THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES

VOLUME II.

THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES

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VOLUME II.
(1) THE ESSENTIAL OIL AND ITS ODOUR
(2) CONSTITUENTS OF ESSENTIAL OILS, SYNTHETIC PERFUMES AND ISOLATED AROMATICS
(3) THE ANALYSIS OF ESSENTIAL OILS

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PREFACE TO THE FOURTH EDITION.

In bringing the second volume of this work up to date, I have to express my thanks to Mr. T. H. Durrans, M.Sc., F.I.C., of Messrs. Boake, Roberts & Co.'s Research Laboratories for contributing the chapter on the Relationship of Odour to Chemical Constitution, a subject to which Mr. Durrans has devoted considerable attention. I have also to thank Mr. Maurice Salamon, B.Sc., and Mr. C. T. Bennett, B.Sc., F.I.C., for reading and revising the chapter on the Analysis of Essential Oils.

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CHAPTER I.

THE ESSENTIAL OIL IN THE PLANT.

An absolutely scientific definition of the term *essential* or *volatile* oils is hardly possible, but for all practical purposes they may be defined as odoriferous bodies of an oily nature obtained almost exclusively from vegetable sources, generally liquid (sometimes semi-solid or solid) at ordinary temperatures, and volatile without decomposition. This definition must be accepted within the ordinary limitations which are laid down by the common acceptation of the words, which will make themselves apparent in the sequel, and show that no more restricted definition is either advantageous or possible. Many essential oils, for example, are partially decomposed when distilled by themselves, and some even when steam distilled.

The volatile oils occur in the most varied parts of the plant anatomy, in some cases being found throughout the various organs, in others being restricted to one special portion of the plant. Thus in the conifers, of which the pine is a type, much volatile oil is found in most parts of the tree; whereas in the rose, the oil is confined to the flower; in the cinnamon, to the bark and the leaves, with a little in the root; in the orange family, chiefly to the flowers and the peel of the fruit; and in the nutmeg, to the fruit. The functions of these bodies in the plant economy are by no means well understood. Whilst it is easy to understand that a fragrant odour in the unfertilised flower may be of great value in attracting the insects with the fecundating pollen, this can have no bearing on the occurrence of odorous bodies in, say, the bark or internal tissues, except in so far as the presence of essential oil in one part of the plant is incidental to, and necessary for, its development, and transference to the spot at which it can exercise its real functions. There may also be a certain protective value in the essential oils, especially against the attacks of insects. At present one is compelled to class the majority of the essential oils as, in general, belonging to the by-products of the metabolic processes of cell life, such as are many of the alkaloids, colouring matters, and tannins; with, possibly, in certain cases, excretionary functions. Some are undoubtedly the results of pathological processes. The structures of the plant which carry the secreted oils occur in the fibro-vascular as well as in the fundamental tissues. Dependent on their mode of origin, the receptacles may be either closed cells containing nothing other than the matter secreted, or they may be vascular structures which have their origin in the gradual absorption of adjacent cell walls, and the consequent fusion of numerous cells into one vessel; or, again, they may be intercellular spaces, large cavities formed in two distinct ways, (1) by the decomposition of a number of adjacent cells, leaving a cavity in their place, whose origin is thus *lysigenous*, (2) by the separation of adjacent cell walls without injury to the cells themselves, thus leaving a space for the secretion, whose origin is *schizogenous*. Sometimes the oils contain a non-volatile resin in solution, forming an oleoresin. For example, isolated cells containing an oleoresin are found in some of the Laurineæ, Zingiberaceæ, and Coniferæ, and intercellular spaces (the so-called *glands*) in some of the Umbelliferæ and Coniferæ.

There are, of course, numerous other functions which the essential oils possess, but in regard to which any views must necessarily be of a highly speculative nature. For example, Tyndall has suggested that, especially where secretion (or excretion) takes place near the surface of an organ, the essential oil has a function which regulates the rate of transpiration. Moisture which is saturated with essential oil has a different heat conductivity from that of moisture alone, so that a plant which gives off much perfume may be protected, during the day, from too great transpiration, and, during the night, from too great reduction of temperature. The high rate of consumption of essential oil during fecundation points, too, to a distinct nutritive value, possibly due to easy assimilation owing to its chemical constitution, of the essential oil.

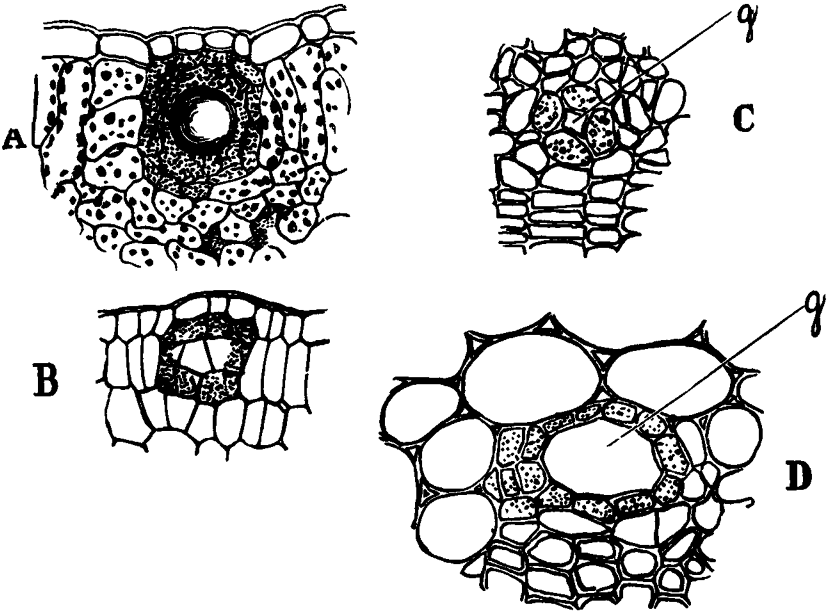

FIG. 1.

In the above diagram A represents an oil cavity below the upper surface of the leaf of *Dictamnus Fraxinella* (× 320). B represents the same in an early stage, and shows the mother cells of the cavity before their absorption (lysigenous). C is an early and D a later stage of the formation of a resin passage in the young stem of the Ivy (*Hedera Helix*) (× 800). In both cases *g* shows the separating cell (schizogenous).

The study of the essential oils *in situ* have hitherto been comparatively restricted, and although much work has been done on a few oils, the results obtained, valuable as they are, must be regarded as of a preliminary nature, indicating possibilities of great interest as research develops.

From a purely practical point of view, the principal problem which requires solution—and which is gradually becoming more understood—is the determination of the external conditions which will enable the grower and distiller to produce the best results, both qualitatively and quantitatively, in regard to any given essential oil.

This problem involves consideration as to the effect of external conditions such as light, heat, moisture, altitude, manuring and other cultural matters, and as is obvious, such considerations may, and do, vary greatly with different plants. Such considerations are to some extent within the scope of the knowledge and skill of the well-trained farmer and the careful distiller. But there are other considerations of a much more abstruse character to be taken into account, and here only the chemist can undertake the necessary investigations. The questions which present themselves for solution are, broadly, some such as the following:—

Where and in what form does the essential oil have its origin? What alterations does it undergo during the life history of the plant? How does it find its way from one part of the plant to another? How can external conditions be controlled so as to vary the character of the essential oil at the will of the cultivator?

These, and similar questions are all-important, if the production of essential oils is to be placed on a really scientific basis

The questions raised in the foregoing paragraphs will be examined briefly, and in principle only, as the detailed account of many of the researches which apply to one plant only, would be outside the scope of this work.

At the outset, attention may be drawn to the fact that the greater part of our knowledge of the development of the essential oil in the plant tissue is due to the painstaking researches of Charabot and his pupils. And a very considerable amount of the information included in this chapter is acknowledged to this source.

From the practical point of view, the principal variation of environment which is definitely under the control of the cultivator, is, of course, the alteration in the composition of the soil, which is brought about by scientific manuring. The analysis of fruits and vegetables will give the ordinary agriculturist much information as to the necessary mineral ingredients to be added to the soil; but in the case of essential oils, the conditions are entirely different. The various parts of the plant tissue are affected in different ways by the same mineral salts, and successful development of the fruit or any other given part of the plant may have little or no relationship with the quantity or quality of essential oil produced. So that it is only by actual distillations of the plant, or portion of the plant, coupled with an exhaustive examination of the essential oil, that informative results can be obtained.

The principles underlying this question are, *mutatis mutandis*, identical for all cases, so that as a typical illustration the case of the peppermint plant may be selected, as this has been worked on by several independent investigators very exhaustively.

Charabot and Hébert[1] carried out an elaborate series of experiments on a field containing 29 rows of peppermint plants, each about 5 yards in length. The normal soil of the field had the following composition:—

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[1] Roure-Bertrand Fils, *Bulletin*, April, **1902**, 5.

Pebbles	250	per mille.
Fine soil, dry	750	,,
Nitrogen (parts per 1000 in the dry fine soil) . .	1·44	,,
Lime (expressed as CaO per 1000 in the dry fine soil)	309·45	,,
Phosphoric acid (expressed as P_2O_5 per 1000 in the dry fine soil)	2·82	,,
Potash (expressed as K_2O per 1000 in the dry fine soil)	1·74	,,

A number of the plants were watered with a solution of 500 grams of sodium chloride in 20 litres of water, and a number with a similar quantity of sodium nitrate. These salts were administered on 23 May, and the following observations were made on the dates specified, on the essential oils obtained under the usual conditions, from the plants normally cultivated, and then treated with the salts above mentioned:—

Plants Cut on 24 July.	Normal.	Sodium Chloride.	Sodium Nitrate.
Optical rotation	- 3° 38′	0°	- 0° 10′
Menthyl esters	12·0 per cent.	12·8 per cent.	12·3 per cent.
Total menthol	38·2 ,,	38·2 ,,	36·7 ,,
Menthone	8·2 ,,	4·0 ,,	6·0 ,,
Plants Cut on 20 August (Green Parts only).			
Menthyl esters	33·3 per cent.	39·6 per cent.	39·2 per cent.
Plants Cut on 16 September (after Fall of Petals).			
Optical rotation	- 5° 30′	- 12° 18′	- 2° 30′
Menthyl esters	27·0 per cent.	30·1 per cent.	28·9 per cent.
Total menthol	47·0 ,,	48·1 ,,	45·8 ,,
Menthone	2·5 ,,	1·1 ,,	2·5 ,,

The oil distilled from plants normally cultivated, which were cut on 18 July, that is six days before the earliest of the above experiments, gave the following results:—

Optical rotation	- 3° 30′
Menthyl esters	8·8 per cent.
Total menthol	41·1 ,, ,,
Menthone	4·0 ,, ,,

The facts established by these experiments are that both sodium chloride and sodium nitrate favour esterification but impede the formation of menthone.

These facts, however, cannot be correctly studied without taking into account a considerable amount of collateral matter. For example, whilst the actual percentage of esters in the essential oils is increased by the use of sodium chloride, this salt has an inhibiting action on the vegetation generally, so that the actual weight of methyl esters per acre is less than when no sodium chloride is used, whilst the reverse is true when sodium nitrate is used.

A very elaborate investigation on the subject has recently been carried out by Gustav Mosler.[1]

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[1] *Pharm. Post*, **1912**, i. 2.

Eight different cultivations were carried out under the following conditions :—

1. Without any manure.
2. With farmyard manure.
3. With sodium nitrate.
4. With sodium nitrate and farmyard manure.
5. With sodium nitrate and calcium superphosphate.
6. With sodium nitrate, calcium superphosphate, and farmyard manure.
7. With sodium nitrate, calcium superphosphate, and potash salts.
8. With sodium nitrate, calcium superphosphate, potash salts, and farmyard manure.

The following are the details of yield of plants and essential oil, with the market values of the product, all being calculated on the same basis :—

	Per Hectare.			
	Dried Plants in Kilos.	Per Cent., Oil.	Weight of Oil in Kilos.	Value.
1	1300	0·77	10·01	500
2	2000	0·88	16·40	820
3	1860	0 74	18·76	938
4	2820	0·81	22·84	1142
5	1940	0·73	14·16	708
6	2320	0·84	19·94	974
7	2200	0·72	15·84	792
8	3140	0·95	29·83	1491

The essential oils, distilled from the plants cut in September had the following characters :—

	1.	2.	3.	4.	5.	6.	7.	8.
Per cent. on dry herb . .	0 87	0·93	0·83	0·91	0·83	0·95	0·83	1·08
Specific gravity	0·9088	0·9092	0·9105	0·9090	0·9100	0·9087	0·9111	0·9099
Optical rotation	– 29·67°	– 29·22°	– 60·25°	– 30·44°	– 31·78°	– 30·41°	– 32·05°	– 30·25°
Acid number .	0·77	0 51	0·78	0·46	6·58	0·50	0·52	0·37
Ester ,, .	37·47	33·49	41·13	43·32	44·14	32·28	45·52	36·75
Menthyl esters .	10·73	9·33	11·74	12·07	12·30	9·27	12·58	10·24
Ester number of acetylated oil	196·05	187·75	197·04	195·24	189·36	194·07	192·70	197·65
Free menthol .	50·13	48·59	48·82	47·76	45·89	30·93	46·08	50·97
Total ,, .	60·86	57·92	60·56	59·83	57·69	60·20	58 66	61·21
Menthone . .	3 52	6·11	0·89	2·94	4·01	1·37	3·75	2·14

It will be noted that the experiments with sodium nitrate confirm the results of Charabot and Hébert, both as regards the increase in menthyl esters and the decrease in menthone in the essential oil.

The influence of sunlight on vegetable growth, and the results of etiolation are, of course, well known to botanical students. There is no room for doubt that the production and evolution of the odour-bearing constituents of a plant are in direct relationship with the chlorophyll and its functions, and that therefore the question of sunlight has a very great effect on the character of the essential oil.

In the case of sweet basil, *Ocimum basilicum,* Charabot and Hébert[1] have examined the essential oils distilled from plants which had been cultivated in full light and from those kept shaded from the light. In the former case the oil contained 57·3 per cent. of estragol and 42·7 per cent. of terpene compounds, whilst in the case of the shaded plants the estragol had risen to 74·2 per cent. and the terpene compounds fell to 25·8 per cent.

A more elaborate investigation on the influence of light was carried out in the case of peppermint plants.[2] The plants were put out at the commencement of May, 1903, and on 10 May a certain area of the field was completely protected from the sun's rays. Many of the plants so shaded died, and in no case did flowering take place. The essential oils were distilled on 6 August, the control plants being deprived of their flowers, so as to make them strictly comparable with the shaded plants. The yield of essential oil was 0·629 per cent. on the dried normal plants but only 0·32 per cent. on the shaded plants. The essential oil of the normal plants contained 18·1 per cent of menthyl esters as against 17·3 per cent. in the oil from the shaded plants. The flowers of the normal plants were distilled separately and yielded 1·815 per cent. on the dried material. It is therefore clear that the restriction of light considerably reduces the proportion of essential oil contained in the plant. This point will become more obvious when the importance of the leaf and its contained chlorophyll is examined.

The effect of altitude on the composition of essential oils has, perhaps, been somewhat exaggerated, since in reality the factors concerned are in the main the sum of the effects of moisture and light, with some slight influence of temperature and rarification of the atmosphere. Gastin Bonnier, in his published works, has shown that the effect of moisture and drought has an equally important effect on plants with that of sunlight and shade. Little experimental work has been carried out in regard to the effect of moisture during cultivation on the essential oils, but there seems no reason to doubt that it is very considerable. As an example one may quote the case of the essential oil distilled from the plants of *Lavandula vera.* When this plant is grown at comparatively high altitudes in the South-East of France and on the Italian frontier it yields an essential oil which contains from 25 to 55 per cent. of linalyl acetate and no cineol. If the same plants grown in England are distilled, the essential oil contains from 6 to 11 per cent. of linalyl acetate, and an appreciable amount of cineol. There are, no doubt, many causes which contribute to this great difference between the essential oils distilled from lavender plants grown in different districts, but there appears to be little doubt that the comparative moisture of the soil in England, and the dryness of the mountainous regions of France in which the lavender plant flourishes, are the dominating factor. Indeed, Charabot has examined an oil distilled from French plants cultivated near Paris and found it to contain only 10·2 per cent. of esters, thus approximating in character to English lavender oil.

The above considerations indicate the great importance of experimental studies on the influence of externally controlled conditions, in

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[1] Charabot and Hébert, 2, **1905**. xxxiii. 584.

[2] Roure-Bertrand Fils, *Bulletin*, April, **1904**, 9.

regard to individual plants, with a view to obtaining from them the greatest amount of essential oil which shall have the characters which are particularly required. It is probable that there is a good deal of unpublished work in this direction, which has been undertaken, but which has been kept secret from commercial motives.

There are many cases in which the action of parasites produces great changes in the anatomical structure of the plant, which changes are usually reflected in the character of the essential oils Molliard has made a careful examination of the effect of the parasite *Eriophyes menthæ* on the peppermint plant. The presence of this parasite causes a practically complete suppression of flowers, the branches which, normally terminated by inflorescences, become luxurious in growth with innumerable branching, but without flowers. Distinct changes in the nervation are also observable, and various other structural changes are to be noticed, all of which profoundly modify the general character of the plant. The essential oil from these sterile peppermint plants is more abundant than in the case of normal plants, but it contains only traces of menthone, and much more of the menthol is in the combined form, as esters. Further, the mixture of esterifying acids is richer in the case of the normal oil, in valerianic acid, than in the case of the oil from the sterile plants.

The essential oil may be secreted in numerous organs, such as cells, hairs, vessels, etc., and may rest stored in the place of secretion; or may be secreted from the cells in which it is produced into organs external to the cells. As pointed out previously, the canals or vessels in which essential oils are formed to a considerable extent are usually termed schizogenous or lysigenous, according to their mode of origin. Many such vessels are schizogenous in the inception, but are enlarged by a later absorption of cell walls. They are then known as schizolysigenous. The mechanism of the actual secretion is by no means well understood, and most views on the subject must be regarded as within the realms of undemonstrated theories. An ingenious explanation of the process of secretion has been advanced by Tschirch.[1] He considers that the external portions of the membranes of the cells which border on the vessel become mucilaginous, and form the first products of the transformation of the cell substance into the essential oil, which then appears in the vessel in the form of tiny drops of oil. This conversion into mucilaginous matter proceeds rapidly until the fully developed vessel is completely surrounded by the secreting cells, whose membranes, on the side bordering on the vessel, is jellified in its external portion forming a mucilaginous layer—the outer layer of which Tschirch terms the resinogenous layer (*Resinogeneschicht*). This resinogenous layer is separated from the cavity of the vessel by a cuticle common to all the cells forming the walls.

The essential oil is formed throughout the resinogenous layer, whence it passes into the vessel, the minute particles uniting to form small oil drops. According to Tschirch, the essential oil is first produced in the inner portions of the resinogenous layer, and has not diffused through the actual cell membrane as essential oil, but in the form of an intermediate product, the actual genesis of the oil as such being in the resinogenous layer.

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[1] Published works, *passim*.

There is, however, a considerable weight of opinion that the essential oil passes through membrane of the cell in which it is secreted. There is, so far as the author can see, no substantial evidence of the existence of Tschirch's resinogenous layer, and there is no doubt that the theoretical need for its existence as assumed by Tschirch is based on a misconception. Tschirch claims that it is not probable that resins and essential oils can diffuse through membranes saturated with water. But he leaves out of consideration the fact that all essential oils are slightly soluble in water, and that diffusion in very dilute aqueous solution is obviously possible and even very probable. On the whole, there does not appear to be much theoretical reason for, nor experimental evidence of, the existence of the resinogenous layer.

An interesting contribution to this question has recently been made by O. Tunmann[1] entitled "Contribution to the knowledge of the cuticular glands," some volatile oils owing their existence to these glands. The author discusses the formation of secretions, and concludes that there is a correspondence between the formation of secretions in the vegetable kingdom and the same process in the glandular tissues of the human skin, that is to say, the sebaceous glands and gland surfaces. The secreted matter is only found outside the glandular cells, as it is divided from the plasma of the cells by a wall of cellulose which is always visible. The first investigator who suggested the resin-secreting layer was Tschirch, who gave, as above stated, to this part of the membrane the name of "resinogenous layer". The determination of this layer in the glands of the skin is easier when the material worked upon has been soaked for one or two months in concentrated aqueous solution of acetate of copper, which hardens it. If fresh material is employed, the *modus operandi*, according to Tunmann, should be as follows: Delicate horizontal cuts should be made, so that the glands may be inspected from above, or in diagonal section. Next add an aqueous solution of chloral hydrate (10, 20, 30, or 40 per cent.). If the layer should not yet be visible the strength of the solution should be increased by degrees until the major part of the resin has been dissolved. Now exert with the finger a gentle pressure upon the side of the covering glass. This will burst the cuticle and push it aside, while the resinogenous layer will be placed either upon the top of the cells, or, separated from the latter, at the side of the gland-head. It is not necessary that all the resin should be dissolved. Staining with diluted tincture of alkanet will show the residual resin, leaving the resinogenous layer uncoloured.

By the aid of the processes described Tunmann claims to have discovered the resinogenous layer in all the plants examined by him. In the course of his investigations he was able to determine various typical forms of the layer. These he divides into three principal types: the rod-type (*Viola Fraxinus*, *Alnus*), the vacuola-type (*Salvia*, *Hyssopus*), and the mesh or grille-type (*Rhododendron*, *Azalea*).

The cuticle of the glands of the skin is partly enlarged by stretching, partly by subsequent development. Its principal purpose is unquestionably to prevent a too rapid exudation or loss of the secretions. In the case of all the persistent glands of the *Labiatæ*, *Pelargoniæ*, *Compositæ*, etc., all of which possess a strong cuticle, a continuous volatilisation of

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[1] *Berichte deutsch. pharm. Ges.*, **18** (1908), 491: from Schimmel's *Report*.

essential oil takes place throughout the whole life of the plant. In the course of this process the chemical composition of the essential oil must of course undergo some modification, but it does not reach a demonstrable process of resinification, because new volatile portions are continuously being formed. Only in autumn, when the period of growth is reaching its end, this formation of volatile constituents ceases, and the remainder of the oil resinifies. Thus it is that autumnal leaves are found to contain in lieu of the usual, almost colourless, highly refractory essential oil, a dark yellow, partly crystalline, partly amorphous, somewhat sparingly soluble lump of resin.

Generally speaking, the view has been accepted that vegetable secretions are decomposition products formed in the course of the metabolism, but Tschirch considers that these secretions are built up to serve quite definite and various biological objects, and in this view he is supported by Tunmann.

In some cases, the formation of essential oil in the plant begins at a very early stage, in fact, before the gland has attained its full development.

In opposition to Charabot, Tunmann considers that the constant change in the chemical composition of vegetable essential oils during the progress of the development of the plant, is chiefly due to the continuous evaporation of the more volatile parts. He agrees with Charabot in deducing, from pharmaco-physiological considerations, that plants in flower cannot yield so valuable an oil as can the young spring leaves.

The solubility of essential oils in water, or in aqueous solutions of other substances is obviously a question of considerable importance in reference to the transference of the oil from one portion of the plant to another, as will be seen in the sequel. From a laboratory point of view, the question has been thoroughly investigated in a number of cases by Umney and Bunker.[1] The following table indicates the results obtained by these observers, the methods adopted by them being (1) the determination of the difference between the refractive index of the dry oil and that of the oil saturated with water, and (2) the determination of the difference between the specific gravity of the dry oil and that of the oil saturated with water :—

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[1] *P. and E.O.R.* **1912**, 101.

I. Essential Oil.	II. S. G. Dried Oil at 15° C.	III. S. G. Watered Oil at 15° C.	IV. Difference.	V. Ref. Ind. Dried Oil at 25° C.	VI. Ref. Ind. Watered Oil at 25° C.	VII. Difference.	VIII. Per Cent. Water from S. G.	IX. Per Cent. Water from Ref. Ind.	X. Per Cent. Water Actually Added.
TYPE I.									
Nutmeg	·9018	·9018	nil	1·4795	1·4795	nil	nil	nil	nil
Juniper	·8734	·8734	nil	1·4785	1·4785	nil	nil	nil	nil
Lemon	·8576	·8576	nil	1·4729	1·4729	nil	nil	nil	nil
Orange	·8539	·8539	nil	1·4715	1·4715	nil	nil	nil	nil
TYPE II.									
Santal	·9756	·9760	·0004	1·5038	1·5035	·0003	1·7 per cent.	0·17 per cent.	0·44 per cent.
Savin	·9139	·9140	·0001	1·4735	1·4732	·0003	0·12 ,,	0·23 ,,	0·23 ,,
Citronella	·9034	·9034	nil	1·4770	1·4769	·0001	nil	0·07 ,,	0·31 ,,
Geranium (Turkish)	·8886	·8898	·0012	1·4723	1·4715	·0008	1·22 per cent.	0·64 ,,	0·82 ,,
TYPE III.									
Lemon-grass	·8820	·8823	·0003	1·4824	1·4823	·0001	0·28 per cent.	0·07 per cent.	0·21 per cent.
Cassia	1·0702	1·0694	− ·0008	1·6003	1·5999	·0004	1·07 ,,	0·14 ,,	0·54 ,,
Citronella (Java)	·8935	·8937	·0002	1·4660	1·4659	·0001	0·21 ,,	0·08 ,,	0·36 ,,
TYPE IV.									
Cinnamon leaf	1·0533	1·0531	− ·0002	1·5315	1·5314	·0001	0·35 per cent.	0·05 per cent.	0·28 per cent.
Clove	1·0509	1·0508	− ·0001	1·5300	1·5295	·0005	0·18 ,,	0·24 ,,	0·41 ,,
Thyme	·9144	·9150	·0006	1·4913	1·4810	·0003	0·78 ,,	0·22 ,,	0·40 ,,
TYPE V.									
Bergamot	·8831	·8835	·0001	1·4634	1·4631	·0003	0·09 per cent.	0·26 per cent.	0·24 per cent.
Geranium (Bourbon)	·9132	·9133	·0001	1·4639	1·4638	·0001	0·12 ,,	0·03 ,,	0·55 ,,
TYPE VI.									
Eucalyptus (Glob.)	·9204	·9209	·0005	1·4602	1·4600	·0002	0·68 per cent.	0·17 per cent.	0·20 per cent.
TYPE VII.									
Caraway	·9135	·9135	nil	1·4847	1·4847	nil	nil	nil	0·13 per cent.

A second series of experiments was carried out to determine the amount of water which the same oils were capable of dissolving. These results are embodied in the following table:—

Essential Oil.	Ref. Ind. at 25° C. of Dried Oil.	Ref. Ind. at 25° C. of "Steamed" Oil.	Difference.	Per Cent. Water.	1 part of Water in (approximately).
Type I.					
Nutmeg	1·4795	1·4795	nil	—	—
Juniper	1·4800	1·4800	nil	—	—
Lemon	1·4729	1·4729	nil	—	—
Orange	1·4715	1·4715	nil	—	—
Type II.					
Santal	1·5040	1·5037	·0003	0·17 °/o	590
Savin	1·4737	1·4733	·0004	0·30 ,,	330
Citronella	1·4800	1·4794	·0006	0·44 ,,	230
Geranium (Turkish)	1·4726	1·4712	·0014	1·13 ,,	90
Type III.					
Lemon-grass	1·4830	1·4824	·0006	0·45 °/o	220
Cassia	1·6017	1·6005	·0012	0·41 ,,	220
Citronella (Java)	1·4666	1·4657	·0009	0·75 ,,	130
Type IV.					
Cinnamon leaf	1·5325	1·5316	·0009	0·42 °/o	220
Clove	1·5305	1·5295	·0010	0·47 ,,	210
Thyme	1·4917	1·4911	·0006	0·41 ,,	220
Type V.					
Bergamot	1·4635	1·4631	·0004	0·34 °/o	300
Geranium (Bourbon)	1·4654	1·4648	·0006	0·49 ,,	200
Type VI.					
Eucalyptus (Glob.)	1·4604	1·4602	·0002	0·16 °/o	620
Type VII.					
Caraway	1·4847	1·4847	nil	—	—

The oils consisting mainly of terpenes do not appear to dissolve water, nor to be soluble in water, or at all events, to any appreciable extent.

It must, however, be remembered that we are here dealing with pure water only, whereas in the plant economy we are dealing with solutions of organic substances, in which essential oils would almost certainly be dissolved more easily than in pure water.

As has been mentioned above, essential oils occur in the most varied parts of the plant anatomy, and in many cases in almost every part of a given plant, whilst in many others the essential oil is restricted to one or two parts of the plant only.

Charabot and Laloue have especially studied the evolution and transference of the essential oil throughout the whole of the plant, and their results form the basis of our knowledge on the subject.

A plant which yielded particularly instructive results on the general question is *Ocimum basilicum*. The investigations were carried out at a number of stages of the plant's growth, the four principal of which were as follows:—

1. 4 July, before flowering. There was a considerable preponderance of leaves which were found to be distinctly richer in odorous constituents than the stems, the essential oil being present as such in the young leaves.

2. 21 July, at the commencement of flowering. The stems now preponderated, and the green parts of the plant showed a smaller percentage of essential oil, whilst the young flowers already contained a larger proportion of essential oil.

3. 26 August, with flowering well advanced. The leaves and flowers were both considerably more numerous than in the preceding stage, and it was found that the percentage of essential oil diminished very sensibly in the green parts of the plants, whilst the flower was fulfilling its functions. The percentage of oil diminished during fecundation in the flowers, but not so considerably as in the green parts of the plant. It is therefore during the period immediately preceding fecundation that the essential oil accumulates most, and during fecundation that it is used up.

4. 15 September, the seed having matured. An increase in the percentage of essential oil in the green plants since the last stage was noted and a diminution in the inflorescences.

The essential oil is therefore formed at an early period of the plant's life, and accumulates most actively towards the commencement of reproduction. Before flowering, the accumulation reaches its maximum and the diminution sets in as reproductive processes proceed, and the transfer of the oil from the green plant to the inflorescences slows down, and when fecundation is accomplished the essential oil, less on the whole, again increases in the green parts and diminishes in the inflorescences. It appears obvious, therefore, that the essential oil, manufactured in the green parts of the plant, is transferred together with the soluble carbohydrates to the flower, probably *not* as nutriment, and, fecundation accomplished, it returns, at all events in part, to the green parts of the plant. The mechanism of this return may possibly be explained by the desiccation of the inflorescence after fecundation, with a consequent increase of osmotic pressure, so that some of the dissolved matter is driven out. Throughout all the stages dealt with no essential oil was detected in the roots.

As another example of the experiments, *Artemisia absinthium* may be selected. The four stages of special interest were as follows:—

1. 26 September. 1904, long before flowering time. The roots did not contain any essential oil. The leaves contained considerably more than the stems—about eleven times as much.

2. 10 July, 1905, commencement of flowering. The roots were now found to be richer in essential oil than the stems. In all the organs the proportion had increased, and in the leaves it had doubled.

3. 4 August, 1905, flowering advanced. The accumulation of essential oil in the roots was still more marked. (This fact does not appear to hold good for any annual plants: *Artemisia* is a perennial

The proportion of essential oil sensibly diminishes in the stems, in the leaves, and especially in the inflorescences, and in the whole plant. The most active formation of essential oil is, therefore, in the early part of the plant's life up to the commencement of flowering.

4. 2 September, 1905, the flowering completed. The percentage of essential oil in the roots has increased still further; a slight increase has taken place in the stems; no alteration is noticed in the leaves, and a diminution has taken place in the inflorescence.

The general conclusions drawn by Charabot and Laloue as the result of these and a number of similar experiments are as follows:—[1]

"The odorous compound first appears in the green organs of the plant whilst still young. It continues to be formed and to accumulate up till the commencement of flowering, but the process becomes slower as flowering advances. The essential oil passes from the leaves to the stems and thence to the inflorescence, obeying the ordinary laws of diffusion. Part of it, entering into solution, passes into the stem by osmosis. Arriving here, and finding the medium already saturated with similar products, precipitation takes place, the remaining soluble portion continuing to diffuse, entering the organs where it is consumed, especially the inflorescence. Whilst fecundation is taking place a certain amount of the essential oil is consumed in the inflorescence. It is possible, and even probable, that at the same time the green organs are producing further quantities of essential oil, but all that can be said with certainty is that a net loss in essential oil occurs when the flower accomplishes its sexual function. This leads to the practical conclusion that such perfume-yielding plants should be gathered for distillation just before the fecundation takes place. This act accomplished, the odorous principles appear to redescend into the stem and other organs of the flower, a movement probably brought about by the desiccation of the flower which follows fecundation, with a resulting increase in the osmotic pressure."

If these assumptions of Charabot and Laloue be correct—and they are borne out by much experimental evidence, after laborious research—the theory of Tschirch and his pupils, which depends on quite opposite assumptions, is clearly unacceptable. According to Charabot and Laloue, the essential oil circulates in the plant in aqueous solution and can traverse the plant from organ to organ in this form, and wherever meeting already saturated media, is precipitated, and the points at which such precipitation occurs are known as secreting organs. This being true, the assumption of a resinogenous layer, based on the hypothesis of the non-solubility of essential oils in water—and in solutions of organic matter—becomes unnecessary and improbable.

Most essential oils appear to be evolved directly in the form of terpenic or non-terpenic compounds separable from the plant tissues in the same form as they exist therein. A considerable number, however, are evolved in the form of complex compounds known as glucosides, in which the essential oil complex is present, but wherein the essential oil itself does not exist in the free state.

The glucosides are compounds, which, under the influence of hydrolytic agents are decomposed into glucose or an allied aldose or ketose, and one or more other bodies, which, in the cases under consideration, form constituents of essential oils. The hydrolytic agents which bring about these changes are soluble ferments, such as diastases, enzymes and similar

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[1] *Le Parfum Chez la Plante*, 233.

bodies, or, where the hydrolysis is produced artifically, dilute acids or alkalis.

The ferments able to decompose particular glucosides are usually found in the plants containing the glucosides, separated from the latter by being enclosed in special cells which do not contain the glucoside, so that the two substances must be brought into contact, in the presence of water, by mechanical means, such as crushing, etc.

Two principal cases of such decomposition are known.

Firstly, there are those cases where the hydrolysis takes place within the plant itself during the life of the plant, so that the essential oil is actually a product, in the free state, of the metabolic processes of the living plant; and secondly, there are those cases where the glucoside is not decomposed except by artificial processes, independent of the life of the plant.

The former case is of particular interest and importance as bearing on the proper method for the extraction of the perfume. Typical instances are those of jasmin and tuberose, which have been carefully investigated by Hesse. This chemist showed that the essential oil of jasmin, which resides in the flower alone, does not, when extracted with a volatile solvent, contain either methyl anthranilate or indole, whereas when the flowers are allowed to macerate in fat by the enfleurage process, and the pomade so obtained extracted, the essential oil does contain both methyl anthranilate and indole; and further, the yield of essential oil obtained by the latter process is at least five times as great as that obtained by extracting the flowers with a volatile solvent. The following considerations arise here. If the detached flowers are treated with a volatile solvent, the living tissues are at once killed, and the actual amount of oil present in the flowers is obtained in the condition in which it exists when they were picked immediately before extraction. But if the detached flowers are macerated in cold fat, the living tissues are not destroyed and the flower continues to live for a certain time. Since a great increase in the quantity of the oil is obtained if, for example, the flowers are exposed to the fat for twenty-four hours, and since new compounds, namely, methyl anthranilate and indole now appear in the oil, it is obvious that much oil and the new compounds are elaborated in the flower during its life after being detached from the plant, quite independently of the chlorophyll-containing organs. There is little reason to doubt that this is the result of a glucosidal decomposition in the flower, the glucoside existing therein at the time of gathering, and steadily decomposing into the essential oil and a sugar so long as the flower is alive, but not when it is killed, as, for example, by the action of a volatile solvent. Hesse has established the same principle in the case of the tuberose, the flowers of which yield about twelve times as much essential oil when exposed to enfleurage as they do when extracted with a volatile solvent. Further, the oil obtained by enfleurage contains far more methyl anthranilate than the oil obtained by extraction with a volatile solvent, and also contains methyl salicylate.

In the case of most plants where the essential oil is due to a glucosidal decomposition, the products are of a non-terpenic character, but this is not invariably the case.

In many plants the glucoside is decomposed during the life of the plant in a manner different from that just described. The conditions are not understood, but in the case of such flowers as the jasmin and tuberose it appears that only a partial decomposition of the glucoside takes place, until the removal of the decomposition products (*e.g.* by enfleurage) when more glucoside is decomposed. In most plants, however, the decomposition is complete, all the essential oil possible is formed, and can be obtained by any of the usual processes without being further increased by more glucosidal decomposition.

One case in which the essential oil does not exist at any stage of the plant's life in the free condition, until the ferment and the glucoside have been brought into contact by artificial means, will suffice to illustrate this type of production of essential oils in the plant. The essential oil of bitter almonds does not exist as such in the kernels, which have no odour such as we ascribe to bitter almonds. The glucoside which gives rise to the essential oil is a body known as amygdalin, of the formula $C_{20}H_{27}NO_{11}$. This body crystallises in orthorhombic prisms with three molecules of water of crystallisation, which are driven off at 110° to 120°. Under the action of the ferment, emulsin (which is rarely, if ever, in contact with the amygdalin in the plant tissues) in the presence of water, amygdalin splits up into glucose, hydrocyanic acid, and benzaldehyde, the characteristic odour-bearer of essential oil of bitter almonds. The reaction (which probably occurs in two stages which need not be discussed here) is as follows:—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Glucose.}}{2C_6H_{12}O_6} + \underset{\text{Benzaldehyde.}}{C_6H\,.\,CHO} + HNC.$$

The above illustration is typical of the method of formation of a large number of essential oils, which need not be discussed here in detail.

The actual genesis of the odoriferous compounds in the living plant has been studied, as indicated above, principally by Charabot and his colleagues, Laloue and Hébert, but interesting work in the same direction has been carried out by Blondel and by Mesnard.

There are three conditions to consider in regard to the physiological activity of the living cell: (1) where the product—the essential oil in the present case—pre-exists in the tissues generally and the function of the phytoblast of the cell is limited to isolating the product at the desired moment. This may be regarded as an *excretion*; (2) where the product has its origin in the cell itself by means of combination and reaction of other bodies transported from other parts of the plant tissue, and (3) where the product is completely built up in the cell, without it being supplied with the materials for the synthesis by transport from other parts of the tissues. These may be regarded as cases of *secretion.*

Numerous theories have been advanced to explain the origin of essential oils in the plant, but the evidence in favour of most of them is in no case at all conclusive, and the question must still be regarded as unsettled.

Flückiger and Tschirch originally suggested that the essential oil was elaborated at the expense of the starch, or possibly even of the cellulose, the intermediate products of which were transported through the tissues to the locality of elimination, undergoing gradual alteration until the final product of transformation was the essential oil. Mesnard regarded the chlorophyll as the parent substance of the essential oils, and Tschirch more recently suggested the tannin as the more probable substance to give rise to essential oils and resins.

One thing is certain, and that is that the chlorophyll-containing parenchyma is, generally speaking, the seat of formation of the essential oils. The physiological activity of the phytoblast of the cell can be demonstrated experimentally, and Blondel has illustrated it in the case of the rose. He took the red rose *General Jaquemінot*, as one having a well-marked odour, and placed two blooms from the same branch, of equal size and development, in vases of water under two bell jars. Into one of the jars a few drops of chloroform on a sponge were introduced. At the end of half an hour the bell jar was lifted, and the weak odour of the rose was found to have given place to an intense odour of the flower. The odour of the rose kept without chloroform was feeble, exactly as at the commencement of the experiment. A similar experiment was carried out with the tea rose *Gloire de Dijon.* In this case the odour of the flower treated with chloroform entirely altered, and was quite disagreeable, with no resemblance to that of the rose itself. In the former case the action of a minute amount of chloroform acts as an irritant, and the stimulus causes a greatly increased secretion of essential oil, whilst in the latter case the functions of the secreting cells were actually changed and a different odorous substance was evolved. With a larger dose of chloroform the contents of the cells are killed and no further exhalation of perfume is noted.

The actual course of the evolution of the essential oil has been particularly studied by Charabot and Laloue in plants, the principal constituents of whose oils belong to four different groups, namely :—

1. Compounds of the linalol group.
2. ,, ,, geraniol ,,
3. ,, ,, thujol ,,
4. ,, ,, menthol ,,

Linalol is a tertiary alcohol of the formula $C_{10}H_{18}O$, which, with its acetic ester (and traces of other esters) forms the basis of the perfume of bergamot and lavender oils. By dehydration linalol is converted into terpenes of which the principal are limonene and dipentene, and by esterification into its acetic ester. The examination of the essential oil at different periods of the development of the bergamot fruit has led Charabot and Laloue to the following conclusions.[1] As the fruit matures the essential oil undergoes the following modifications :—

1. The amount of free acids decreases.
2. The richness in linalyl acetate increases.
3. The proportion of free linalol and even of total linalol decreases to a very sensible extent.
4. The quantity of the terpenes increases, without the ratio between the amounts of the two hydrocarbons limonene and dipentene being altered.

The fact that the amount of total linalol decreases whilst the richness in linalyl acetate increases, proves that linalol appears in the plant at an earlier period than its acetic ester. Further, the free acetic acid acting on the linalol esterifies a portion of it, whilst another portion of this terpene alcohol is dehydrated with the production of limonene and dipentene, which are the usual resultants of linalol in presence of certain dehydrating agents. This view is corroborated by the fact that the quantity of the mixed terpenes increases during the esterification, without the slightest variation being observed in the ratio between the

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[1] Roure-Bertrand Fils, *Bulletin*, March, 1900, 12.

amounts of the two terpenes, which shows that their formation is simultaneous and is the result of one and the same reaction.

The practical conclusion to be drawn from this is as follows: Oil of bergamot having a value which increases according to the richness in ester, it will be profitable to gather the harvest at the period at which the fruit is fully ripe.

The same compound, linalol, is the parent substance of oil of lavender. The study of the progressive development of this oil in the plant tissues was carried out on three samples which were distilled at intervals of a fortnight, the first from flowers in the budding stage, the second from the fully flowering plants, and the third from the plants with the flowers faded. The essential oils thus obtained had the following characters:—

	Oil from the Plants with—		
	Buds.	Flowers.	Faded Flowers.
Specific gravity at 15° C.	0·8849	0·8854	0·8821
Optical rotation	− 6° 32′	− 6° 48′	− 6° 50′
Acidity, as acetic acid per litre of water collected during distillation	0·5241 gm.	0·4716 gm.	0·3846 gm.
Ester per cent.	36·6	40·4	39·75
Free linalol per cent.	21·0	16·7	18·9
Total „ „	49·8	48·4	50·3

Hence, the acidity decreases in the course of vegetation; the proportion of free linalol and the proportion of total linalol also decrease in the essence up to the time when the flowers are fully opened, whilst the proportion of ester increases: then, when the flower fades, the essential oil becomes richer in linalol, whilst, on the other hand, its ester-content decreases.

Thus as in the case of oil of bergamot, esterification is accompanied by a decrease in the total proportion of linalol and in the proportion of free acid. These facts prove that, here also, the esters originate by the direct action of the acids on the alcohols. Under these conditions, as the plant develops, part of the linalol is esterified whilst another portion is dehydrated. So that not only does the proportion of free alcohol, but also that of the total alcohol decrease. But as the esterification process is completed, which happens when the flower commences to fade, the total alcohols increase at a fairly rapid rate.

The progressive development of the geraniol compounds in essential oils has been principally studied in the case of oil of geranium.

The typical plant which was selected for investigation in the case of the geraniol compounds was the ordinary geranium. The principal alcohol present in this oil is geraniol, $C_{10}H_{18}O$, and this is accompanied by a smaller amount of citronellol, $C_{10}H_{20}O$. A ketone, menthone, is also present.

An oil was distilled from the green plants on 18 July, and a second sample from the still green plants on 21 August. These two samples had the following characters:—

	Product Collected—	
	On 18 July.	On 21 August.
Density at 15° C.	0·897	0·899
Rotatory power in 100 mm. tube	− 10°	− 10° 16′
Coefficient of saturation of the acids	43·8	41·0
Esters (calculated as geranyl tiglate)	5·8	10·0
Free alcohol (calculated as $C_{10}H_{18}O$)	64·0	62·1
Total alcohol	67·8	68·6

It will be seen that (1) the acidity decreases during the maturing of the plant; (2) as in all the cases previously considered, oil of geranium becomes richer in esters during vegetation; (3) the proportion of total alcohol increases slightly and the quantity of free alcohol decreases, but not to an extent corresponding with the increase of esters, so that in the course of esterification, which takes place in this case without dehydration, a small quantity of alcohol is produced.

Practically no menthone was found in either oil, but in the oil obtained from the plant after flowering and complete maturation, an appreciable quantity of menthone was found. It is thus clear that the menthone is formed, as would be expected, principally during the period of the greatest respiratory activity.

The thujol group, in reference to these studies, is represented by the absinthe herb (*Artemisia absynthium*), which contains a secondary alcohol thujol, $C_{10}H_{18}O$, and its esters, and its corresponding ketone, thujone, $C_{10}H_{16}O$. The conclusions drawn in this case are as follows:—

From the early stages of vegetation, before the influence of flowering is seen, an essential oil is present in the chlorophyll-containing organs, which is already rich in thujol, but which contains very little thujone. Esterification steadily increases up to the time of flowering, and then diminishes, and afterwards increases again as new green organs develope. The amount of thujol diminishes during the evolution of the plant, but increases again when new green organs are developed. The thujone gradually increases up till the time of flowering, and then steadily decreases owing to consumption in the flowers themselves.

It is therefore probable that the alcohol is formed in the first instance, which is afterwards esterified to thujyl esters and oxidised to thujone.

The last of these investigations to which reference will be made is that of the peppermint, as representing the menthol group of compounds. Four samples of essential oil were examined:—

1. That distilled from young plants not exceeding 50 cm. in height, the inflorescence having formed, but the buds not having made their appearance.
2. That distilled from the plant when the buds were commencing to appear, but from which the inflorescences were removed.
3. That distilled from the inflorescences so removed.
4. That distilled from the normal plant in full flower.

The oils in question had the following characters:—

	1. Oil Extracted before the Formation of the Buds.	Oil Extracted after the Formation of the Buds.		4. Oil Extracted from the Flowering Plants.
		2. Leaves.	3. Inflorescences.	
Specific gravity at 18° C. . .	0·9025	0·9016	0·9081	0·9200
Optical rotation at 18° C. in 100 mm. tube .	− 24° 10′	− 26°	− 20° 15′	− 2° 37′
Ester (calculated) as menthyl acetate) . .	3·7 per cent.	10·3 per cent.	7·5 per cent.	10·7 per cent.
Combined menthol . . .	2·9 ,,	8·1 ,,	5·9 ,,	8·4 ,,
Free menthol .	44·3 ,,	42·2 ,,	29·9 ,,	32·1 ,,
Total ,, .	47·2 ,,	50·3 ,,	35·8 ,,	40·5 ,,
Menthone . .	5·2 ,,	4·2 ,,	16·7 ,,	10·2 ,,

After allowing for the relative weights of the leaves and inflorescences, the composition of the average oil which would have been yielded by (2) and (3) if distilled together would have been as follows:—

Esters	9·6 per cent.
Combined menthol	7·6 ,,
Free menthol	39·0 ,,
Total ,, ...	46·6 ,,
Menthone	7·5 ,,

It is thus apparent that at the commencement of vegetation of the peppermint the oil is rich in menthol, but only a small amount is present in the esterified condition. Menthone only exists in small quantity. As the green parts of the plant develope, the proportion of esterified menthol increases, as has been found to be the case with other alcohols. This esterification, however, only takes place in the leaves, and when the essential oil extends towards the flowering tops, it becomes poorer in esters.

The net result is an increase in esters in the total essential oil distilled from the whole of the plant, owing to the development of the green parts. The menthone increases during the development of the inflorescences, whilst the menthol decreases correspondingly. So that the oil obtained from plants systematically deprived of their inflorescences only contains a small amount of menthone, but is very rich in free menthol and in esters. The oil, however, distilled from the flower shoots, even at an early stage of their development, contains a considerable quantity of menthone and comparatively small quantities of free menthol and esters. It is therefore seen that the formation of the esters of menthol takes place in the green parts of the plant, whilst the menthone originates more especially in the flowers. This latter point is further corroborated by the fact that if the peppermint becomes modified by the puncture of an insect so as to suffer mutilation, the greater part of the menthone disappears, as well as the flowers.

These observations throw light on the mechanism which governs the transformation in the plant of the compounds belonging to the menthol group. This alcohol being produced simultaneously with the green parts of the plant, is partially esterified in the leaves; the esterification here again is manifested as a consequence of the disappearance of the chlorophyll. Then, when the heads bearing the buds and later the flowers are formed, a certain quantity of oil accumulates and the menthol, both in the free and combined state, is there converted into menthone by oxidation.

Investigations of the character detailed above lead to the following conclusions. The esters are principally formed in the green parts of the plant by the action of free acids on the alcohols. The latter easily losing water are, at the same time partially dehydrated without combining with acids and so give rise to terpenes. Isomerisation is also going on, so that starting from the compound linalol, we see the following compounds formed : linalyl acetate by esterification, terpenes by dehydration, and the isomeric alcohols geraniol and nerol by isomerisation. All three reactions can be effected artificially in the laboratory, as they are naturally in the plant tissues. The alcohols and their esters are easily converted into aldehydes and ketones, especially when the inflorescence appears, since it is in these organs that oxygen is fixed to a maximum extent.

Whatever may be the complex functions of the chlorophyll in the plant, so far as the essential oils is concerned, there can be no doubt that it favours the process of dehydration. Gaston Bonnier has shown that under the influence of a mountain climate the green parts of a plant undergo considerable modification. The leaves are thicker and of a more rich green colour, and the assimilatory tissues of the stem are better suited for the exercise of the chlorophyll functions. The green palissade tissue is more strongly developed, either by the cells being longer, or because the number of layers of palissade cells is greater, so that the chlorophyll bearers are larger and more numerous. Under similar conditions, plants grown at low altitudes have a lower chlorophyll function than the same plants grown at high altitudes. Charabot's observations are supplementary to these, and prove that the more intense the chlorophyll function, the greater the power of dehydration of the alcohols, and therefore the greater the ester value of the oil. This has been demonstrated clearly in the case of lavender oil, when it is generally true that the higher the altitude at which the plants are grown, the higher the ester content. Grown in the neighbourhood of Paris, as before mentioned, the plants yield an essential oil with so low an ester value that it approximates to English lavender oil in composition. The influence of the altitude appears to be due to (1) greater light; (2) drier atmosphere, and (3) lower temperature. The first two of these influences tend to assist esterification, whilst the third acts in a contrary sense, and may even neutralise the others.

In the esterification of an alcohol, water is always formed, according to the equation—

$$\underset{\text{Alcohol.}}{ROH} + \underset{\text{Acid.}}{AH} = \underset{\text{Ester.}}{RA} + \underset{\text{Water.}}{H_2O}$$

This action is reversible, so that to maintain the ester value it is obvious that the removal of water is advantageous. As a matter of fact, if transpiration is increased, or the absorption of moisture by the roots is diminished, the esterification is more rapid.

In regard to the distribution of the essential oil from one organ of the plant to another, it has been established that there is a circulation of the odorous compounds from the green portions of the plant into the flowers, which may be regarded as the consuming organs, and that the constituents which travel through the tissues are, as would be expected, the most soluble present in the oil. Hence as Charabot, Hébert, and Laloue have shown,[1] it results that this phenomenon of circulation and that which governs the chemical transformations which modify the composition of the essential oils, combine their effects when the aldehydes or ketones in question are relatively soluble constituents. In such a case the essential oil of the inflorescences will be appreciably richer in aldehydic principles than the essential oil of the leaves. This is what was found in the case of verbena in which the citral is one of the most soluble constituents of the oil, as clearly indicated from the fact that the portion extracted from the waters of distillation is richer in citral than the portion which is decanted. The essential oil of the inflorescences contains an appreciably higher proportion of citral than the essential oil extracted from the green parts of the plants.

If, on the other hand, the aldehydic or ketonic portion of the essential oil is sparingly soluble, the effects of the phenomenon of circulation on the composition of the essential oils from the various organs will be the reverse of those produced by the chemical changes which take place in the inflorescence, since the principles which are displaced are principally those which are most soluble. The relative insolubility of such ketones and aldehydes will tend to make the oil of the leaves richer in these compounds on account of their restricted power of circulation, and on the other hand, to make the oil of the inflorescences richer in alcoholic principles, whilst the actual formation of these compounds in the inflorescence will have the effect of increasing the proportion of aldehydes or ketones in the inflorescence. The net result depends on which of the two features predominates.

It has been shown while studying the formation and circulation of the odorous products in the wormwood, that the ketone thujone is, contrary to the usual rule for ketones, one of the most insoluble constituents of the oil, and this is why, in spite of the tendency which thujol possesses to become converted into thujone in the inflorescence by oxidation, the essential oil from the leaves is richer in thujone than the flower oil. This is due not only to the fact that the insoluble thujone passes very slowly from the leaves to the flowers, but also to the fact that the thujone which does so circulate, and also the thujone actually formed in the flowers, being already a partially oxidised product on the way to degradation, is the one which is principally consumed by the flower in the exercise of its life function, namely, the fecundation process. In the case of peppermint, the nature of the actual chemical transformations which occur in the green organs has a predominant influence on the distribution of the odoriferous constituents. This was demonstrated by distilling 200 kilos of the plant and collecting 200 litres of distillation water. This water was exhausted by shaking three successive times with petrolium ether, which on evaporation yielded 35 grams of essential oil which had been originally dissolved in the water. The oil obtained by decantation, and that by extraction from the distillation waters gave the following results on analysis :—

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[1] Roure-Bertrand Fils, *Bulletin*, May, **1908**, 4.

	Essential Oil	
	Separated by Decantation	Extracted from the Waters
Specific gravity at 15° C.	0·9194	0·9140
Solubility in 80 per cent. alcohol	Soluble in 1 vol., becoming opalescent on the further addition of alcohol	Soluble in 1 vol., separation of crystals on the further addition of alcohol
Rotatory power	– 11° 28'	– 17° 36
,, ,, of the acetylated oil	– 20° 12'	– 35° 28
Colour	Pale green	Reddish-brown
Acid number	0·2	12·8
Saponification number	43·9	39·1
Ester number	43·7	26·3
Menthyl acetate	15·5 per cent.	9·3 per cent
Combined menthol	12·2 ,,	7·3 ,,
Saponification number of acetylated oil	161·7	198·3
Esters in acetylated oil	57·2 per cent.	70·1 per cent.
Free menthol in original oil	37·4 ,,	56·3 ,,
Total ,, ,, ,,	49·6 ,,	63·6 ,,
Saponification number of the reduced and acetylated oil	188·1	215·9
Saponification number corresponding to the menthone	26·4	17·6
Menthone in original oil	7·4 per cent	4·9 per cent.

Comparing the undissolved essential oil with that which was dissolved in the waters, it is seen that the former is richer in esters, poorer in free menthol and total menthol, and richer in menthone than the second. In other words the relatively sparingly soluble constituents are esters and menthone, whilst menthol is particularly soluble.

The earlier researches of Charabot have shown that the essential oil of the flowers is richer in menthone than the essential oil of the leaves. And it is in spite of a circulation of menthol, a soluble principle, from the leaf to the inflorescence, that this latter organ contains an essential oil particularly rich in menthone. It must therefore be that the menthol is there converted into menthone by oxidation.

The differences in composition between the two essential oils examined show well, if they be compared with those which exist between the essential oils of the leaves and the inflorescences, that the distribution of the odorous principles between the leaf, the organ of production, and the flower, the organ of consumption, tends to take place according to their relative solubilities. But this tendency may be inhibited, or on the other hand, it may be favoured by the chemical metamorphoses which the substances undergo at any particular point of their passage or at any particular centre of accumulation. Thus, in the present case, some of the least soluble principles, the esters of menthol, are most abundant in the oil of the leaves, whilst another, menthone, is richest in the oil of an organ to which there go, by circulation, nevertheless, the most soluble portions. This is because this organ (the flower) constitutes the medium in which the formation of this insoluble principle is particularly active.

Some highly interesting conclusions as to the relationship of essential oils to the botanical characters of the plant have been drawn by Baker

FIG 2 —Types of eucalyptus leaf venations which indicate the presence of certain chemical constituents in the oil. (*Baker and Smith*) For explanation see next page and Smith,[1] as a result of their exhaustive researches on the eucalypts of Australasia These investigators have shown that there is a marked agreement between the chemical constituents of the essential oils of these trees, and the venation of the lanceolate leaves of the several species, so marked, indeed, that in the majority of cases it is possible to state what the general character of the essential oils is by a careful examination of the leaf venation There are three principal types of venation, which are shown in the accompanying illustration (see previous page)

The first type is representative of those eucalyptus trees whose oils contain the terpene pinene in marked quantity, cineol either not at all or only in small amount, and from which phellandrene is absent

The second type is characteristic of trees yielding oils which contain pinene, but are more or less rich in cineol and free from phellandrene

The third type represents trees in which phellandrene is an important constituent

There appears reason to suppose that with the eucalypts a gradual deviation from a type has taken place, and that the formation of characteristic constituents in these oils has been contemporaneous with the characteristic alteration or deviation of the venation of their leaves That the constituents have been fixed and constant in the oils of the several eucalypts for a very long period of time is demonstrated by the fact that whenever a species occurs over a large area of country the constituents of the oil are practically identical also, only differing in about the same amount as is to be expected with the oils from trees of the same species growing together in close proximity to each other. The venation of the leaves of individual species is comparatively similar throughout their geographical distribution, and their botanical characters show also a marked constancy All this comparative constancy is probably accounted for by the long period of time that must have elapsed before a particular species could have established itself as such over so extensive a range over which they are found to-day

EXPLANATION OF PLATE.

1 Leaf of *Eucalyptus corymbosa*, Sm.—This venation is indicative of the presence of pinene in the oil Note the close parallel lateral veins, the thick mid-rib, and the position of the marginal vein close to the edge of the leaf The yield of oil from leaves showing this venation is small, there not being room between the lateral veins for the formation of many oil glands

2 Leaf of *Eucalyptus Smithii*, R T B —This venation is characteristic of species whose oil consists principally of eucalyptol and pinene. Note the more acute lateral veins which are wider apart, thus giving more room for the formation of oil glands, the yield of oil is thus larger in these species The marginal vein is further removed from the edge and is slightly bending to meet the lateral veins

3 Leaf of *Eucalyptus radiata*, Sieb —This venation is characteristic of those species whose oil consists largely of phellandrene and the peppermint ketone Note the still more acute and fewer lateral veins. The marginal vein has also become so far removed from the edge that a second one occurs and the slight bending, as seen in 2, has culminated in this group in a series of loops The spaces for the formation of oil glands are also practically unrestricted and a large yield of oil is thus obtainable

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[1] *Journ and Proc Roy Soc* N S W, xxxv 116, and *Report* to British Association, Section B, Manchester, **1915**

CHAPTER II.

THE RELATIONSHIP BETWEEN ODOUR AND CHEMICAL CONSTITUTION.

THE connections between chemical constitution, on the one hand, and colour or physiological action on the other have been continually studied for many years, but the allied property of odour has only engaged occasional attention within quite recent times.

The reason for this apparent neglect is not far to seek and lies largely in the fact that no adequate means have yet been devised for measuring and classifying odours.

The most noteworthy attempts to remedy this defect are those of Zwaardemaker, C. van Dam,[1] and Fournie,[2] but for details of the "olfactometers" devised by them the original papers should be consulted. These instruments are of distinct value for the matching of perfumes but they all suffer from a fundamental defect inasmuch as they make no allowance for the relative vapour pressures of the substances under examination.

The strength of an odour, up to a certain point, will depend upon the amount of substance which reaches the nostrils; it is therefore necessary that this factor should be taken into account when comparing odours. In the ordinary manner of smelling we have to deal with a mixture of the vapour of the substance and air. The maximum amount of substance which can thus be conveyed depends on the vapour pressure of the substance and this in turn depends on the temperature, being greater when hot and lesser when cold. In order therefore to make any comparisons of a fundamental nature the vapour pressure factor must be allowed for.

It is the almost universal practice to record the nature and strength of an odour at the particular temperature which may obtain at the time of examination. Substances at their temperatures of boiling have a common vapour pressure equal to that of the atmosphere, but it is clearly impossible to smell a substance in such a condition, whereas, if we could go to the other extreme, the absolute zero, it is probable that no vapour would exist as such and for this reason alone, apart from any physiological one, no odour would be discernible.

To operate at a fixed definite vapour pressure is also an obvious impossibility, since this would involve a large range of temperature sufficient to cause physiological complications.

H. Erdmann[3] considers that the volatility of a perfume does not depend on its vapour tension alone but also on its specific solubility in the air. This he deduced from the fact that certain bodies lose, more or less completely, their odours in liquid air, but that on shaking the mixtures the odours become strongly apparent. He argues therefore that

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[1] *Jour. Chem. Soc.*, A. i. **1917**, 606.

[2] *P. and E.O.R.*, **1917**, viii. 278.

[3] *Jour. Prakt. Chem.*, **1900**, 225.

the perfumes dissolved in the liquid air evaporate with it in spite of the fact that the temperature is in the region of – 190° C.

This is a doubtful conclusion since if temperature-vapour tension curves for volatile substances be examined it will be seen that at low temperatures the rate of diminution of the vapour tension falls off rapidly and hence the vapour tension at – 190° C. is often not vastly different from what it is at normal temperature, and hence is not by any means negligible when we take into account the very small quantity of substance that needs to be inspired in order for its odour to be perceptible.

It has been satisfactorily demonstrated by Henning that the vapours of odoriferous substances obey the general gas laws, and there is consequently no need to assume any additional factor of the nature of specific solubility.

A. Durand[1] attributes the sense of smell to "odourant ions". He found that bodies such as musk and camphor greatly increase the condensing power of dust free air for aqueous vapour and that the more strongly odorous the air is, the greater becomes that effect, the amount of condensation being proportional to the number and the size of the ions in the air. He considers that it is upon these "odourant ions" that the sense of smell depends, and that this accounts for the fact that hygrometric conditions influence the sense. When air containing the perfume is inspired, the odourant ions are retained in the olfactory region and give rise to the sensation of smell.

The fact that the hygrometric state of the air influences the sense of smell is probably more validly explained by the fact that moist air is capable of carrying a larger proportion of the vapour of a volatile substance than is dry air.

It is interesting in this connection to note that Zwaardemaker[2] has found that dilute aqueous solutions of odorous substances when sprayed from an earthed sprayer yield a cloud having a positive charge of electricity. He found that on diluting these solutions to such an extent that the electrical phenomenon is only just appreciable, the odour is also just appreciable, but he found that the phenomenon is exhibited by other substances which are inodorous but physiologically active. In a similar manner Backmann[3] compared the smallest quantities of benzene, toluene, xylene, cumene, and durene that can be detected by the olfactory organ. He found that the quantity diminishes as the number of substituent methyl groups increases, also that the electrical charge produced by spraying equimolecular aqueous solutions increases from benzene to xylene and then diminishes.

In spite of the coincidences shown above it is doubtful if there is any connection between odour and electrical charge. Heller[4] discards the view that odour is of an electrical nature and criticises very severely an electronic theory put forward by Tudat.[5]

Teudt considers that the nasal sensory nerves have electron vibrations which are increased by resonance when odoriferous substances having corresponding intramolecular electron vibrations are inspired with air, and he concludes that a chemical element can the more readily induce odour in

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[1] *Comptes Rendus*, **1918**, 166, 129.

[2] *Jour. Chem. Soc.*, **1917**, A. ii. 63; **1918**, A. ii. 351; **1920**, A. ii. 74.

[3] *Ibid.*, **1917**, A. i. 498.

[4] *P. and E.O.R.*, **1920**, 38.

[5] *Ibid.*, **1920**, 12; and *Jour. Chem. Soc.*, **1919**, A. i. 607.

its compounds in proportion as its electrons are more firmly united to the atomic nucleus

While there is little reason seriously to consider Teudt's first conception, yet there is some justification for his second one, because the osmophoric elements are all grouped together in the periodic table and are therefore likely to have a fundamental common characteristic

Of historical interest is Tyndall's observation,[1] made so long ago as 1865, that gases with an odour possess the power of absorbing radiant heat to a marked degree Grijns[2] in 1919 was not able to detect any relation between the intensity of the odour and its power of absorbing radiant heat, and he therefore concluded that the stimulation of the olfactory apparatus is not effected by the liberation of energy absorbed from radiant heat.

The actual mechanism or process involved in the operation of smelling is not exactly known The most important investigation in this direction is that of Backmann[3] He observed that in order that a substance may be odorous it must be sufficiently soluble in both water and in the lipoid fats of the nose cells The odours of the saturated aliphatic alcohols first increase as the molecular weight increases and then decrease The lower alcohols are comparatively odourless because of their low degree of solubility in the lipoid fats, while on the other hand the highest members are odourless because of their insolubility in water The intermediate alcohols which are soluble in both fats and water have powerful odours. Backmann used olive oil in his experiments as a substitute for the lipoid fats.

This explanation is probably applicable to the results recorded by Passy,[4] who found that with the homologous aliphatic acids the strength of the odour—as measured by the reciprocal of the smallest quantity that could be perceived—of formic acid is comparatively small, a maximum is reached with butyric acid and after diminution to the weak œnanthic acid, another maximum is reached with pelargonic acid, thereafter the odour diminishes very rapidly

Backmann's conclusions are of the highest importance and give a reasonable explanation of many facts concerning the odours of substances, such as the almost invariable rule that substances of high molecular weight are odourless, the increase in the strength of the odours of members of a homologous series to a maximum and subsequent diminution, the lack of odour with the sugars and so on Possibly also the consistent lack of odour of polyhydroxy alcohols generally and of polycarboxylic acids may be satisfactorily explained in a similar manner

In this connection it is interesting to recall Kremer's experiments[5] By means of a spectroscopic method, Kremer demonstrated that when air saturated with an odoriferous substance such as pyridine or camphor is bubbled through a liquid containing a lipoid—such as a suspension of lecithin of a fatty animal tissue in Ringer's solution—more of the odoriferous substance is adsorbed than when the saturated air passes through water only

It appears from this that some sort of reaction, physical or chemical, takes place between odoriferous bodies and the lipoid fats of the

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[1] *Heat as a Mode of Motion*, London, **1865**, 366

[2] *Jour Chem. Soc* , A i **1919**, 423

[3] *J Physiol Path général*, **1917**, 17, 1 , *Jour Chem. Soc* , A i **1918**, 88.

[4] *Zeit Angew Chem.*, **1900**, 103

[5] *Jour Chem Soc* , A. i. **1917**, 607.

olfactory organ. Ruzicka[1] goes so far as to define an odoriferous body as one which is soluble in the air (*i.e.* volatile) and which reacts chemically with substances in the mucous membrane of the nose stimulating the nose nerves. Haller[2] also considers that the action is undoubtedly of a chemical nature and that the odoriferous molecule undergoes a change of some kind.

That odoriferous bodies must undergo a change in the nose follows from the simple fact that the sensation only lasts for a short while after the removal of the source of odour. The substances in the mucus membrane by means of which the odoriferous body is "fixed" are termed "osmoceptors" by Ruzicka.

The well-known phenomenon of smell-fatigue is explained by the theory that actual chemical reaction takes place between the odoriferous body and some reacting material in the nose; thus it can easily be conceived that some sort of addition reaction takes place and that directly the osmoceptor in the nose becomes saturated no further reaction is possible and no further odour can be appreciated until fresh osmoceptor has been formed. Ruzicka has suggested that two such osmoceptors are involved since substances inspired in a concentrated state have odours different to those perceived in a dilute condition. He suggests that one osmoceptor reacts more readily than the other and in consequence is the more readily saturated or consumed, this osmoceptor is responsible for the sensation produced when dilute odours are inspired. If the odour be concentrated, the first osmoceptor is saturated almost instantaneously and then the sensation produced is the result of the reaction between the odoriferous substance and the second osmoceptor.

These conceptions fit in very well with the facts and are probably not far from the truth.

It seems likely that the sequence of events in the process of smelling is, after the odoriferous substance has reached the nostrils, first for the substance to dissolve in the aqueous outer layer, thence passing to the lipoid fats, wherein an addition reaction takes place, causing a change of energy which produces a sensation perceptible to the nervous centre.

It will be realised that the strength of an odour may suffer successive diminutions in the process of smelling. It will be governed firstly, by the vapour pressure of the odoriferous body, secondly, by the degree of solubility of the substance in water, thirdly, to its relative solubility in the lipoid fats with respect to that in water, and, lastly, to the speed of the chemical reaction. To a less extent the type of odour is similarly governed and this may account for the many "shades" of odour that exist. It is obvious that too much importance must not be placed on the chemical aspect of the problem, especially as regards the strength of an odour.

The first publication of importance regarding the relationship between odour and chemical constitution *per se*, is that of Klimont,[3] who attempted an explanation on the lines of Witt's colour theory.[4] Klimont introduced the term "aromataphore" to designate groups which carry a pleasant odour with them.

Rupe and Majewski[5] renamed such groups "osmophores" and de-

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[1] *P. and E.O.R.*, **1920**, 37. [2] *Ibid.*, 39.

[3] *Die Synthetische und Isolierten Aromatea*, Leipzig, **1899**.

[4] *Berichte*, **1876**, 522 and **1888**, 325. [5] *Ibid.*, **1897**, 2444, and **1900**, 3401.

fined them as groups which confer a characteristic odour; such groups are:—

$—OH$; $—O—$; $—CHO$; $—CO.CH_3$; $—OCH_3$; $—NO_2$; $—CN$; $—N_3$.

They stated that the influence of these groups is not easily definable with exactness and that the presence of other groups may modify profoundly their effect, even so far as entirely to suppress the odour.

Rupe and Majewski attempted to determine by experiment the influence of the relative positions of osmophores on each other in the same molecule. In the case of the three methyl tri-azo-benzoates no great difference in the type of odour exists, only a difference in the strengths, the para compound being the strongest and the ortho the weakest. Of the three methoxy-acetophenones, as another example, the meta isomer is almost odourless in comparison with the ortho and para.

Rupe also found that one osmophore can be replaced by another without greatly altering the type of the odour, thus vanilline, *p*-nitroguaiacol, and *p*-cyanoguaiacol all have similar odours but varying in strength.

Cohn[1] instanced a similar phenomenon in the similarity of the odours of, benzaldehyde, nitro-benzene, benzonitrile, azimidobenzene, and phenyldi-imide. He developed the "osmophore" theory and introduced the terms "kakosmophore" and "enosmophore" to indicate those groups which impart an upleasant and a pleasant odour respectively. The kakosmophore groups are :—

$—SH$; $—S—$; $—NC$; $—As=$but $—CN$ is enosmophoric.

Cohn also drew attention to the fact that the molecular weight must not be excessive if the substance is to have an odour, and that it frequently happens that the addition of more osmophores to an odoriferous molecule results in odourlessness due to an excessive molecular weight.

It should be noticed that the similarity between the osmophore theory and Witt's chromophore colour theory does not extend much beyond the initial conception and there seems to be no connection between the odour and the colour of a body, it is indeed quite the exception for a body to have both a strong odour and a strong colour. Two prolific sources of colour, *viz.* the diazo group and a large molecule have no counterpart as regards odour, and it is probably only by chance that quinone and chroman both have pronounced odours and are the sources of colour.

The lack of connection between the two phenomena is, of course, to be expected since colour is an objective phenomenon whereas odour is subjective, or, as Ruzicka puts it, colour has a physical and odour a chemical influence on the human senses.

Cohn points out that position isomerism is of the greatest importance as regards the odours of isomerides, this is strikingly instanced in the case of the tri-nitro tertiary butyl xylenes since the only one possessing the powerful musk odour is that in which the nitro groups are situated each in the meta position to the two others; again the ortho-amidobenzaldehyde has a strong odour but the meta and para isomerides are odourless.

Cohn concludes that with benzenoid bodies "side chains" only impart odour when they occupy the ortho or para positions relatively to one another, and he further states that the 1.3.4 positions are the most

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[1] *Die Riechstoffe*, **1904**.

favourable for the production of odour. Many instances can be quoted in refutation of these statements. It is, however, an undoubted fact that the para isomers tend to possess stronger and more pleasant odours than either the ortho or the meta.

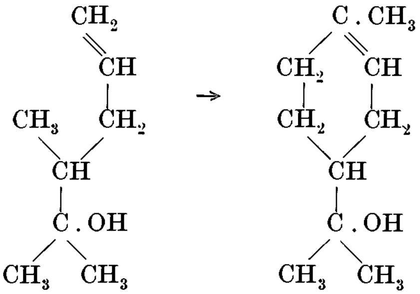
One of the most important publications on this subject, considered from the chemical side, is that of Gertrude Woker.[1] This investigator drew attention to the importance of multiple bonding. The double bond is often accompanied by a pleasant, but the triple or acetylenic linkage generally produces a disagreeable smell: a multiplicity of double bond can produce an effect equivalent to a triple bond.

Inasmuch as the terms pleasant and disagreeable are merely relative, these statements are not capable of being accurately examined, but without doubt there is a strong tendency for multiple bonding to produce a strengthening of the odours.

Woker attributes this fact to an internal tension or strain caused by the multiple bonding and the consequent increase in the volatility of the body. Thus by loading one and the same carbon atom in a molecule with the same or similar groups each having the same "polarity,"—as in the case of tertiary compounds—great intramolecular repelling forces are set up, and this results in the well-known camphor type of odour which almost invariably accompanies compounds with tertiary carbon atoms. A group of opposite "sign" operates against the other three and has a great influence, thus —COOH will greatly weaken the effect of three methyl groups.

Woker attempts to apply this strain theory to ring compounds, and considers that the five carbon atom ring produces less strongly odoured substances than any other and points out that, according to Baeyer's strain theory, the five carbon ring has the least internal tension. It is very doubtful if this contention is correct, since the penta-methylenes do not seem to be less strongly odoured than other polymethylene ring compounds.[2]

Woker points out that the closing of a chain compound to form a ring compound does not affect the odour much, thus the aliphatic terpineol of W. H. Perkin, Jr.,[3] 2·3 di-methyl 5 hexenol 2 has a very similar odour to α-terpineol, their respective formulæ being :—



2·3 di-methyl 5 hexenol 2. α-Terpineol.

If the closing of the chain involves the disappearance of double bonds

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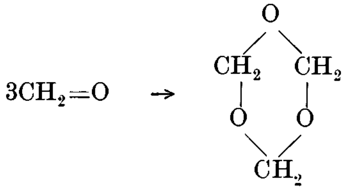
[1] *Jour. Phys. Chem.*, **1906**, x. 455

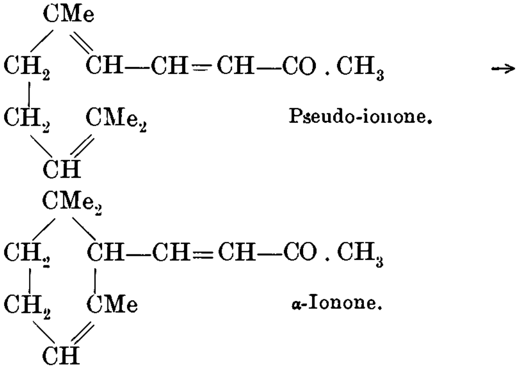
[2] *Cf. P. and E.O.R.*, May, **1919**, 115, 123.

[3] Schimmel's *Report*, April, **1907**, 113.

the odour also diminishes, thus formaldehyde polymerises to the odourless trioxymethylene.



Woker has apparently overlooked the classic example of the conversion of pseudo-ionone to ionone.



Pseudo-ionone.

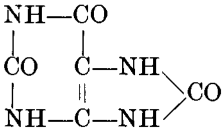
α-Ionone.

This transformation involves both the closing of the ring and the disappearance of a double bond, and the result is an enormous strengthening of the odour.

Woker considers the cases of elements other than carbon, hydrogen and oxygen, and shows that if the last be replaced by sulphur the odour becomes more marked and less pleasant; also that nitrogen when functioning as a trivalent element, frequently imparts a characteristic ammoniacal odour; if it be bound to another atom by two bonds the odour is intensified and deteriorates in quality. Phosphorous likewise frequently imparts a disgusting odour to its compounds, and the odour of hydrogen phosphide becomes progressively more penetrating when its hydrogen atoms are successively replaced by alkyl, phenyl, or tolyl radicles, the tertiary phosphines causing positive pain when smelt, but this last fact is probably due to the reaction which takes place between tertiary phosphines and water in the nose.

Arsenic, antimony, and bismuth all impart unpleasant odours to their compounds, and Woker points out a highly important fact that it is only when the total valency of these elements is not employed that these odours are produced.

Woker points out the apparent anomaly presented by uric acid.



Uric acid is odourless in spite of three carbonyl groups, four trivalent nitrogen atoms and a double bond, and that it is similarly colourless in spite of four chromophores. Measurements of its refractive and dispersive properties indicate that it is a saturated body which suggests that molecular attraction exists between the various groups.

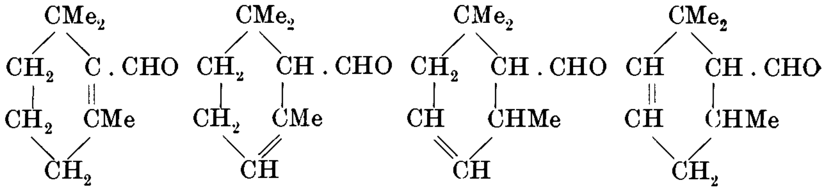
The explanation of the odourlessness of this acid probably rests on physical grounds. It is extremely insoluble in water and in oils, and is practically non-volatile.

In 1909 Mehrling and Welde[1] investigated experimentally the cause of the "violet" odour of the ionones.

They formulated the rule that:—

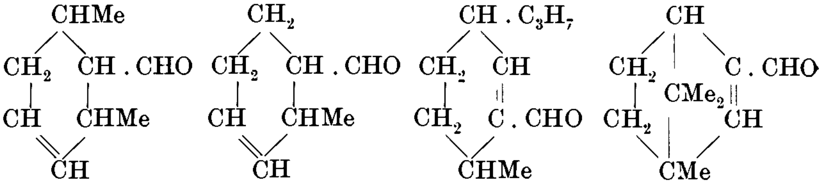
"The aldehydes of cyclogeraniolene (or Δ^{6} 1 · 3 · 3 tri-methyl cyclohexene) form with acetone, bodies having a violet odour, so long as the aldehyde group is next to the methyl or to the di-methyl group or to both, and the intensity of the violet odour increases with the number of aldehyde groups in the neighbourhood of the methyl. The odour of the acetone condensation product disappears when the aldehyde group is removed from the neighbourhood of the methyl."

Thus in the case of the four cyclocitrals:—



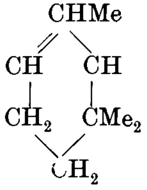
their acetone condensation products all have an odour of violets, being respectively β-ionone; α-ionone; α-irone; and β-irone.

Mehrling and Welde first determined if hydro-aromatic ring aldehydes in general gave violet like odours when condensed with acetone, and it was found that in the case of the four following aldehydes only the first yields a body having a violet odour:—

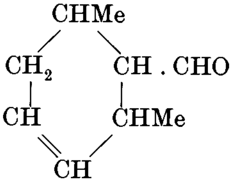


the other yielding bodies having odours of fenchone and camphor.

They concluded, therefore, that in order to obtain the violet odour the side chain must be connected to a cyclogeraniolene ring, *e.g.*:—



or



etc.

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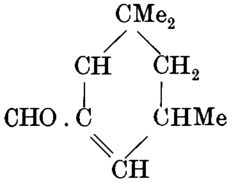
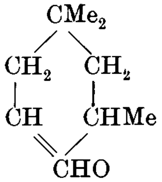
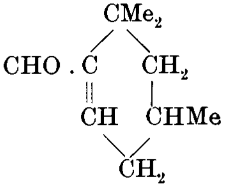
[1] *Annalen*, 366, 119.

In order to determine if any other condition is necessary they condensed acetone with the following isomers of the cyclocitrals :—







and so obtained isomers of the ionones and irones.

The first of these cyclocitrals yielded an almost odourless product, but the two others gave violet odoured bodies, hence they concluded that the violet odour is only obtained when the side chain $—CH{=}CH . CO . CH_3$ is next to a methyl group in the cyclogeraniolene ring.

To the conditions enunciated by Mehrling and Welde might be added that the side chain must be unsaturated since di-hydroionone only has a faint odour, and also that the violet odour is occasionally present with bodies of quite different structure from the ionones, for instance Δ′ 2·2·4 tri-methyl-tetra-hydro-benzaldehyde.

They next determined if the property of forming this violet odour rests in the grouping—CMe_2—C(CHO)—CMe—such as occurs in the cyclocitral ring, but it was found that the simplest aldehyde with this grouping, *viz.* iso-propyl butyl aldehyde, $CHMe_2 . CH(CHO)CH_2Me$ when condensed with acetone yields a body having only a floral and not a violet odour.

Austerweil and Cochin[1] in 1910 published the results of an experimental investigation into the chemical nature of bodies having a rose odour. The citronellol molecule was modified by the introduction of various groups, but it was found that no very profound change results when one or two methyl groups are introduced by substituting the hydrogens attached to the carbon atom adjacent to the hydroxyl group. Thus, citronellol,[2] $CMe_2{=}CH . CH_2 . CH_2 . CHMe . CH_2 . CH_2 . OH$, has a rose like odour ; 1 methyl citronellol,

$$CMe_2{=}CH . CH_2 . CH_2 . CHMe . CH_2 . CHMeOH,$$

has the same odour but more pronounced, and suggestive of tea roses. 2 Di-methyl-citronellol, $CMe_2{=}CH . CH_2 . CH_2 . CHMe . CH_2CMe_2OH$, has the rose odour but is also slightly camphoraceous (as is to be expected with a tertiary alcohol) ; 1 ethyl citronellol has a very fine odour of roses and 2 di-ethyl-citronellol is like the di-methyl compound but the rose odour is more pronounced ; 1 phenyl citronellol is very strong.

They concluded that the rose odour accompanies the alcoholic group whether primary, secondary, or tertiary, that is to say is represented by the group $—CH_2CRROH$, where R is either a hydrogen atom or an alkyl or aryl group. Semmler[3] had previously noticed that the rose odour is only evinced with an eight carbon atom chain in combination with the group $—CH_2 . CRR . OH$, thus di-methyl-heptenol,

$$CMe_2{=}CH—CH_2—CH_2 . CMe_2 . OH,$$

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[1] *Comptes Rendus*, 150, 1693.

[2] There is some doubt concerning the formulæ quoted here, but the conclusions are no· vitiated thereby.

[3] *Die Aetherischen Oele*, Vol. I, 249 250.

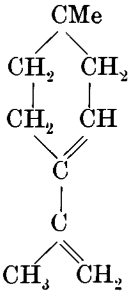
has a fruity but not a rose odour. It should be noted, however, that saturated alcohols with eight and nine carbon atom chains such as octyl and nonyl alcohols do not have a rose odour, and it seems as if the presence of a double bond is also necessary for a distinct rose odour to exist.

Similar results with geraniol were published in the following year.[1] It was found that 1 methyl geraniol,

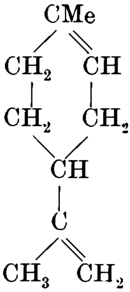
$$CMe_2{=}CH\,.\,CH_2\,.\,CH_2\,.\,CMe{=}CH\,.\,CHMeOH,$$

has a pronounced odour of geraniums, 1 ethyl and 2 di-ethyl-geraniol are more like the original alcohol. Austerweil and Cochin concluded that the more the group —CRR . OH increases in importance the less the influence of the neighbouring double bond since 1 phenyl geraniol has a geranium odour strongly reminiscent of roses; further that the odour changes from the rose to the geranium type on the introduction of a second double bond.

W. H. Perkin, Jr., and his collaborators during the course of an extended investigation into the synthesis of the terpenes recorded some interesting facts. It was found that $\Delta^{3\cdot 8/9}$ *p*-menthadiene has an even more pronounced lemon odour than $\Delta^{1\cdot 8/9}$ *p*-menthadiene (dipentene)



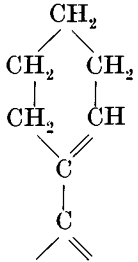
$\Delta^{3\cdot 8/9}$ *p*-menthadiene.



Dipentene.

and the conclusion was drawn that the lemon odour was independent of the position of the double bond. On removing the double bond from the ring there results $\Delta^{8/9}$ *p*-menthene and the lemon odour disappears, giving place to a faint parsley odour; similarly Δ^{3} *p*-menthene which has one double bond in the ring and none in the side chain also only have a faint odour. It follows that both double bonds are necessary for the lemon odour to be manifest.

The methyl group, para to the isopropyl, modifies, but is not essential for, the production of the lemon odour since $\Delta^{3\cdot/89}$ nor-menthadiene is very like lemons in odour.



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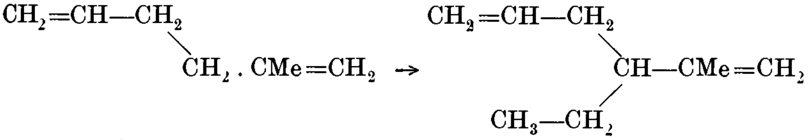
[1] *Comptes Rendus*, 151, 440.

It should also be noted that the lemon odour is not confined to the para isomers, as it is even more pronounced in several of the ortho and meta bodies, although generally modified.

Perkin pointed out that open chain compounds, which are analogous in structure to a terpene, show a certain similarity in behaviour, thus the addition of an ethyl group to 2-methyl 1 5-hexadiene by converting it into 2-methyl 3-ethyl 1·5-hexadiene changes the unpleasant acrid odour into a pleasant one reminding of lemon and peppermint



$$\mathrm{CH_2{=}CH{-}CH_2{-}CH_2\,.\,CMe{=}CH_2} \rightarrow \mathrm{CH_2{=}CH{-}CH_2{-}CH(CH_2{-}CH_3){-}CMe{=}CH_2}$$

2-methyl 1 5-hexadiene. 2-methyl 3-ethyl 1·5 hexadiene

Turning again to the theoretical aspect. Electrical theories have been advanced by Teudt,[1] Aronsohn, Zwaardemaker, and others, but little attention need be paid to these

Durrans[2] in 1919 attempted to develop a theory based on the examination of the odours of substances considered class by class, and expressed the opinion that, from a chemical point of view, odour is caused primarily by the presence of unsatisfied or residual affinity, but that the possession or otherwise of an odour by a body depends on physiological and physical as well as chemical properties. This theory, which is named the "Residual Affinity Theory of Odour," demands that if a substance has an odour, it must answer to the following requirements —

1. It must possess free or residual affinity.

2 It must be sufficiently soluble in both the water and the lipoid fats of the nose

3 It must be volatile in order that it can reach the nostrils

If a body be what we term odourless, its odourlessness may be due to its failure to satisfy any one or more of these demands.

The second of the premises of the residual affinity theory has already been dealt with here, the third is obvious, it remains therefore only to consider the first

The "Residual Affinity Odour Theory" can have both a qualitative and a quantitative conception since the nature, distribution, and amount of affinity may vary from substance to substance. It is well known that bodies of similar type and construction frequently have similar odours This fact was drawn attention to by Parry[3] who instanced the various types of odoriferous alcohols —

1. The fruity odours of the higher fatty alcohols

2. The soft rose-like and similar odours of the di-olefinic alcohols of the geraniol type.

3. The soft heavier odours of the cyclo substituted aliphatic alcohols such as benzyl and phenyl-ethyl alcohols

4 The sharp (camphoraceous ?) alcohols of the terpene alcohols of the borneol type.

5 The heavy "oriental" odours of the sesquiterpene alcohols

6. The phenolic odours

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[1] *P and E O R* , Jan. **1920**, 12, Feb. **1920**, 38.

[2] *Ibid* , 21 May, **1919**, and Dec. **1920**, 391.

[3] *Ibid.*, May, **1916**, 129.

As other instances of typical "class" odours might be quoted:—

Para substituted phenol ethers	Aniseed
Ring substituted dihydroxy benzenes	Quinone
Cyclohexane alcohols	Menthol
Menthenols	Terpineol
Menthadienes	Lemons
Ketenes	Piercing
Aldehydrates	Intense lemon
Acetals	Soft ethereal
1·2-di-ketones	Quinone.

Very many other examples might be quoted, but these suffice to show that each of the classes of substances quoted has some common inherent characteristic quite apart from questions of volatility, solubility, or physiological action.

Durrans attributes this concurrence to the unsatisfied or residual affinity of the molecules, the residual affinity of each molecule being comparable with that of other molecules of the same type, any variation of odour between the substances of one type or between the types being due to variations in the residual affinity either in kind, quantity, or distribution.

This theory takes account of the view that the sensation of odour is the result of a chemical reaction in the nose, since in order for a body to be able to enter into chemical reaction the possession of residual affinity is probably a *sine qua non*, but it should be noted that the converse does not hold.

It is easy to conceive that a class of similar bodies possessing similar residual affinities would react with the osmoceptors of the nose in similar manners and in consequence produce similar odours.

It is not easy exactly to determine the amount or distribution of the residual affinity of a molecule, but certain examples afford satisfactory ground for surmise.

Consider the benzene molecule. When not overpowered by other osmophores, it generally imparts a typical "aromatic" odour, but directly the nature of the ring—with all the possibilities of its six "fourth affinities"—is upset by the introduction of two or more hydrogen atoms which are themselves non-osmophoric, an entirely different but still characteristic class odour results. A large change in the residual affinity of the molecule has been accompanied by a large change of odour.

Mere substitution of hydrogen, by a weak osmophore methyl, for instance, does not produce any striking change of odour; this corresponds with the fact that the affinities of the benzene ring are only slightly interfered with in this case. It should also be noted that the hydrobenzenes no longer possess the chemical properties of benzene, being more like aliphatic bodies. This fact is again in accordance with the idea that odour is the result of a chemical reaction in the nose.

Another interesting example to examine is that of the ketenes. These bodies of extremely piercing odour have the general formula $RR'C{=}CO$, and they give ample evidence of unsatisfied affinity, polymerising with exceptional rapidity, combining easily with water and alcohols and condensing with other substances in many ways. If the double bond of the ketenes be hydrogenated there result the corresponding ketones, which are much milder in odour, much less reactive, and which show much less evidence of unsatisfied affinity.

Unsaturated bodies, generally, have stronger odours than the corresponding saturated compounds and are known to possess more residual affinity than the latter, and to be more reactive chemically. Thus for example the very pungent dipropargyl or 1·5-hexadiine, which is very reactive chemically, corresponds to the stable and nearly odourless saturated hexane; other pairs which might similarly be enlarged upon are allyl and *n*-propyl alcohols; carbon suboxide and propylene glycol; crotonic aldehyde and *n*-butylaldehyde, and so on.

The effect of a particular element on the odour of its compound seems also to lend support to the "residual affinity" theory, for it is only the elements which possess residual affinity in certain of their compounds, which function as osmophores. Oxygen, nitrogen, sulphur, phosphorous, halogens, arsenic, antimony, bismuth, etc., whose valencies vary under certain conditions are powerfully osmophoric whereas carbon, hydrogen, and many others which have a constant valency are practically non-osmophoric, and it is very instructive to note that the element is osmophoric when it is not employing its full number of valencies and theretore has free affinity.

By far the larger number of elements are non-osmophoric because they or their compounds fail to satisfy one or more of the three essential conditions of the residual affinity theory. Thus the majority of salts cannot have an appreciable odour because of two reasons—non-volatility and non-solubility in the lipoid fats, also in many cases the chance of the existence of free, residual affinity is remote. These defects are not necessarily inherent in the atom itself but may be due to its manner of combination; thus arsenic, when functioning as a metal, does not yield odoriferous compounds, for example, arsenious chloride, in spite of its high volatility, is odourless. But when it is part of a radical, it frequently gives rise to bodies of great pungency such as cacodyl As_2Me_4; the fact that cacodyl readily takes fire in air is good evidence that it possesses unsatisfied affinity.

The osmophoric elements are all closely associated in the periodic table and are therefore likely to have a fundamental common characteristic and the property of varying valence is one of their common characteristics, whereas it seldom occurs with the non-osmophoric elements.

If in an odoriferous body the atoms with which the possibility of free affinity exists be replaced by others where such possibility does not exist the odour is removed. Thus cacodyl would yield the odourless ethane; methyl iodide would give methane; ethyl hydro-selenide would yield ethane, and so on.

It seems evident therefore that the unsatisfied affinity of an odoriferous body plays a fundamental part in the production of its odour by reason of one or more chemical reactions taking place in the olfactory organ; the reactions must necessarily be complicated and rapid. They are at present entirely unknown and problematical, but no very great progress in the knowledge of this subject is likely to be made until the chemical properties of the osmoceptors have been determined.

CHAPTER III.

THE following groups of compounds will be described in the present chapter:—

1 Hydrocarbons.
2. Sesquiterpenes.
3 Alcohols.
4 Esters
5 Aldehydes.
6 Ketones.
7 Phenols and phenolic compounds
8 Oxides and lactones.
9 Nitrogen compounds.
10 Sulphur ,,
11. Free acids.

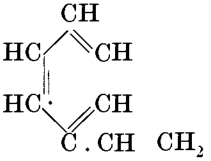
1. HYDROCARBONS.

HEPTANE.

The aliphatic hydrocarbon heptane, C_7H_{16}, has recently been discovered as a constituent of the oil obtained by the distillation of the resinous exudation of *Pinus Sabiniana*, *Pinus Jeffreyi*, and a few other essential oils. It is a highly volatile liquid of specific gravity 0·688 and boils at 98° to 99°. It has, probably, the lowest specific gravity of all liquids found naturally in essential oils

STYROLENE

Styrolene, C_8H_8, also known as styrol, is phenyl-ethylene, of the constitution.



It is a very aromatic oil, useful in some bouquets, and is found naturally in storax and other balsamic substances. It is prepared by various methods, amongst them being the heating of cinnamic acid with lime to 200°. It is a colourless, highly refractive liquid having the following characters —

Specific gravity	0·9074
Refractive index	1·5403
Boiling point	140° to 145°

It yields two sets of halogen derivatives, the α-derivatives—for example, bromostyrolene, $C_6H_5CH : CHBr$—and the β-derivatives, such as $C_6H_5CBr : CH_2$. The β-products are useless in perfumery, but the α-products are highly odorous bodies, possessing a powerful odour of hyacinths. α-chlorostyrolene is obtained by the action of caustic alkali on dichlorethyl-benzene. α-bromostyrolene is obtained by boiling dibrom-hydrocinnamic acid with water. α-chlorostyrolene boils at 199°, and α-bromostyrolene melts at 7° and boils at 220°.

Styrolene yields a dibromide, $C_6H_5\ CHBr . CH_2Br$, melting at 74° to 74·5°.

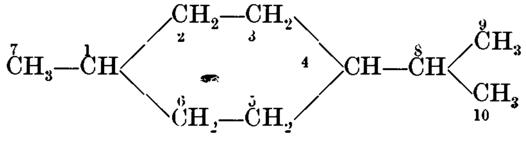
DIPHENYL-METHANE.

This hydrocarbon, $C_6H_5 . CH_2 . C_6H_5$, is a synthetic body, with an odour which is in the main that of geranium leaves, but which also has a suggestion of oranges. It has lately come into considerable vogue, together with the corresponding body, diphenyl-oxide, as the basis of artificial geranium oil. It can be prepared by treating benzyl chloride and benzene with zinc-dust; or from methylene chloride, benzene, and aluminium chloride; or by the reduction of benzophenone with zinc-dust. It is a crystalline body melting at 26·5°, and boils at 261°.

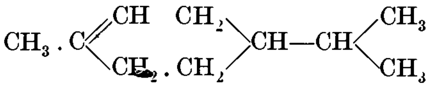
TERPENES.

The terpenes proper are mostly volatile liquids—rarely solids—all having the formula $C_{10}H_{16}$; they form the principal portion, from a quantitative point of view, of an enormous number of essential oils, but rarely have any great odour value. They are easily decomposable, especially under the influence of air, moisture, and light, and it is the decomposition of the terpenes in an essential oil, due to age or faulty storage, which is the most frequent cause of the oil spoiling. Since most terpenes boil within a comparatively narrow range, it is somewhat difficult to separate them in a state of purity. Even when converted into crystalline compounds from which the terpene is regenerated, there is a possibility of molecular rearrangement, so that the regenerated terpene may be different from the original. Hence the fact that numerous terpenes have been described from time to time, which are in reality impure forms of a well-known terpene with traces of some other body. This is especially true of pinene which has been described under numerous other names. The ease with which molecular rearrangement takes place in many terpenes, renders evidence of constitution based on analytical reactions of these bodies of doubtful value, and it is only in the case of those terpenes which have been synthesised that their constitution can be regarded as definitely settled.

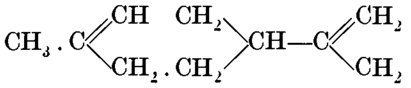
The type substance upon which the nomenclature of the terpenes is based is hexahydro-*p*-cymene, which is termed *p*-menthane, the carbon atoms being numbered as shown in the following formula:—



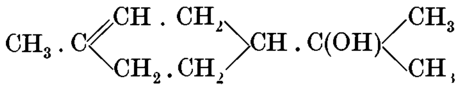
Following the usual rules of chemical nomenclature, the examples below are readily understood —



containing one double linking, is $\Delta\ ^{1}$*p*-menthene.

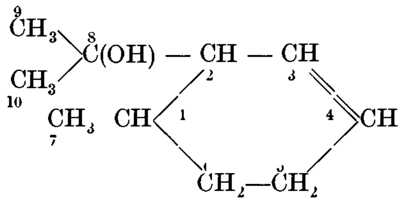


or limonene, containing two double linkings, is $\Delta\ ^{1}\ ^{8}(^{9})$-*p*-menthadiene.

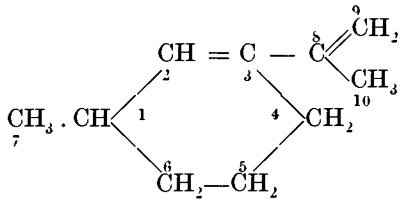


or terpineol is $\Delta\ ^{1}$-*p*-menthenol (8), the (8) referring to the ol, or hydroxy group.

The abbreviated nomenclature of the compounds of the *ortho* and *meta*-series follows the same rules. For example —



is Δ^{3}-*o*-menthenol 8.



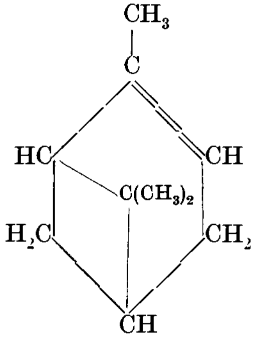
$\Delta\ ^{2\cdot 8}.(^{9})$-*m*-menthadiene

Pinene.

There are four distinct terpenes known under this name, namely, α-pinene, β-pinene, δ-pinene, and isopinene. It must be emphasised, however, that they are all of different constitution, and the customary nomenclature is ill-chosen, as they should be known by entirely different names.

Pinene in one form or another has been described under numerous names, such as terebenthene, australene, eucalyptene, laurene, olibene, and massoyene, all of which are more or less impure forms of α-pinene or β-pinene.

α-pinene is the most commonly occurring terpene found in nature, and, according to most modern views, has the following formula —



α-pinene is an optically active terpene, which occurs both in the dextro-rotatory and the laevo-rotatory forms, but is not found in the inactive form, except as a mixture in unequal quantities of the two active forms, with a varying specific rotation.

It is obtained from American turpentine as dextro-α-pinene, or from French turpentine as laevo-α-pinene. It is also obtained in a very pure form as dextro-α-pinene from Greek oil of turpentine. Optically inactive α-pinene can be obtained by regeneration from the nitrosochloride. The purest specimens of α-pinene yet obtained have the following characters:—

	Dextro-α-Pinene.	Laevo-α-Pinene.
Boiling-point	155° to 156°	155° to 156°
Specific gravity at 15°	0·864	0·865
Refractive index at 20°	1·4656	—
Specific rotation	+ 48·4°	- 48·6°

Optically inactive α-pinene can be obtained by heating α-pinene nitrosochloride with aniline.[1] It has the following characters:—

Boiling-point	155° to 156°
Specific gravity	0·862
Refractive index	1·46553
Optical rotation	± 0°

Wallach [2] has also obtained laevo-α-pinene by heating nopinol-acetic acid in a current of hydrogen.

α-pinene forms a number of well-defined crystalline compounds, several of which serve for its identification. Of these one of the best known is the nitrosochloride. This body was discovered by W. A. Tilden, who prepared it in the following manner: the pinene is dissolved in two to three times its volume of petroleum ether, cooled to 0°, and an 8 per cent. solution of nitrosyl chloride in equal volumes of petroleum ether and chloroform added with constant stirring, care being taken that the temperature is kept as near 0° as possible. When the reaction is over alcohol is added, and the crystalline precipitate is separated, washed with alcohol, and dried at 50°. The melting-point of the compound is usually given as 103°, but by careful crystallisation from a chloroform solution it can be raised to 115°. It is possible that the true melting-point is about 109°, and that higher figures may be due to decomposition into nitroso-pinene. Tilden stated that only very small yields of the nitrosochloride, which is optically inactive, could be obtained from

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[1] Wallach, *Annalen*, **252**, 132; **258**, 343.

[2] *Ibid.*, **368**, 1.

α-pinene with a high optical rotation: the lower the optical rotation of the pinene used, the higher is the yield of nitrosochloride obtained. The formula for pinene-nitrosochloride has been assumed to be $C_{10}H_{16}NOCl$, but Baeyer showed it to be a bi-molecular compound of the formula $(C_{10}H_{16}NOCl)_2$, and always consists of equal quantities of the nitrosochlorides of the two optically active forms of α-pinene. Hence its optical inactivity. Where the pinene, from which it is derived, is highly optically active, that is, contains much excess of one of the optically active forms, the nitrosochloride of that active form is the result of the reaction. This body, however, is very unstable and tends to become inverted to optical inactivity, but during the inversion so much heat is liberated that the bulk of the nitrosochloride is decomposed. This, then, is the explanation of the fact that the yield of nitrosochloride is in inverse ratio to the optical activity of the α-pinene.

In the preparation of the nitrosochloride, Wallach proposed to use pinene in glacial acetic acid and amyl nitrite. Ehestadt has recently proposed the following method, which is very simple and yields excellent results: The pinene (or oil of turpentine) is diluted with its own volume of ether, the solution cooled with ice, and the gas generated by dropping a saturated solution of sodium nitrite into concentrated hydrochloric acid passed through the solution. Fine crystals of pinene-nitrosochloride soon commence to separate out. Schimmel & Co. obtained the following yields of nitrosochloride by the methods quoted:—

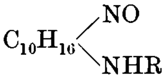
Rotation of Pinene.	Per Cent. (Tilden).	Per Cent. (Wallach).	Per Cent. (Ehestadt).
+ 11° 10'	10 per cent.	30-31·4 per cent.	37·5 per cent.
+ 40° 23'	—	4 ,,	4·6 ,,
− 33° 42'	—	9-11 ,,	10 ,,
± 0°	—	20 ,,	22 ,,

Nitroso-pinene is obtained from pinene-nitrosochloride by the action of alcoholic potash,

$$C_{10}H_{16}NOCl + KOH = C_{10}H_{15}NO + KCl + H_2O.$$

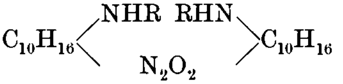
Nitroso-pinene may be prepared for identification purposes as follows: To a solution of 12 grams of sodium in 30 c.c. of 90 per cent. alcohol, 100 grams of pinene-nitrosochloride are added. The mixture is boiled on a water-bath, under a reflux condenser, until the reaction is complete. Water is added, the clear solution filtered from insoluble impurities, and the filtrate poured into excess of acetic acid. The nitroso-pinene separates as an oil which solidifies to a yellowish mass in a few days. This is broken up, washed with water, and dried on a porous plate. It can be recrystallised from acetic ether, when it is obtained in the pure condition, and then melts at 132°.

Pinene-nitrosochloride forms a series of compounds with various bases, such as propylamine, amylamine, benzylamine, etc., known as pinene-nitrolamines. If two molecules of benzylamine in alcoholic solution be allowed to act on one molecule of pinene-nitrosochloride, pinene nitrol-benzylamine separates on the addition of water, and on recrystallisation from a mixture of ether and alcohol, forms beautiful rhombic crystals melting at 122° to 123°. *Dextro*-α-pinene and *laevo*-α-pinene yield the same optically inactive nitrolamines. The corresponding nitrol-piperidine melts at 118° to 119°. Wallach considers the formula for the nitrolamines to be—



$$C_{10}H_{16}\Big\langle\begin{matrix}NO\\ NHR\end{matrix}$$

whilst Baeyer considers them to be bi-molecular and to have the formula—



$$C_{10}H_{16}\Big\langle\begin{matrix}NHR\quad RHN\\ N_2O_2\end{matrix}\Big\rangle C_{10}H_{16}$$

An important compound for the identification of pinene is the hydrochloride $C_{10}H_{16}HCl$, a body once known as artificial camphor, on account of its odour being very similar to that of natural camphor. This body is obtained by saturating well-cooled perfectly dry pinene with dry hydrochloric acid gas. If the reagent is moist or the temperature be allowed to rise, the terpene molecule suffers rearrangement and some dipentene dihydrochloride is formed. Pinene hydrochloride is a volatile substance, having a camphor-like odour, and melts at 127°. The optical properties of pinene hydrochloride are peculiar. Wallach states that the hydrochloride from *laevo*-pinene is laevo-rotatory, whilst that from *dextro*-pinene is optically inactive. Long,[1] however, has shown that this is not correct, and in this has recently been fully confirmed by Tsakalotos and Papaconstantinou.[2] The laevo-rotatory hydrochloride prepared by Wallach had a specific rotation $-30{\cdot}7°$, and the last-named chemists have prepared numerous samples from *dextro*-pinene, whose specific rotation varied only between $+33°$ and $+33{\cdot}4°$.

Pinene hydrobromide, $C_{10}H_{16}HBr$, is prepared in a manner similar to that described for the hydrochloride. It melts at 80° and has a specific rotation of about $+30°$ or $-30°$, according to the rotation of the pinene from which it is prepared.

Sometimes, on account of the difficulty in preparing the nitrosochloride from a highly active α-pinene, it is necessary to examine the oxidation products before it is possible to come definitely to a conclusion as to the presence or absence of the hydrocarbon. Pinene yields numerous acids as the result of oxidising processes, so that the method of preparing the product to be examined must be rigidly adhered to if useful results are to be obtained. The terpene is transformed into pinonic acid, $C_{10}H_{16}O_3$, in the following manner: A solution of 233 grams of potassium permanganate in 2000 c.c. of water is placed in a flask, and an emulsion of 100 grams of the hydrocarbon in 600 c.c. of water is gradually added in small portions. The mixture is kept cool by means of a current of cold water, and shaken continuously. The oxidation products are then treated as follows: The liquid is filtered from manganese oxide, and evaporated to about 1000 c.c., saturated with carbon dioxide, and the neutral and unaltered compounds removed by extraction with ether in the usual manner. The crude pinonic acid is separated from its potassium salt by sulphuric acid and is then extracted with ether. If β-pinene be present, nopinic acid will be present

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[1] *Jour. Amer. Chem. Soc.*, **21**, 637.

[2] *Jour. de Pharm. et de Chim.*, **1916**, 97.

amongst the oxidation products. This forms a highly insoluble sodium salt, and is removed in this form.

There appear to be either several isomerides of pinonic acid, or such closely related oxidation products as to render the purification of the acid a matter of great difficulty. The characters of the *dextro-* and *laevo-*rotatory forms of this acid have, however, been settled by the researches of Barbier and Grignard[1] and Schimmel & Co.[2]

By oxidation of *d-* and *l-*pinene of high rotatory power, Barbier and Grignard obtained the optically active forms of pinonic acid. *l-*pinene from French turpentine oil (boiling-point 155° to 157°, $\alpha_D - 37\cdot2°$; 157° to 160°, $\alpha_D - 32\cdot3°$) was oxidised with permanganate. From the product of oxidation, which (after elimination of the volatile acids and of nopinic acid) boiled at 189° to 195° under 18 mm. pressure, *l-*pinonic acid separated out in long crystalline needles, which, after recrystallisation from a mixture of ether and petroleum ether, melted at 67° to 69°. The acid was easily soluble in water and ether, fairly soluble in chloroform, and almost insoluble in petroleum ether. Its specific rotation is $[\alpha]_D - 90\cdot5°$ in chloroform solution. Oximation produced two oximes; one, laevo-rotatory, melting-point 128°; and the other, dextro-rotatory, melting-point 189° to 191°.

*d-*pinene from myrtle oil (boiling-point 155° to 158°; $d\frac{14°}{4°}$ 0·8635; n_D 1·46977; $[\alpha]_D + 39\cdot4°$) yielded upon oxidation a mixture of racemic and *d-*pinonic acids. The latter melted at 67° to 68° and showed the same properties as the acid described above, except as regards its specific rotatory power, which was found to be $[\alpha]_D + 89\cdot0°$. By mixing the two active pinonic acids the inactive form, melting-point 104°, was obtained. Oximation produced the two oximes corresponding to the above. A preparation obtained by Tiemann from α-dihydroxy-dihydrocampholenic acid by means of distillation, and described as *l-*pinonic acid (melting-point 98° to 99°; oxime melting-point 147°) possibly represents, according to Barbier and Grignard, a stereo-isomeric acid.

Schimmel & Co. have published the following method, based on the oxidation of α-pinene to pinonic acid, and β-pinene to nopinic acid, for the identification of pinene in mixtures, such as, for example, with limonene in the case of lemon oil: Five c.c. of the oil or fraction of the oil containing pinene is shaken with 12 grams of powdered potassium permanganate, 2·5 c.c. of sodium hydroxide, and 700 c.c. of iced water for about three hours. The mixture is then saturated with carbonic acid gas and distilled with steam to remove any unoxidised products. After filtration the liquid is evaporated in a current of carbon dioxide to about 200 c.c. and repeatedly extracted with chloroform to remove impurities. Gradually, on further evaporation, a crystalline incrustation appears, which is principally the highly insoluble sodium salt of nopinic acid, the oxidation product of β-pinene. This is separated by means of a suction filter and treated with dilute sulphuric acid, when nopinic acid, $C_{10}H_{16}O_3$, readily separates out in crystals which melt at 125°. If nopinic acid be oxidised by passing a current of steam through water in which the acid and lead peroxide are suspended, the ketone, nopinone $C_9H_{14}O$, is produced. This substance is a liquid ketone of unmistakable odour, forming a semicarbazone melting at 188·5°. The oxidation products of α-pinene remain in

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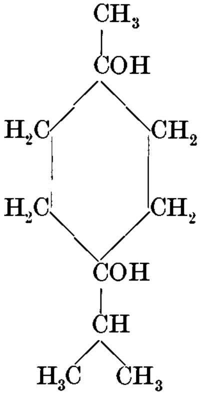
[1] *Comptes rendus*, 147 (**1908**), 597.

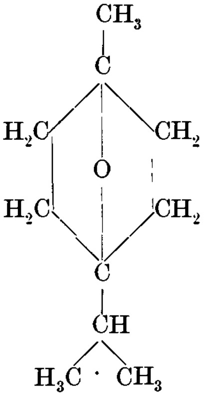
[2] *Report*, April, **1909**, 120.

the mother liquor after filtering off the sodium nopinate. At present, however, no satisfactory method has been devised for separating this, unless it be present in a comparatively large amount, when its semicarbazone can be prepared, which melts at 204°.

The hydration product of α-pinene is particularly interesting. If pinene be allowed to remain in contact with dilute mineral acid for some time, at ordinary temperature, terpin hydrate, $C_{10}H_{18}(OH)_2 + H_2O$, is formed. The best method for the preparation of this body is as follows: A mixture of 8 parts of pinene, 2 parts of alcohol, and 2 parts of nitric acid, of specific gravity 1·250, is placed in a flat evaporating basin. After standing for several days the liquid is poured off from the crystalline crust which is formed, and neutralised with alkali, when a second crop of crystals is obtained. The successful preparation of this compound depends largely on the temperature of the atmosphere, and the best yield is obtained during the cooler part of the year. Terpin hydrate, which also results from the oxidation of limonene and dipentene, under suitable conditions, crystallises from alcohol in transparent, well-defined monoclinic prisms, soluble in 200 parts of cold water and in 22 parts of boiling water. It melts at 116° to 117°. When distilled, or dried over sulphuric acid, anhydrous terpin is formed. This body, $C_{10}H_{18}(OH)_2$, melts at 104° to 105°, and probably has the constitution indicated below, which suggests that it is the hydrated compound of cineol or eucalyptol:—



Terpin.



Cineol.

It is convenient to here mention the hydrocarbon verbenene, $C_{10}H_{14}$, on account of its relationship with pinene. It results from the action of acetic anhydride on verbenol, the alcohol corresponding with the ketone, verbenone. So produced it is laevo-rotatory. The dextro-rotatory and racemic varieties are also known.[1] The sesquiterpenes have the following characters when regenerated from their respective dibromides:—

	l-Verbenene.	*d*-Verbenene.
Specific gravity	0·8866	0·8867
Specific rotation	− 100·61°	+ 100·71°
Refractive index	—	1·4980

They yield beautifully crystalline dibromides melting at 70° to 72° and having a specific rotation ± 298°. The racemic dibromide melts at 50° to 52°.

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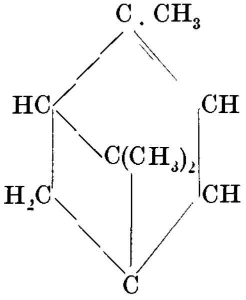
[1] *Berichte*, 1921, **54**, 887; *Annalen*, 1913, i., 495.

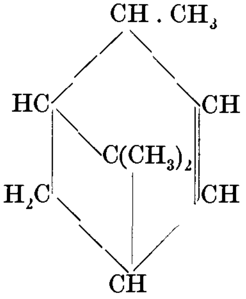
l-Verbenene is reduced by sodium and alcohol to dihydroverbenene, which is so closely related to pinene that it has been named δ-pinene. This body has the following characters —

Boiling-point	158° to 159° at 762 mm.
Specific gravity	0·865
Refractive index	1·4662
Specific rotation	+ 36·52°

It yields ordinary pinene hydrochloride when treated in the usual manner with hydrogen chloride. Verbenene and δ-pinene have the following constitutions —



Verbenene.



δ Pinene.

β-pinene, which is also known as nopinene, is found associated with α-pinene in turpentine oil, and in numerous other terpene-containing essential oils. The properties of β-pinene, in as pure a state as it has been obtained, are as follows —

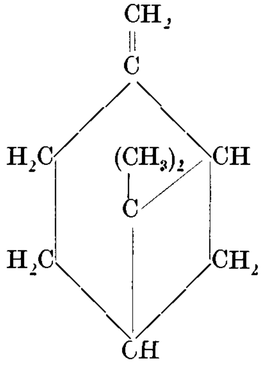
NATURAL β-PINENE (FROM HYSSOP OIL).

Boiling point	164° to 166°
Specific gravity	0·865
Optical rotation	− 19° 29′
Refractive index	1 4755

The artificially obtained terpin, prepared as described below, has the following characters —

	(1)	(2)
Boiling-point	162° to 163°	162° to 163°
Specific gravity	0·866	0·8675
Refractive index	1·4724	1·4749
Optical rotation	− 22° 20′	− 22° 5′

β-pinene has the following constitution .—



Wallach[1] has prepared this terpene artificially in the following manner: The starting-point for the preparation of the hydrocarbon was the ketone nopinone, which is the oxidation product of nopinic acid, which itself results from the oxidation of β-pinene or nopinene. By treating nopinone with bromacetic acid in the presence of zinc-dust, the ethyl ester of nopinolacetic acid was obtained. This body, on dehydration by means of acetic anhydride yields, together with other products, β-pinene, which has the characters given above.

β-pinene does not yield a nitrosochloride. By treatment with dry hydrochloric acid it yields a mixture of bornyl chloride and dipentene dihydrochloride. The terpene is best identified by oxidation to nopinic acid, as described under α-pinene, or, when existing in more than very small quantity by the following method of procedure :—

Three parts of the oil or fraction containing much β-pinene are well shaken with a solution of 7 parts of potassium permanganate in 90 parts of water, with 1·5 parts of caustic soda. When reaction is complete, the product is steam distilled, and the residue, after removal of unaltered products, filtered from the manganese oxide. The filtrate is reduced to 30 parts by evaporation, and the nopinate of sodium separated by cooling the liquid. Excess of dilute sulphuric acid is added, and the nopinic acid so released is extracted by benzene, from which it crystallises in fine needles melting at 125° to 127°. The identification can be completed by the further oxidation of the nopinic acid to the ketone nopinone. Ten grams of the nopinate of sodium are dissolved in 100 c c. of boiling water, and a solution of 3 grams of potassium permanganate in 75 c.c. of water is added, and then 2 grams of sulphuric acid in 20 c.c. of water. The ketone is obtained from the reaction mass by distillation with steam. It yields a semicarbazone melting at 188° to 189°.

Varon[2] considers that α-pinene and β-pinene exist in the following approximate proportions in French, American, and German turpentine oils :—

French Oil.

	Rotation $[\alpha]_j$	Per Cent.
α-pinene	– 39·5°	63
β-pinene	– 19 8°	37

American Oil.

	Rotation $[\alpha]_j$	Per Cent
α pinene	+ 24°	73
β-pinene	– 19·8°	27

German Oil.

	Rotation $[\alpha]_j$	Per Cent.
α-pinene	+ 7·5°	72
β-pinene	– 18·3°	28

Isopinene is a name which has been applied to at least two terpenes. Of these the earliest so-named is that isolated by Aschan[3] by decomposing the liquid chlorides obtained in the process of preparing pinene hydrochloride, by the action of bases. He thus obtained a hydrocarbon which he termed pinolene, $C_{10}H_{16}$, boiling at 145° to 146°. By converting pinolene into its hydrochloride, and then removing the hydrochloric acid by means of aniline, he prepared a terpene, which he termed isopinene,

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[1] *Annalen*, **245**, 251.

[2] *Comptes rendus*, 149 (**1909**), 997.

[3] *Berichte*, **40** (1907), 2250.

boiling at about 156°. Both terpenes yielded a hydrochloride melting at 36° to 37°, which appear to be identical.

Further investigations showed that the two hydrochlorides are identical in all respects. Moreover, pinolene is not a single body, but a mixture of at least two hydrocarbons which the author has called α-and *β-pinolenes*. The separation of the two isomerides may be effected by the action of potassium permanganate at 60° to 80° C.: α-pinolene is completely destroyed, whilst the β-isomeride persists.

β-pinolene has the following characters :—

Boiling-point	142° to 144°
Optical rotation	+ 0° 28'
Specific gravity	0·8588
Refractive index	1·4477

Its molecular refraction is 42·37, appearing to indicate a tricyclic compound, whilst the value calculated for a tricyclic body $C_{10}H_{16}$ is 41·83.

β-pinolene, when saturated in ethereal solution with dry hydrogen chloride, at 15° C., yields a very readily liquifiable *hydrochloride*, melting at 25° to 26° C., which does not appear to be identical with the hydrochloride obtained from crude pinolene. Aniline converts it into pure *isopinene.*

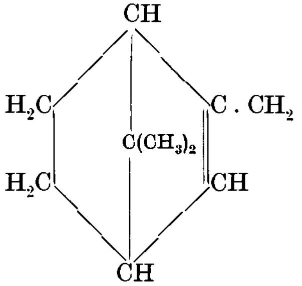
The isopinene used in subsequent researches was obtained by fractionating the pinolene boiling at 144° to 145° C., a mixture of the α- and β-isomeride, then treating it with hydrogen chloride and removing this acid by means of aniline. The hydrocarbon obtained was purified by oxidation with permanganate in acetone solution. It possesses the following constants :—

Boiling-point	154° to 156°
Specific gravity	0·8677 at $\frac{20°}{4°}$
Optical rotation	+ 2° 30′
Refractive index	1·47055

When purified by conversion into its hydrochloride and regenerated by means of aniline, its properties were practically unaltered, as follows :—

Boiling-point	154·5° to 155·5°
Specific gravity	0· 658 at $\frac{20°}{4°}$
Optical rotation	+ 2·61°
Refractive index	1·47025

According to Aschan the formula for isopinene is—

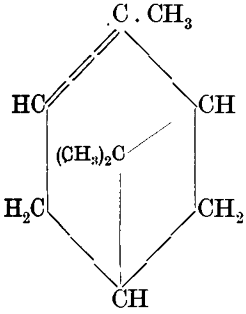


which is the formula proposed by Wallach for fenchene. The relationship of this body to Wallach's fenchene is still a matter of uncertainty, and requires further investigation (*see vide* under Fenchene, p. 55).

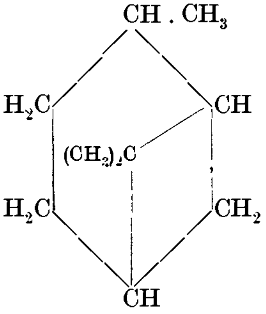
Zelinsky,[1] apparently overlooking Aschan's isopinene, has imprŏperly appropriated the same name to a quite different terpene.

He prepared this in the following manner:—

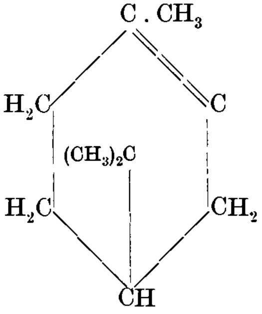
l-α-pinene (boiling-point 155° to 155·5°; $d\,\frac{20^\circ}{4^\circ}$ 0·8587; $[\alpha]_D$ − 43·81°; n_{D20° 1·4652) in absolute ethereal solution was allowed to react with palladium black. After a few hours hydrogen was passed into the liquid at ordinary temperature, giving rise to a terpene possessing the following constants: boiling-point 158·5° to 159·5°; $d\,\frac{20^\circ}{4^\circ}$ 0·8573; $[\alpha]_D$ − 38·09°; n_{D20° 1·4641. It does not form a crystalline hydrochloride or nitrosochloride. Zelinsky assumes that α-pinene first absorbs hydrogen, with the formation of hydropinene, and that *iso*pinene results from the latter, according to the following formulæ:—



α-Pinene.



Hydropinene.



*Iso*pinene.

The behaviour of α-pinene towards palladium black is very different when it is exposed for a period of four weeks to the action of hydrogen under very low pressure. In this case it yields hydropinene (boiling point 167·5° to 168°; $d\,\frac{20^\circ}{4^\circ}$ 0·8567; $[\alpha]_D$ − 19·84°; n_{D20° 1·4605).

FIRPENE.

Firpene is a terpene, which may be a chemical individual, but which may be an impure terpene not yet definitely characterised. It was isolated from the turpentine of the "Western fir," by Frankforter and Frary,[2] who found it to have the following physical characters:—

Boiling-point	152° to 153·5°
Specific gravity	0·8598 at 20°
Refractive index	1·47299
Specific rotation	− 47·2°

It yields a crystalline hydrochloride melting at 130° to 131°. This compound is much more easily volatilised than pinene hydrochloride. With chlorine it yields a dichlor-firpene hydrochloride, whilst pinene yields no similar compound. It also yields a crystalline hydrobromide melting at 102°. No crystalline nitrosochloride has been prepared. The melting

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[1] *Berichte*, **44** (1911), 2782.

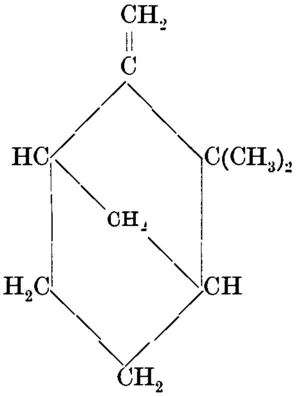
[2] *Jour. Amer. Chem. Soc.*, **1906**, xxviii. 1461.

points of the halogen compounds are barely sufficient to prove that they are not mixtures of pinene and other hydrochlorides, and it is well recognised that the nitrosochloride is extremely difficult to prepare when the pinene is of high optical activity. Hence further evidence is necessary before firpene can be regarded as a terpene of established individuality.

CAMPHENE.

Camphene is the only well-recognised terpene which occurs in nature in the solid condition. It occurs, like pinene, in both optically active forms. The constitution of this terpene has been a matter of considerable difference of opinion, and the constitution assigned to it by Semmler based on its similarity to bornylene was thought by many to be finally accepted. Recent researches, however, have clearly established that the formula assigned to it by Wagner is the correct one.

Wagner's formula is as follows:—



The synthetic evidence in favour of this formula is now quite indisputable.[1]

Camphene has the following characters:—

Melting-point	50° to 52°
Boiling-point	159° ,, 161°
Specific rotation	± 104° (*sed quære*)
Refractive index	1·4550 at 50°
Specific gravity	0·8555 ,, 40°

Camphene is extremely difficult to separate in the solid condition from essential oils, and it may therefore be taken for granted that natural camphene is rarely prepared in the pure condition. The figure given above for the specific rotation is for a sample artificially prepared from pinene hydrochloride.

Camphene is prepared artificially by the isomerisation of pinene with sulphuric acid or by the withdrawal of HCl from pinene monohydrochloride, or by the action of heat in the presence of acetic anhydride on bornylamine, $C_{10}H_{17}NH_2$, which causes the withdrawal of ammonia and leaves camphene, as follows:—

$$C_{10}H_{17}NH_2 = C_{10}H_{16} + NH_3.$$

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[1] Lipp, *Berichte*, **47** (1914), 891; Komppa, *Berichte*, *ibid.*, 934; Haworth and King, *Journ. Chem. Soc.*, **1914**, 1342.

It is best prepared, however, by converting the alcohol, borneol, into bornyl chloride. The bornyl chloride is carefully dried and then gently warmed with an equal weight of aniline. The mixture is then heated to the boiling-point of aniline when the reaction, which is suddenly violent, is quickly completed. The reaction mass is neutralised by hydrochloric acid and distilled over in a current of steam. Camphene is rapidly condensed and solidifies to a crystalline mass.

Camphene is not very stable at high temperatures, and when kept at 250° decomposes to a considerable extent, yielding other terpenes.

The identification of camphene is best carried out by its conversion into isoborneol under the influence of acetic acid in the presence of sulphuric acid. In order to effect this conversion, 100 grams of the fraction containing the terpene in substantial quantity are mixed with 250 grams of glacial acetic acid and 10 grams of 50 per cent. sulphuric acid. The mixture is heated for two to three hours on a water-bath to a temperature of 50° to 60°. At first the liquid separates into two layers, but soon becomes homogeneous and takes on a pale red colour. Excess of water is added, and the oil which is precipitated, and which contains the isoborneol in the form of its acetate, is well washed with water repeatedly. It is then saponified by heating with alcoholic potash solution on a water-bath. The liquid is then evaporated and extracted with water, and the residue recrystallised from petroleum ether.

The isoborneol so formed melts at 212°, but the determination must be carried out in a sealed tube, as the melting-point is very close to the temperature of sublimation. It is, however, very rarely that the isoborneol so prepared is free from impurities, and the melting-point will often be found to be as low as 203° to 205°. It is therefore necessary to prepare derivatives of the isoborneol in order to identify it with certainty. The compound with bromal melts at 71° to 72°. Other compounds will be found mentioned under "isoborneol". By dehydration by means of zinc chloride, isoborneol is easily converted into camphene, melting at about 49° to 50°.

A number of characteristic derivatives of camphene have been prepared of which the following are the most important.

Camphene hydrochloride, $C_{10}H_{16}HCl$, is prepared by passing dry hydrochloric acid into an alcoholic solution of camphene. When recrystallised from an alcoholic solution containing excess of hydrochloric acid, it melts at 155° (or possibly a few degrees lower). Melting-points from 149° to 165° have been recorded for this compound, but the products examined were probably not in a state of purity.

It is possible, however, that camphene hydrochloride is not a uniform body, but that some of the terpene suffers some rearrangement in the molecule by the action of hydrochloric acid, and that the hydrochloride consists of a mixture of α-camphene hydrochloride and β-camphene hydrochloride; there is, however, no evidence to suggest that camphene itself is a mixture of two terpenes, so that the two camphenes are not known to exist. Aschan[1] obtained an alcohol, camphene hydrate, by acting on camphene hydrochloride with milk of lime, a reagent which does not produce molecular rearrangement in the terpene nucleus.

In the same way bornyl and *iso*bornyl chlorides react with milk of lime. But, whereas bornyl chloride gives an almost quantitative yield of

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[1] *Annalen*, **383** (1911), 1.

camphene hydrate, *iso*bornyl chloride yields camphene with traces of camphene hydrate. Camphene hydrochloride yields about equal quantities of camphene and camphene hydrate so that Aschan assumes it to be a mixture of two hydrochlorides, α- and β-camphene hydrochloride, of which the α-modification when treated with alkalis yields camphene hydrate, while the β-modification yields camphene. Assuming this view to be correct, bornyl chloride would consist chiefly of α-, and *iso*bornyl chloride, chiefly of β-camphene hydrochloride.

Aschan has not succeeded in separating α- and β-camphene hydrochloride.

Camphene hydrobromide, $C_{10}H_{16}HBr$, forms well-defined crystals melting at 133°, and the hydriodide melts at about 50°.

Monobromcamphene, $C_{10}H_{15}Br$, is prepared by treating a solution of camphene in four times its weight of alcohol and four times its weight of ether, with the equivalent of two atoms of bromine. Monobromcamphene is also produced by treating camphene hydrochloride with bromine and distilling the product with quinoline. It has, according to Jünger and Klages,[1] the following characters:—

Boiling-point	226° to 227°
Specific gravity	1·265 at 15°
Refractive index	1·5260 ,, 15°
Molecular refraction	52·36

Camphene dibromide, $C_{10}H_{16}Br_2$, is obtained by bromination, and subsequent purification from the monobromcamphene formed. It crystallises from alcohol in colourless prisms, melting at 90°. It is best formed by slowly adding bromine to a solution of camphene in petroleum ether, the mixture being cooled to $-10°$.

Camphene forms a well-defined nitrite, and a nitroso-nitrite, when treated in the following manner: A well-cooled solution of camphene in petroleum ether is mixed with a saturated solution of sodium nitrite, and dilute acetic acid is added. The mixture is well stirred, being kept cool all the time. Camphene nitrosonitrite, $C_{10}H_{16}N_3O_5$, separates and on recrystallisation forms crystals which decompose at about 149°. The petroleum ether solution, which has been filtered off from this compound, is shaken with a concentrated solution of potassium hydroxide, which removes camphene nitrosite, $C_{10}H_{16}N_2O_3$, in the form of its potassium salt. When this is decomposed with acids it yields the free nitrosite. This compound is a greenish oil, with a pleasant odour, easily decomposing when heated to 50°.

After having separated the nitrosonitrite and the nitrosite, the residual solution in petroleum ether is evaporated. There then separates camphene nitrite, $C_{10}H_{15}NO_2$, in fine needles which melt at 66°, and boil at 147° at a pressure of 12 mm.

The oxidation products of camphene are of considerable interest, but as they vary very considerably according to the exact method of oxidation employed, they are not of very great use in the characterisation of the terpene.

When pinene hydrodide is heated with 40 per cent. alcoholic potash at 170° for four hours, a mixture of camphene and a second hydrocarbon is produced. This body, $C_{10}H_{16}$, melts at 97·5° to 98° and has been termed bornylene by its discoverer, Wagner.[2] It is closely related to

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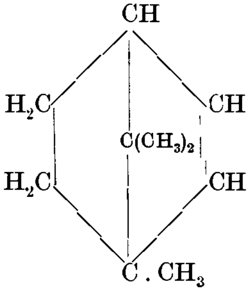
[1] *Berichte*, **29**, 544.

[2] *Ibid.*, **33**, 2121.

camphene, and Wagner proposed to term camphene *iso*bornylene. It is quite certain that the two bodies are different in constitution, since bornylene on reduction by the method of Sabatier and Senderens yields dihydrobornylene, identical with camphane, whilst camphene yields dihydrocamphene which is not identical with camphane. Both camphene and bornylene yield camphenanic and isocamphenanic acid on oxidation, so that they are obviously closely related.

According to Buchner and Weigand,[1] bornylene has the constitution—



FENCHENE.

This terpene is not found in nature, or it so, only to a very minute extent, possibly being present in traces in turpentine and in oil of *Eucalyptus globulus*. It may be prepared by reducing the ketone, fenchone $C_{10}H_{16}O$, to its alcohol, fenchyl alcohol, $C_{10}H_{17}OH$, from which the elements of water can be separated by means of potassium bisulphate at a high temperature, when fenchene, $C_{10}H_{16}$, results. It is, however, certain that the terpene so obtained is a mixture of probably two chemical and several stereo-chemical isomers. According to Wallach[2] fenchene thus prepared is a liquid boiling at 155° to 156°, of specific gravity 0·867 and refractive index 1·4690 at 20°. According to Gardner and Cockburn its boiling-point is 150° to 152°, its specific gravity 0·8667 at 18°, and its optical rotation $-$ 6·46°. Wallach[3] found that when *l*-fenchyl alcohol prepared from *d*-fenchone is treated with phosphorus pentachloride, it yields two fenchyl chlorides, and these in turn yield two fenchenes, one *laevo*- and the other *dextro*-rotatory. They are both derived from dextrofenchene, and Wallach designated them D-*dextro*-fenchene and D-*laevo*-fenchene.

The corresponding hydrocarbons obtained from *l*-fenchone were termed by Wallach L-*d*-fenchene and L-*l*-fenchene, the capital letter being used to indicate the rotation of the parent fenchone, and the small letter that of the terpene.

A terpene yielding isofenchyl alcohol on hydration, which Wallach considers to be one of the fenchenes, was artificially prepared by converting nopinone into a hydroxy ester by means of bromoacetic ester and zinc-dust. The hydroxy ester is dehydrated by potassium bisulphate, and so yields an unsaturated ester, which on saponification yields an acid from which the terpene results by distillation. This fenchene has the following characters:—

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[1] *Ber.chte*, **46**, 2108.
[2] *Annalen*, **(263)**, 149; **(302)**, 376.
[3] *Ibid.* **(302)**, 371; **(315)**, 273.

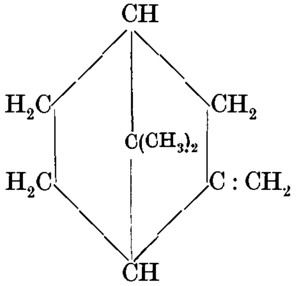
Specific gravity	0·863
Optical rotation	+ 15·93°
Refractive index	1·4699
Boiling-point	158°

By using *d*-fenchone a D-*l*-fenchene was prepared, having an optical rotation − 32°, and yielding a dibromide melting at 87° to 88°.

Up to this point no evidence was forthcoming that any one of the fenchenes prepared was pure, as the optical rotation of nearly every specimen was different. Wallach[1] has, however, more recently prepared fenchene by treating fenchyl-amine with nitrous acid. The resulting terpenes were separated by fractional distillation into two main portions, one of which had the following characters:—

Boiling-point	156° to 157°
Optical rotation	− 32° 12′
Specific gravity	0·869 at 19°
Refractive index	1·4724 ,, 19°

This is the purest D-*l*-fenchene prepared, and it yielded a dibromide $C_{10}H_{16}Br_2$, melting at 87° to 88°. Wallach considers that D-*l*-fenchene has the following constitution:—



Bertram and Helle[2] some years ago prepared a fenchene, which they termed isofenchene, by splitting off water from isofenchyl alcohol. L-*d*-fenchene prepared from *l*-fenchone in a similar manner was found to have an optical rotation + 29°.

By treating D-*l*-fenchene with ozone, a portion of it is converted into D-*d*-fenchene.

Komppa and Roschier[3] now propose a revision of the nomenclature of the fenchene terpenes, Wallach's D-fenchene being termed *α*-fenchene, D-*l*-fenchene becoming *l*-*α*-fenchene, and D-*d*-fenchene becoming *d*-*α*-fenchene. The fenchene obtained by Bertram and Helle's method, by dehydrating fenchyl alcohol with potassium bisulphate, is now termed *β*-fenchene. This nomenclature is certainly preferable as it contains no suggestion that the two bodies are identical in chemical constitution, nor is there any particular evidence that D-*l*-fenchene and L-*l*-fenchene are not the same actual terpene, and equally so in the case of D-*d*-fenchene and L-*d*-fenchene.

Accepting the later nomenclature, *β*-fenchene can be prepared almost free from the *α*- variety by heating fenchyl alcohol with $KHSO_4$. After repeated fractionation over sodium, *β*-fenchene has the following characters:—

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[1] *Annalen* (362), 174.

[2] *Jour. prakt. Chem.* 61 (1900), 303.

[3] *Chem. Zentr.* (1917), i. 407.

Boiling-point	151° to 153°
Specific gravity	0·366
„ rotation	+ 10·7°

On oxidation it yields hydroxyfenchenic acid melting at 138° to 139°. The derivatives of fenchene are not in most cases crystalline, but the optically active α-fenchenes form a dibromide, $C_{10}H_{16}Br_2$, which crystallises well, and melts at 87° to 88°. The racemic form melts at 62°.

By hydration with acetic and sulphuric acids, isofenchyl alcohol is formed, and this can be oxidised to isofenchone.

The following are the characters of various derivatives of the active and the racemic forms :—

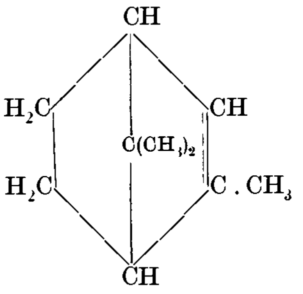
	Melting points of	
	Active Compound.	Racemic Compound.
Fenchene dibromide	87° to 88°	62°
Urethane of isofenchyl alcohol	100° „ 107°	94°
Isofenchone semicarbazone	221° „ 222°	223° to 224°
„ oxime	82°	133°
Monobrom-isofenchone	56° to 57°	46° to 47°
Isofencho-camphoric acid	158° „ 159°	174° „ 175°

Fenchene is more resistant to the action of nitric acid than other terpenes, and may be regarded as of particularly stable constitution.

On page 49 the possible relationships of isopinene and fenchene were mentioned. Komppa and Roschier[1] have prepared a fenchene from α-fencho-camphorone, which they had previously prepared synthetically. The complete synthesis of this fenchene has, therefore, been achieved. α-fencho-camphorone is converted by magnesium methyl iodide into the corresponding alcohol, which is dehydrated by distillation at atmospheric pressure, yielding α-fenchene having the following characters :—

Boiling-point	154° to 156°
Specific gravity at $\frac{20°}{4°}$	0·866
Refractive index	1·47045
Molecular refraction	43·93

It yields a hydrochloride melting at 35° to 37°, which when treated with aniline regenerates the same hydrocarbon, which is identical in all respects with isopinene. The admixture of this fenchene hydrochloride with that prepared from isopinene causes no depression of the melting-point, and Komppa regards the identity of inactive α-fenchene and isopinene as established. He assigns the following constitution to α-fenchene (isopinene) :—



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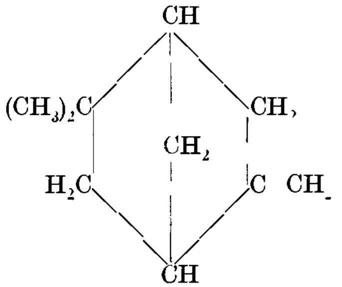
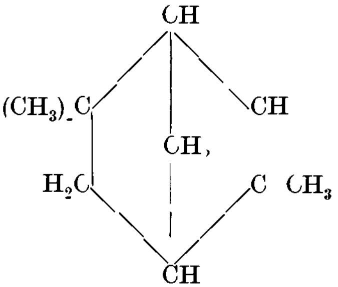
[1] *Ann. Acad. Sci. Fennicae*, 1916, [A], **10**, iii. 3-15; *Journ. Chem. Soc*, 1917 *Abst.*, i. 466.

The latest contribution to the chemistry of this abstruse subject is contained in papers by Komppa and Roschier,[1] and by Roschier.[2] They have obtained a fenchene by treating methyl-β-fenchocamphorol with potassium bisulphate, which is the inactive form of β fenchene, mixed with a small amount of a terpene they term γ-fenchene. β-fenchene (identical with D-*d*-fenchene of Wallach), and γ-fenchene have the following constitutions:—



β Fenchene.



γ Fenchene

Several other synthetic fenchenes are also described.

SABINENE.

This terpene occurs principally in oil of savin, but has also been found in marjoram, cardamom, shô-gyû and a few other essential oils. It is obtained from the fraction of oil of savin which boils below 195°, which amounts to about 30 per cent. of the oil. It has probably not been isolated in a state of absolute purity, but its characters are approximately as follows:—

Boiling point	162° to 166°
Specific gravity	0.846
Optical rotation	+ 66°
Refractive index	1.4675

By systematic fractionation of a large quantity of sabinene obtained from oil of savin, Schimmel & Co. separated the crude terpene into the following fractions:—

Per Cent.	Boiling point.	Specific Gravity.	Rotation.
20	162° to 163°	0.8481	+ 59° 30
49	163° ,, 164°	0.8480	+ 63° 50
31	164° ,, 165°	0.8482	+ 68° 54

By the action of hydrochloric acid gas on sabinene dissolved in acetic acid, terpinene dihydrochloride is produced, melting at 52°. If no trace of moisture is present the monohydrochloride alone is yielded.

By oxidising sabinene with ice-cold solution of potassium permanganate, sabinene glycol, $C_{10}H_{16}(OH)_2$, results. This body melts at 54°, and, together with the above-described hydrochloride serves for the characteri-

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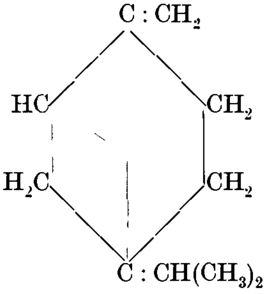
[1] *Ann. Acad. Sci. Fennicae*, 1917, [A], **15**, x. 1-15.

[2] *Ibid.*, 1919 [A], **10**, i. 1.

sation of the terpene. During the oxidation there is also formed sabinenic acid, $C_{10}H_{16}O_3$, an oxyacid which crystallises from water and melts at 57°. If this acid be oxidised with peroxide of lead, sabinene ketone, $C_9H_{14}O$, is formed, which is quite characteristic of the terpene. It has the following characters :—

Boiling-point	213°
Specific gravity	0·945
Refractive index	1·4629
Specific rotation	− 18°

To prepare sabinenic acid for the identification of the terpene, Wallach[1] operates as follows: 10 grams of the crude terpene are mixed with the theoretical amount of potassium permanganate in water at ice temperature. The oxide of manganese is filtered off, the liquid rendered acid and extracted with ether, and the ethereal solution shaken with caustic soda solution. The sodium salt is very sparingly soluble, and is precipitated, collected, and decomposed with dilute sulphuric acid and purified by a further solution in ether. It must be well dried in a desiccator before its melting-point is determined. Sabinene has the following constitution :—



Sabinene appears to be fairly closely related to thujene (tanacetene), since both α-thujene and β-thujene yield the same body, thujane $C_{10}H_{18}$, as does sabinene when reduced by hydrogen in the presence of platinum black.

Considerable difference of opinion exists as to the relationships of sabinene to terpinene, and the conversion of sabinene into terpinene hydrochloride is to be explained by a molecular rearrangement, and cannot be said to be evidence of relationship.[2]

By treating sabinene with formic acid at reduced temperatures Semmler has obtained an alcohol of the formula $C_{10}H_{18}O$ which has the following characters :—

Boiling-point at 11 mm.	93° to 96°
Specific gravity at 20°	0·926
Refractive index	1·48033
Optical rotation	+ 14°

This alcohol is probably identical with the alcohol "origanol" discovered by Wallach in marjoram oil and termed by him terpineol.

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[1] *Annalen*, **357** (1907), 78.

[2] *Ibid.*, **350** (1906), 162; *Berichte*, **39** (1906), 4416, and **40** (1907), 2959.

THUJENE.

Thujene has not been isolated from any essential oil, and the numerous terpenes described under this name are in all probability non-uniform bodies.

The body originally known under this name was prepared by the dry distillation of thujylamine or isothujylamine hydrochloride, and is identical with Semmler's tanacetene.[1]

Tschugaeff prepared thujene by distilling thujyl xanthogenate.[2] This body had the following characters:—

Specific gravity	0·8275 at $\frac{20°}{4°}$
Boiling-point	151° to 152·5°
Refractive index	1·4504

According to its discoverer, this body is the true terpene of the thujone series, and he prefers to call Semmler's thujene or tanacetene, isothujene, as being the true terpene of the isothujone series.

By the dry distillation of trimethyl-thujylammonium hydroxide, Tschugaeff obtained a thujene quite similar to the above, but of considerably higher optical rotation. He therefore considers that two stereoisomers may result from different methods of preparation from thujone.

A hydrocarbon was also prepared by Kondakoff, to which he gave the name thujene, which may have been a crude mixture of the two stereoisomers. The characters of these bodies are summarised in the following table:—

Boiling point	Specific Gravity	Rotation	Refractive Index
Semmler's Thujene—			
60° to 63° (14 mm.)	0·8508 at 15°		1·47600
Wallach's Thujene—			
170° to 172° (760 mm.)	0·8360 „ 15°		1·47145
Tschugaeff's Thujene—			
151° to 152·5° (670 mm.)	0·8275 „ 15°		1·45042
Kondakoff's Hydrocarbon—			
1. 147° to 150°	8·8258 „ 18°	+ 48° 32	1·44929
2. 150° „ 151·5°	0·8260 „ 18°	+ 40° 15	1·45001
3. 151·5° to 152·5°	0·8279 „ 17°	+ 28° 12′	1·44999
4. 152·5° „ 156°	0·8286 „ 17°	+ 12° 1′	1·44909
5. 156° to 168°	0·8286 „ 17°	+ 3° 33′	1·45259

Kondakoff and Skworzow[3] have recently reinvestigated the subject and are of the opinion that all the thujenes so described are mixtures and not uniform bodies. They consider that the lower boiling fractions prepared from thujyl xanthogenate consist of two stereoisomers, and the higher boiling fractions to consist of isothujene with some terpinene. They do not consider that any pure thujene has been prepared, but dextro-thujene in as great a state of purity as they have been able to prepare it has the following characters:—

Specific gravity	0·822
Optical rotation	+ 109°
Refractive index	1·44809

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[1] *Berichte*, **25**, 3345.

[2] *Ibid.*, **33**, 3118.

[3] *Chem. Zentral.*, 1910, ii. 467.

Isothujene dihydrochloride is stated to have the following characters:—

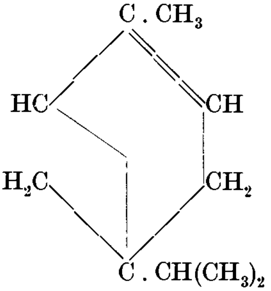
Boiling-point	121·5° to 122·5° at 16 mm.
Specific gravity at 20°	1·0697
Specific rotation	+ 1·86°
Refractive index	1·48458

When this is treated with sodium acetate in alcoholic solution, it yields a hydrocarbon (isothujene?) having the following characters:—

Boiling-point	176° to 180°
Specific gravity at 18°	0·854
Specific rotation	+ 3·11°
Refractive index	1·47586

It is obvious that the chemistry of the thujene isomers requires further investigation.

The following formula has been suggested for thujene, which is in accord with its obvious relationship with sabinene:—



DIPENTENE AND LIMONENE.

Dipentene is the racemic form of the optically active *d*-limonene and *l*-limonene, terpenes which are found to a very large extent in essential oils. Since an equal mixture of *d*-limonene and *l*-limonene is dipentene, it is obvious that whenever optically active limonene is found with a rotation below the maximum, it must contain dipentene. Mixtures of equal quantities of a compound of the optically active limonenes are identical with the corresponding compound prepared from dipentene. It is therefore obvious that the nomenclature is unfortunate and dipentene should be termed *i*-limonene.

Limonene occurs freely in nature, forming the greater part of oils of lemon and orange, and found to a large extent in caraway, dill, bergamot, and many other essential oils.

It has frequently been stated that dipentene has a higher boiling-point than its optically active components, but this is not so, any observation in this direction being undoubtedly due to the presence of minute traces of impurities.

The following are the characters of the most highly purified specimens of limonene which have been prepared:—

	d-limonene.	*l*-limonene.
Boiling-point	175° to 176°	175° to 176°
Specific gravity	0·850	0·8472
Optical rotation	+105°	− 105°
Refractive index	1·4750	1·4746

A specimen obtained by the reduction of limonene tetrabromide by Godlewski and Roshanowitsch[1] had a specific rotation + 125° 36′ which is practically equal to an observed rotation of + 106° 30′, thus confirming the purity of the specimens prepared by fractional distillation.

For the identification of limonene, one of the most useful compounds is the crystalline tetrabromide, $C_{10}H_{16}Br_4$. This body is best prepared as follows: the fraction of the oil containing much limonene is mixed with four times its volume of glacial acetic acid, and the mixture cooled in ice. Bromine is then added, drop by drop, so long as it becomes decolorised at once. The mixture is then allowed to stand until crystals separate. These are filtered off, pressed between porous paper, and recrystallised from acetic ether. Limonene tetrabromide melts at 104.5° and is optically active, its specific rotation being ± 73.3°. The inactive, or dipentene, tetrabromide melts at 124° to 125°. In the preparation of the tetrabromide traces of moisture are advisable, as the use of absolutely anhydrous material renders the compound very difficult to crystallise.

When the limonene to be identified is of high optical rotation, that is, of a high degree of purity in one of its optical forms, the tetrabromide is easy to identify, but in the presence of much dipentene, it is necessary to recrystallise the compound repeatedly before a pure limonene tetrabromide is obtained.

Both limonenes yield nitrosochlorides, $C_{10}H_{16}NOCl$, each of which can be separated into two modifications. There are thus four limonene nitrosochlorides; they are known as the α- and β- varieties of the *dextro-* and *laevo-*rotatory forms of the terpenes. The α- and β- forms, however, yield the same carvoxime on treatment with alcoholic potash.

Here, as in every other case, the only difference between the derivatives of the two limonenes is that they are equally active optically in the opposite directions, and differ in the usual way in crystalline form. The nitrosochlorides, on boiling with alcoholic potash, yield nitroso-limonenes, $C_{10}H_{15}NO$. These are identical with the two carvoximes, and their constitution is probably $C_{10}H_{14}$ NOH. They both melt at 72°. The carvoxime prepared from *dextro*-limonene-nitrosochloride is *laevo*-rotatory, whilst that from *laevo*-limonene-nitrosochloride is *dextro*-rotatory.

Tilden and Leech have prepared nitrosocyanides of limonene by the action of potassium cyanide on the nitroso compounds. The table on opposite page gives the melting-points and optical rotation of the principal of these and other limonene compounds.

For the preparation and separation of the limonene nitrosochlorides the following method should be employed:—

Five parts of the terpene, 7 of amyl nitrite, and 12 of glacial acetic acid are mixed and cooled with ice and salt, and a mixture of 6 parts of hydrochloric acid and 6 parts of glacial acetic acid added in small quantities at a time. Five parts of alcohol are then added and the mixture allowed to stand in a freezing mixture for a time. A mass of crystals separates, which consists of the crude nitrosochlorides. This is filtered off and washed with alcohol. When perfectly dry 100 grams of the crystals are digested with 200 c.c. of chloroform for a few moments and at once filtered. The chloroform dissolves α-nitrosochloride, which is precipitated by the addition of excess of methyl alcohol. The crude compound is filtered off, dried and digested with anhydrous ether for

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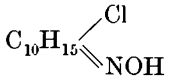
[1] *Chem Zentral*, 1899 i 1241

fifteen minutes, the ethereal solution filtered off and the ether allowed to evaporate spontaneously. The α-nitrosochloride separates in large crystals, which are again dissolved in ether and methyl alcohol added in small quantity. The solvent is now allowed to evaporate slowly, when the pure compound crystallises out. It melts at 103° to 104°.

Compounds.	Dextro- and Laevo Melting-point.	Inactive Melting-point.	Specific Dextro-Rotation.	Specific Laevo-Rotation.
Limonene	—	—	+ 125°	− 125°
α-nitrosochloride	103° to 104°	103° to 104°	+ 313·4°	− 314·8°
β-nitrosochloride	100°	—	+ 240·3°	− 242·2°
α-nitrosocyanide	90° to 91°	81°	+ 152·7°	− 152·2°
Benzoyl-α-nitrosocyanide	108°	96°	+ 126·3°	− 127·2°
β-nitrosocyanide	140° to 141°	159° to 160°	− 31·6°	+ 30·6°
Benzoyl-β-nitrosocyanide	121°	98°	− 108·2°	+ 108·7°
α-amide	138°	155°	+ 174·9°	− 174°
Benzoyl-α-amide	152°	150°	+ 241·7°	− 242°
α-carboxylic acid	97°	116°	+ 102·9°	− 103·9°
Dihydro-carvoxime	88·5°	115°	+ 9·46°	− 9·25°
Tetrabromide	104°	125° to 126°	+ 73·3°	− 76·4°
Carvoxime	72°	93°	− 39·3°	+ 39·7°
Monohydrochloride	—	—	− 40°	+ 39·5°
Nitrobenzylamine	92°	110°	+ 163·8°	− 163·6°

The portion of the mixture of crude nitrosochlorides which was not dissolved by chloroform consists of crude β-nitrosochloride. This is dissolved by shaking with ten times its weight of chloroform. The solution is then filtered and methyl alcohol added and the precipitate filtered off, washed with ether, and dried. The dried compound is dissolved in ether and on evaporation of the solvent pure β-nitrosochloride separates. This body melts at 100°.

According to Wallach the nitrosochlorides are physical isomerides of the formula :—



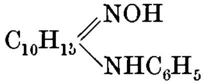
$$C_{10}H_{15}\begin{cases} Cl \\ NOH \end{cases}$$

Very characteristic derivatives are obtained by the action of organic bases on the limonene nitrosochlorides. If *d*-α-limonene nitrosochloride be so treated, two nitrolamines are obtained, α-nitrolamine (dextro-rotatory), and β-nitrolamine (laevo-rotatory). If *d*-β-limonene nitrosochloride be treated in the same manner, exactly the same reaction products are obtained. If, on the other hand *l*-α-nitrosochloride or *l*-β-nitrosochloride be treated in the same manner, a mixture of α-nitrolamine (laevo-rotatory) and β-nitrolamine (dextro-rotatory) is obtained.

The anilides and piperidides are the most characteristic of these compounds. They are prepared by similar methods, of which that for the piperidides is as follows: 20 grams of purified α-limonene nitrosochloride are mixed with 20 grams of piperidine and 60 grams of alcohol, and gently warmed with frequent shaking. When the solution is clear, the warm liquid is poured into an evaporating dish and a small amount of water added. On cooling, crystals of the sparingly soluble impure β-base separate. These are filtered off, and water added to the filtrate which precipates the more soluble α-base. The crude α-compound is dissolved in acetic acid, filtered, and precipitated by ammonia. It is thrown out as an oil, which afterwards solidifies, and is then dissolved in a little petroleum ether, which leaves traces of the β-compound undissolved, and the α-base separates on evaporation of the petroleum ether, and is recrystallised from alcohol. The crude β-compound is dried, digested with cold petroleum ether, which dissolves any α-base present, and the undissolved portion recrystallised from warm petroleum ether with the addition of a little methyl alcohol.

α-limonene nitrol-piperdide forms orthorhombic crystals melting at 93° to 94°, whilst β-limonene piperidide melts at 110° to 111°.

The nitroanilides are very characteristic crystalline compounds of limonene. These have the constitution—



$$C_{10}H_{15}\begin{cases}NOH\\NHC_6H_5\end{cases}$$

To prepare them, 20 grams of pure α-limonene, nitrosochloride are powdered and warmed with 20 c.c. of aniline and 30 c.c. of alcohol, under a reflux condenser. The mixture is heated with constant shaking, and after violent reaction is over the mass is allowed to cool, and when cold, excess of concentrated hydrochloric acid is added. The resulting crystals are filtered off and washed with ether-alcohol. They consist of the hydrochloric acid salt of α-limonene nitrolanilide, and on treatment with ammonia the free base is liberated. When recrystallised from alcohol it melts at 112° to 113°. The filtrate from the hydrochloric acid salt of the α-base is poured into a large volume of water containing free ammonia. The β-anilide gradually becomes solid and is dissolved in three times its weight of warm benzene in order to remove traces of aniline. The β-anilide separates from this solution and forms fine needles melting at 153°.

Limonene forms a monohydrochloride, which is a liquid, and which exists in both optically active modifications. By the action of moist hydrochloric acid on the acetic or alcoholic solution of limonene, no optically active dihydrochloride is formed, the terpene becoming inactive and dipentene dihydrochloride, $C_{10}H_{16}2HCl$, results. This body is prepared when limonene is mixed with half its volume of glacial acetic acid, and a current of hydrochloric acid gas is passed *over* (not *into*) the well-cooled liquid, with frequent shaking. The resulting mass is pressed on a porous plate, dissolved in alcohol, and precipitated with water. It melts sharply at 50°.

Forster and van Gelderen[1] have prepared a characteristic nitro-derivative of dipentene by treating dipentene nitrosochloride with sodium azide. The resulting body, $C_{10}H_{15}(NOH)N_3$, dipentene nitroso-azide, melts at 72° to 73°. The corresponding active limonene derivatives melt at 52° to 53°.

Dipentene, the inactive form of limonene, not only occurs naturally in essential oils, but results by the action of heat on several other terpenes, and to a considerable extent by the action of sulphuric acid on pinene.

Pure dipentene may be prepared by boiling 1 part of pure dipentene dihydrochloride with 1 part of anhydrous sodium acetate and 2 parts

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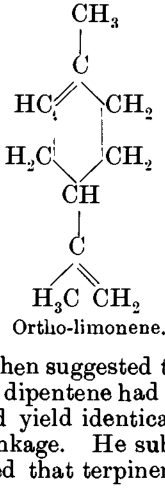
[1] *Proc. Chem. Soc.*, **27** (1911), 195.

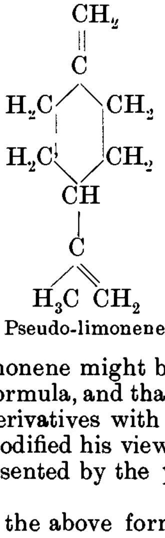
of glacial acetic acid for half an hour under a reflux condenser. The dipentene is distilled with steam and then heated with caustic potash and finally redistilled.

The weight of chemical evidence is strongly in favour of dipentene, being actually *i*-limonene, that is, merely the racemic form of the active limonenes. Semmler has suggested, however, that a slight difference may exist between the constitutions of these terpenes.

He suggested a nomenclature for the terpenes by which those compounds which contain a double linkage between the nucleus and the side chain should be called pseudo-compounds, whilst the compounds with the double linkage in the nucleus should be the ortho-compounds. He suggested the following formulæ:—



Ortho-limonene.

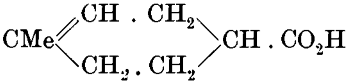


Pseudo-limonene.

Semmler then suggested that ortho-limonene might be ordinary limonene, and that dipentene had the pseudo-formula, and that both these compounds would yield identical halogen derivatives with the breaking of the double linkage. He subsequently modified his view to some extent and considered that terpinene was represented by the pseudo-limonene formula.

There seems no room for doubt that the above formula for "ortho-limonene" is the correct formula for limonene, and the classical synthesis of dipentene by W. H. Perkin, Jun., and his colleagues has proved beyond doubt that it is the correct formula for dipentene or *i*-limonene.

These researches on the synthesis of the terpenes were commenced in 1900, and has been carried on with considerable success and conspicuous ability ever since. It was considered necessary to synthesise terpineol, and so establish the formula which analytic reactions supported. The first necessary step was to synthetically prepare the 1-methyl-Δ'-cyclohexene-4-carboxylic acid,[1] of the formula—



$$\mathrm{CMe}\left\langle\begin{matrix}\mathrm{CH}\,.\,\mathrm{CH_2}\\ \mathrm{CH_2}\,.\,\mathrm{CH_2}\end{matrix}\right\rangle\mathrm{CH}\,.\,\mathrm{CO_2H}$$

and as this acid was at that time unknown, the first problem was to discover some means by which its synthesis could be accomplished.

The acid was prepared in considerable quantities by the following rather complicated series of reactions.[2] When ethyl β-iodopropionate and the sodium derivative of ethyl cyanacetate are allowed to interact in

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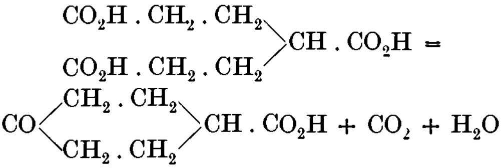
[1] W. H. Perkin, *Lecture to the Pharmaceutical Society*, May, 1912.

[2] *Jour. Chem. Soc.*, **85** (1904), 416 and 654.

molecular proportions at the ordinary temperature, a reaction takes place which results in the formation of ethyl γ-cyanopentane-αγε-tricarboxylate and regeneration of half of the ethyl cyanoacetate :—

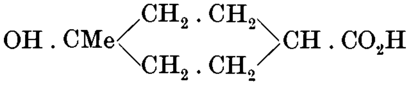
$$2CO_2Et.CHNa.CN + 2ICH_2.CH_2.CO_2Et =$$
$$CO_2Et.C(CN)(CH_2.CH_2.CO_2Et)_2 + CO_2Et.CH_2.CN + 2NaI.$$

This cyano-ester is hydrolysed by boiling with concentrated hydrochloric acid with the formation of pentane-αγε-tricarboxylic acid, $CO_2H.CH(CH_2.CH_2.CO_2H)_2$ and when the sodium salt of this acid is heated with acetic anhydride and distilled, decomposition takes place with the formation of δ-ketohexahydrobenzoic acid or cyclohexanone-4-carboxylic acid—



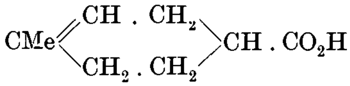
$$\begin{matrix}CO_2H.CH_2.CH_2\\CO_2H.CH_2.CH_2\end{matrix}\rangle CH.CO_2H =$$
$$CO\langle\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\rangle CH.CO_2H + CO_2 + H_2O$$

The next step was to convert cyclohexanone-4-carboxylic acid into 1-methyl-cyclohexanol-4-carboxylic acid, and this is readily accomplished by heating the ester of the ketonic acid with magnesium methyliodide in the usual manner—



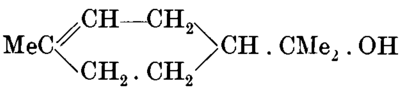
$$OH.CMe\langle\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\rangle CH.CO_2H$$

If the hydroxy-acid is heated with hydrobromic acid, it is converted into 1-methyl-1-bromocyclohexane-4-carboxylic acid, and this is decomposed by boiling with sodium carbonate with loss of hydrogen bromide and with formation of 1-methyl-Δ' cyclohexene-4-carboxylic acid—



$$CMe\langle\begin{matrix}CH.CH_2\\CH_2.CH_2\end{matrix}\rangle CH.CO_2H$$

The last step was to convert the unsaturated acid into its ester and to act on this with an ethereal solution of magnesium methyl iodide, when an almost quantitative yield of an oil was obtained which, on examination, proved to be *terpineol*—

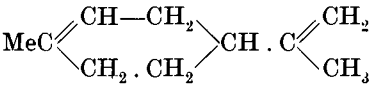


$$MeC\langle\begin{matrix}CH—CH_2\\CH_2.CH_2\end{matrix}\rangle CH.CMe_2.OH$$

the change being simply the conversion of the $—CO_2Et$ group into the group $—CMe_2.OH$.

In order that there might be no doubt as to the identity of the synthetical product, it was converted into the *nitrosochloride*, $C_{10}H_{18}O, NOCl$ (melting-point 122°), and *phenylurethane*, $C_{10}H_{17}O.CO.NH.C_6H_5$ (melting-point 113°), and these were compared with specimens made from ordinary terpineol, with the result that the preparations obtained from the two sources were found to be absolutely identical.

The next step was to convert the synthetic terpineol into dipentene, which was readily accomplished by heating with potassium hydrogen sulphate, when water was eliminated and dipentene formed—



Dipentene.

The *dipentene* produced in this way was converted into the *tetrabromide*, $C_{10}H_{16}Br_4$ (melting-point 125°), the *dihydrochloride*, $C_{10}H_{16}$, 2HCl (melting-point 48° to 50°), and the *nitrosochloride*, $C_{10}H_{16}$, NOCl (melting-point 106°), and these derivatives were compared with the corresponding specimens obtained from ordinary dipentene, with which they were found to be identical in all respects.

Attempts to prepare the active limonenes were unsuccessful, as during the reactions, even when the various acids and the terpineol were separated into their active components, racemisation takes place during the dehydration and the most active product obtained had a rotation of − 5°, so that it consisted essentially of dipentene, with a very small amount of laevo-limonene.

CARVESTRENE AND SYLVESTRENE.

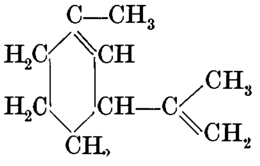
Sylvestrene is a well-recognised terpene, which is found in various turpentine and pine oils, but only in its dextro-rotatory form. Carvestrene is merely the optically inactive variety of sylvestrene, and is another instance of unfortunate nomenclature: it should be properly called *i*-sylvestrene.

There appear to exist two very closely allied terpenes, which have so similar constitutions and characters that it is almost impossible, if not quite so, to separate them when existing together naturally. The synthetically prepared sylvestrene is, of course a distinct individual, the constitution of which will be dealt with directly.

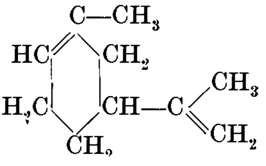
To prepare natural sylvestrene, the fraction of Swedish oil of turpentine boiling between 175° to 180° is diluted with an equal volume of ether which has been previously saturated with hydrochloric acid gas. The mixture is allowed to stand for two or three days, the ether distilled off, and the residue is left in a very cold place for some months, when sylvestrene dihydrochloride is obtained. This body, $C_{10}H_{16}2HCl$, when recrystallised from alcohol melts at 72° and has an optical rotation $[\alpha]_D$ = + 22°. If this body be distilled with aniline it yields sylvestrene, which has the following characters :—

Boiling-point	176° to 180°
Specific gravity	0·851
Refractive index	1·4757 to 1·4779
Optical rotation	+ 60° „ + 80°

This body, so isolated is probably a mixture of the two isomerides, the optical rotation varying with the relative proportions of the two bodies. The two isomers have the following constitutions :—



Sylvestrene.



Isosylvestrene.

They are therefore *meta*-menthadienes.

Sylvestrene yields the following characteristic reaction If a drop of concentrated sulphuric acid be added to a solution of one drop of sylvestrene in acetic anhydride, a deep blue coloration results No other terpene appears to give this reaction

Sylvestrene is a very stable terpene, but on heating to 250° it is partially polymerised In addition to the dihydrochloride mentioned above, it yields the following characteristic compounds —

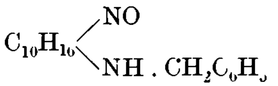
The dihydrobromide, $C_{10}H_{16}2HBr$, is obtained in a similar way to the dihydrochloride It melts at 72° and has a specific rotatory power + 17 9°

The dihydriodide $C_{10}H_{16}2HI$ is prepared in a similar manner, and melts at 66° to 67°.

Sylvestrene tetrabromide, $C_{10}H_{16}Br_4$, is prepared when pure sylvestrene, regenerated from its dihydrochloride and dissolved in acetic acid, is heated with bromine until a permanent yellow colour is produced Water is added to the reaction product, but not sufficient to precipitate the bromide, and the vessel allowed to stand in a cold place The bromide separates and can be purified by recrystallisation from alcohol It forms monosymmetric crystals melting at 135° to 136°, and having a specific rotation + 73 7°

Sylvestrene nitrosochloride, $C_{10}H_{16}$ NOCl, is prepared from pure sylvestrene, regenerated from the dihydrochloride in the following manner Four volumes of the terpene are dissolved in six of amyl nitrite and five volumes of strong hydrochloric acid are added, with constant shaking The heavy oil which separates is shaken with a little ethyl alcohol, when it solidifies, and can be purified by dissolving it in chloroform and precipitating it with petroleum ether It is finally recrystallised from methyl alcohol, when it melts at 106° to 107°

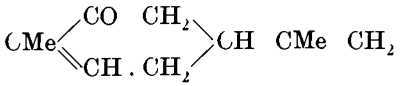
When the last-described body is warmed with benzylamine, in alcoholic solution, sylvestrene nitrol-benzylamine



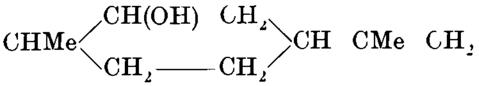
$$C_{10}H_{16}\begin{cases}NO\\NH\,.\,CH_2C_6H_5\end{cases}$$

is formed This, when recrystallised from methyl alcohol, forms well-defined crystals melting at 71° to 72° and having a specific rotation + 185 6°

Carvestrene, or *i*-sylvestrene, was first prepared by Baeyer[1] from carvone, the ketone characteristic of oil of caraway This body, when reduced with sodium and alcohol yields dihydrocarveol, which, on oxidation is converted into dihydrocarvone The formulæ of these three bodies are as follows —



Carvone



Dihydrocarveol

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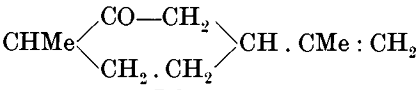
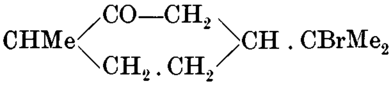
[1] *Berichte* **27**, 3485.

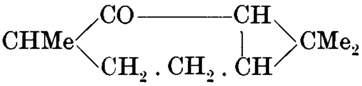


Dihydrocarvone.

Hydrobromic acid converts dihydrocarvone into a hydrobromide, $C_{10}H_{17}OBr$, which, when treated with cold alcoholic potash, readily loses hydrogen bromide. Instead, however, of the unsaturated substance, dihydrocarvone, being regenerated as the result of this decomposition, a remarkable formation of a *cyclo*propane ring takes place and *carone* is produced—

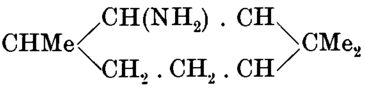


Hydrobromide of dihydrocarvone.

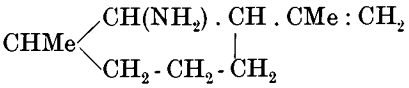


Carone.

Carone is then converted into its oxime, which is reduced by sodium and alcohol, and yields carylamine, $C_{10}H_{17}NH_2$, which has the following constitution :—



Carylamine is decomposed when its solution in dilute acids is evaporated, during which process the dimethyl*cyclo*propane ring suffers disruption and the unsaturated isomeric base, *vestrylamine*,

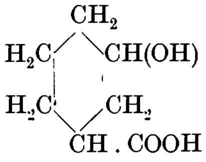


is formed. The hydrochloride of vestrylamine is readily decomposed on distillation, with elimination of ammonium chloride and formation of *carvestrene.*

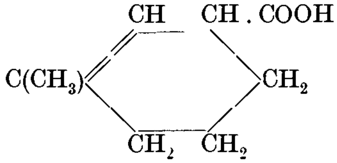
The properties of carvestrene or *i*-sylvestrene are as follows :—

Boiling-point	178°
Dihydrochloride melting-point	52·5°
Dihydrobromide „	48° to 50°

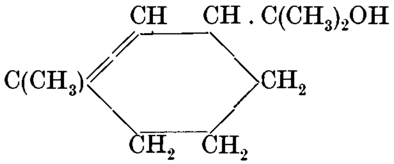
The constitution of carvestrene has been determined, subject to the limitation above referred to as to the constitution of isocarvestrene, by the masterly synthesis achieved by W. H Perkin, Jr., and his colleagues. The starting-point of this synthesis was *m*-hydroxy-benzoic acid, which was reduced by sodium and alcohol to cyclohexanol-3-carboxylic acid, of the formula—



By oxidation with chromic acid, this is converted into cyclohexanone-3-carboxylic acid, in which the —CH . OH— group is converted into the —CO— group. This is converted into its ethyl ester and treated with magnesium methyl iodide, and the product, on hydrolysis, yields 1-methyl-cyclohexane-1-ol-3-carboxylic acid, which is converted by hydrobromic acid into 1-bromo-1 - methyl - cyclohexane - 3 - carboxylic acid. When this is digested with pyridine, hydrobromic acid is eliminated and yields 1-methyl-Δ'-cyclohexane-3-carboxylic acid of the formula—



The ethyl ester of this acid was treated with magnesium methyl iodide, and thus yielded dihydrocarvestrenol—



which on dehydration with potassium bisulphate yields carvestrene.

A further synthesis of carvestrene has been effected by Perkin and Fisher.[1]

It is probable that the carvestrene so synthesised is in reality a mixture of the two bodies described above as carvestrene and isocarvestrene.

The active variety of the terpene *d*-sylvestrene has been prepared synthetically by preparing the methyl-cyclohexane-carboxylic acid described above, and recrystallising its brucine salt. The acid contains a small quantity of the Δ^6 acid, although the Δ^1 variety predominates. The Δ^6 acid was resolved by the brucine crystallisations, and an acid of rotation + 90° obtained. The synthetic process was then proceeded with, and the resulting terpene was found to be *d*-sylvestrene, having a rotation of + 66°.

PHELLANDRENE.

Two isomeric terpenes are known under the name of phellandrene. Before the distinction between the two bodies was recognised, phellandrene had been discovered and reported in a number of essential oils, so that in many cases it is impossible at present to decide which isomer is that actually present in a given oil. The two terpenes—still another case of the absurd nomenclature which has been retained for so many of the terpenes—are known as α-phellandrene and β-phellandrene. The constitutions of the two hydrocarbons are probably as follows :—

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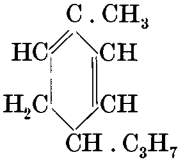
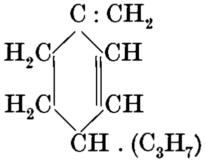
[1] *Jour. Chem. Soc.*, **93** (1908), 1876.



α-Phellandrene.



β-Phellandrene.

These terpenes have been exhaustively studied by Wallach,[1] who particularly examined phellandrenes from the following sources :—

1. *l*-phellandrene from eucalyptus oil.
2. *d*-phellandrene from elemi oil.
3. *d*-phellandrene from bitter fennel oil.
4. *d*-phellandrene from water fennel oil.

He found that the *d*-phellandrene from elemi and bitter fennel oils were identical, and that *l*-phellandrene from eucalyptus oil is the laevorotatory variety of the same terpene. To these he assigned the names *d*-α-phellandrene and *l*-α-phellandrene. The *d*-phellandrene from water fennel oil differs from these and is named *d*-β-phellandrene. The following are the characters of the purest specimens of natural phellandrene yet obtained :—

	d-α-phellandrene.	*d*-β-phellandrene.	*l*-α-phellandrene.
Specific gravity .	0·844 at 19°	0·852 at 20°	0·848 at 15°
Refractive index .	1·4732	1·4788	1·4769
Boiling-point . .	61° at 11 mm.	—	50° to 52° at 5 mm.
" " . .	175° " 760 mm.	—	174° at 760 mm.
Optical rotation .	+ 40° 40'	+ 14° 45' to + 18° 30'	− 84° 10'

All varieties of phellandrene are somewhat unstable and are easily susceptible of isomerisation.

All varieties readily yield a nitrite of the formula $C_{10}H_{16}N_2O_3$, which is prepared in the following manner, and is a most useful compound for characterising these terpenes. A solution of 5 grams of sodium nitrite in 8 c.c. of water is added to a solution of 5 c.c. of the fraction of the oil containing much phellandrene in 10 c.c. of petroleum ether, and 5 c.c. of glacial acetic acid is slowly added to the mixture with constant stirring. The resulting crystals are filtered, washed with water and methyl alcohol, and purified by dissolving in chloroform and precipitating with methyl alcohol. The final purification is effected by triturating the crystals with a cold mixture of methyl alcohol and ether, and recrystallising several times from acetic ether. The phellandrene nitrite so obtained is not a homogeneous substance, but a mixture of two physical isomerides, which is true for both α- and β-phellandrene. These physical isomerides are known as the α- and β-varieties, so that the following very confused nomenclature arises, the specific rotation and melting points of the six known modifications being given :—

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[1] *Annalen*, **324** (1902), 269, and **336** (1904), 9.

	Specific Rotation.	Melting-point.
Dextro-α-phellandrene α-nitrite	– 138·4°	112° to 113°
Laevo-α-phellandrene α-nitrite	+ 135·9°	112° ,, 113°
Dextro-α-phellandrene β-nitrite	+ 45·9°	105°
Laevo-α-phellandrene β-nitrite	– 40·8°	105°
Dextro-β-phellandrene α-nitrite	159·3°	102°
Dextro-β-phellandrene β-nitrite	+ 0°	97° to 98°

As laevo-β-phellandrene has not yet been isolated, the corresponding two nitrites have not, of course, been prepared.

The separation of the physical isomerides is effected in the following manner: the mixed nitrites are dissolved in acetone and precipitated by the addition of water, the mixture being cooled to 0°. This process is repeated several times, when eventually the more soluble or β-nitrite is separated from the less soluble or α-variety.

β-phellandrene, which was originally obtained from water fennel oil, is also found in the essential oil of *Bupleurum fruticosum.*[1] Francesconi and Sernagiotto have prepared from it the corresponding physically isomeric nitrosochlorides. They find that the yield of nitrosochlorides prepared in the same way as pinene nitrosochloride (*q.v.*), is greater as the optical rotation of the terpene is lower. Through a series of recrystallisations, the two isomers were separated, and found to have the following characters :—

	Specific Rotation.	Melting-point.
β-phellandrene-α-nitrosochloride	– 175°	101° to 102°
β-phellandrene-β-nitrosochloride	– 285°	100°

No crystalline nitrosochlorides have, so far, been prepared from α-phellandrene.

If α-phellandrene be oxidised by potassium permanganate, the principal body resulting is α-oxy-β-isopropyl glutaric acid. If β-phellandrene be oxidised, closely related acids result, but if a 1 per cent. solution of permanganate be used and the oxidation effected very carefully in the cold, with the terpene always in excess, a glycol, $C_{10}H_{16}(OH)_2$, results, which when dehydrated with dilute sulphuric acid yields tetrahydrocuminic aldehyde.

This aldehyde is identical with the naturally occurring phellandral, an aldehyde found in oil of water fennel. If the nitrosochloride of β-phellandrene be decomposed by acetic acid, dehydrocuminic aldehyde and carvacrol result.

The phellandrene nitrites are converted, by heating with strong hydrochloric acid at 40°, into mono- and di-chlorthymo-quinone.

If the α-phellandrene nitrite be heated with an alcoholic solution of potash, it is converted into nitrophellandrene, $C_{10}H_{15}(NO_2)$. This body is converted by reduction with sodium and alcohol into tetrahydrocarvone, or by less energetic reduction with zinc and acetic acid, into carvotanacetone. The relationship between these bodies is shown by the following formulæ :—

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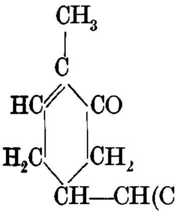
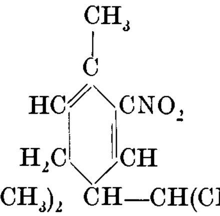
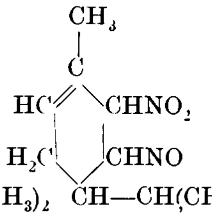
[1] *Gazz. Chim. Ital.*, **46** (1916), 119.



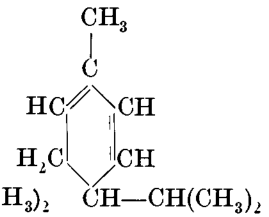
Carvotanacetone.



Nitro-α phellandrene



α Phellandrene nitrite.



α Phellandrene.

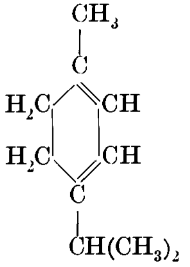
Wallach[1] has prepared α-phellandrene synthetically from sabinenic acid by oxidising it to sabina ketone with potassium permanganate This ketone was converted into its semicarbazone, and the latter compound treated with dilute sulphuric acid, when sabina ketone is not regenerated, but an isomer, which was found to be isopropyl-hexenone. By the interaction of this body with methyl-magnesium iodide, loss of water occurs with a simultaneous conversion into α-phellandrene, which appears to be a mixture of the *dextro-* and *laevo-* varieties This synthetically prepared α-phellandrene has the following characters —

Boiling-point	175° to 176°
Specific gravity at 22°	0·841
Refractive index at 22°	1·4760
Melting point of nitrite	113°

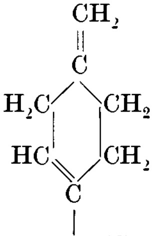
Clover[2] has isolated a terpene from elemi oil, which he claims to be pure α-phellandrene, and which has an optical rotation of + 129·8°.

TERPINENE.

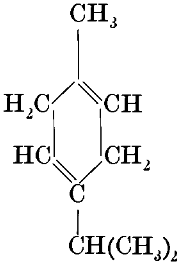
The chemistry of the hydrocarbons known under this name is in a very unsettled condition. There are at least three well-defined terpenes known by this name, α-terpinene, β-terpinene, and γ-terpinene, which have the following constitutions —



α-Terpinene



β Terpinene.



γ Terpinene.

Apparently only α-terpinene and γ-terpinene have been found occurring naturally in essential oils. All the terpinenes are formed artificially from other terpinenes, or from geraniol, cineol, terpin hydrate, linalol, dihydrocarveol, and numerous other compounds.

In 1908-1909 F. W Semmler[3] made a critical study of the question of the characters of the terpinenes with a view to clearing up some of the

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[1] *Annalen*, **359**, 265

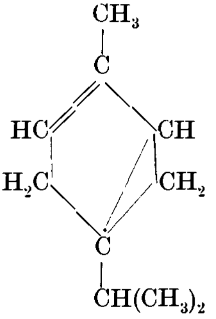
[2] *Amer Chem Journal*, **39**, 612.

[3] *Berichte*, **41** (1908), 4474 , **42** (1909), 522

contradictory statements which had been published in regard to them. By acting on carvenone with phosphorus pentachloride and reducing the carvenene chloride formed, he obtained a hydrocarbon which he termed carvenene, which by its method of production should be a dihydrocymene, and is considered by Semmler to be α-terpinene, possibly mixed with some of the other modifications. By boiling carvenene for two hours with alcoholic sulphuric acid, he inverted it to isocarvenene, which Semmler considers to be β-terpinene. Wallach, however, does not consider that these bodies are identical with the α-terpinene and β-terpinene above mentioned. Semmler's two terpinenes (carvenenes) have the following characters:—

	Carvenene (α-terpinene).	Isocarvenene (β-terpinene).
Specific gravity at 20°	0·844	0·845
Boiling-point	180° at 735 mm.	—
,, ,, ...	61° to 63° at 10 mm.	59° to 62°
Refractive index	1·4910	1·4800

Auwers[1] has paid considerable attention to the terpinene question, and especially in regard to the fact that the molecular refraction of the terpinenes shows considerable variation according to the method of preparation, and often appears to indicate that the terpinenes are exceptions to Brühl's laws of refraction. He came to the conclusion that the terpinenes are usually mixtures of more than one modification, together with a certain amount of a hydrocarbon of the formula:—



Auwers considers that terpinene produced from terpin hydrate is a mixture in which α-terpinene cannot be regarded as the characteristic constituent. From the terpinene hydrochloride, the α-terpinene-content cannot be expected to exceed 50 per cent. in the most favourable case. For obtaining α-terpinene which, although not pure, is of a comparatively high percentage, Auwers regards the method from carvone *via* dihydrocarveol as the best. Semmler regards carvenene as a particularly pure α-terpinene, but Auwers does not agree with this, because in its preparation the action of nascent hydrochloric acid produces conditions which afford no guarantee of a uniform final product. Carvenene does not appear to be identical with α-terpinene from o-cresol which Auwers prepared by acting on o-cresol with chloroform and alkali, thus producing methyl-dichloromethyl-keto-dihydrobenzene. This body was converted into its higher homologues by the action of magnesium alkyl iodide, and the resulting bodies were isomerised by concentrated sulphuric acid, and the

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[1] *Berichte*, 42 (1909), 2404, 2424.

isomers, on treatment with alcoholic potash yield the corresponding hydrocarbons. By using magnesium propyl iodide, he obtained $\Delta^{1\,3}$ menthadiene, *i.e.* α-terpinene. Auwers and his pupils have also prepared α-terpinene synthetically by other methods, and find it to have the following characters :—

Boiling-point	65° to 66° at 13·5 mm.
Specific gravity at $\frac{19°}{4°}$	0·8353
Refractive index at 19°	1·47942

Henderson and Sutherland[1] have prepared a hydrocarbon synthetically which is possibly a modification of terpinene. They reduced thymohydroquinone, thus obtaining menthane-2-5-diol, which was heated for half an hour with twice its weight of sulphate of potash under a reflux condenser, and so yielded a terpene boiling at 179°, of specific gravity about 0·840 and refractive index 1·4779.

It may be accepted that α-terpinene has characters falling within the following limits :—

Specific gravity	0·842 to 0·846 at 20°
Boiling-point	175° to 181°
Refractive index	about 1·4720 to 1·4800

A specimen of γ-terpinene obtained by Schimmel & Co. from coriander oil, and probably consisting of a mixture of the α- and γ-varieties, had the following characters :—

Boiling-point	177° to 178°
Optical rotation	+ 0° 32′
Specific gravity	0·8485 at 15°
Refractive index	1·4765

The most characteristic derivative for the identification of α-terpinene is the nitrosite, $C_{10}H_{16}N_2O_3$, which melts at 155°. It is prepared as follows: 2 to 3 grams of the product to be identified are dissolved in an equal volume of petroleum ether, and an aqueous solution of 2 to 3 grams of sodium nitrite added. Glacial acetic acid is then added gradually with constant stirring, the vessel being immersed in warm water for a few moments and then allowed to stand in a cool place. Terpinene nitrosite separates, usually in a few hours, but always in two days. The crystals are filtered off, washed with water, and then with cold alcohol, and dried on a porous plate. The crystals can be purified by recrystallisation from hot alcohol, and melt sharply at 155°. With piperidine, it yields a nitrolpiperidine melting at 153° to 154°, and with benzylamine a nitrolbenzylamine melting at 137°. These two compounds are prepared in the same manner as the corresponding pinene derivatives (*q.v.*).

It is probable that γ-terpinene has not been isolated in a state of purity, but it can be recognised, by yielding erythritol melting at 236° to 237°, on oxidation with potassium permanganate. In order to obtain this, 140 grams of the product to be identified are shaken for several hours with 280 grams of caustic potash and 660 grams of potassium permanganate, 8 litres of water, and 8 kilos of ice. The erythritol resulting is recrystallised from 25 per cent. alcohol, when it melts at 236° to 237°. γ-terpinene does not yield a crystalline nitrosite.

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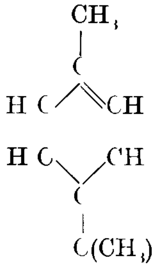
[1] *Jour. Chem. Soc.*, **97** (1910), 1616.

TERPINOLENE

This terpene is very rarely met with in nature, but is formed by the dehydration of various alcohols, such as terpineol and linalol. It has been identified in the essential oil of Manila elemi.

The constitution of terpinolene is probably as follows:—



This terpene was discovered by Wallach[1] and was prepared by heating turpentine oil with alcoholic sulphuric acid. It is also yielded in satisfactory quantity by dehydrating terpineol by means of oxalic acid. Melted terpineol (melting-point 35°) is added very gradually to a boiling saturated solution of oxalic acid, through which a current of steam is passed. About 1 gram of terpineol should be added drop by drop, per minute, so that dehydration is complete, and the resulting terpinolene is at once removed by the current of steam before it is isomerised to any extent.

Semmler[2] has succeeded in preparing pure terpinolene by the reduction of terpinolene tetrabromide by means of zinc dust in alcoholic medium (not in presence of acetic acid, as in that case a mixture of hydrocarbons is obtained). The constants of the pure hydrocarbon are:—

Specific gravity at 20°	0.854
Refractive index	1.484
Boiling point at 10 mm	67° to 68°
,, ,, ,, 760 mm	183° ,, 185°
Optical rotation	± 0°

Terpinolene therefore appears to be of all the monocyclic terpenes, the one which possesses the highest specific gravity and the highest boiling point.

For the identification of terpinolene, its tetrabromide is the most characteristic compound. This body is prepared by adding gradually four atoms of bromine to a solution of the terpene in glacial acetic acid maintained at a low temperature. Terpinolene tetrabromide, $C_{10}H_{16}Br_4$, melts at 116° to 117°, when recrystallised from alcohol.

ORIGANENE

This terpene has been isolated from the oil of *Origanum hirtum* by Pickles.[3] It is an oil possessing a distinct odour of lemons and has the following characters:—

Boiling point	160° to 164° at 750 mm
Specific gravity	0.847
Refractive index	1.4800
Optical rotation	+ 1° 50'

[1] *Annalen*, **227**, 283; **230**, 262.

[2] *Berichte*, **42**, 4644.

[3] *Jour. Chem. Soc.*, **93** (1908), 862.

It is possible that this slight optical rotation may be due to traces of impurities.

Origanene yields a crystalline nitrosochloride, melting at 91° to 94°, and a nitrolpiperidine melting at 198°. These derivatives are prepared in the same manner as the corresponding compounds of pinene (*q.v.*).

Pickles has suggested that origanene has the constitution which Wallach has assigned to α-terpinene, but there is not sufficient experimental evidence to support this suggestion.

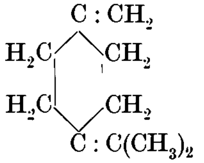
CRITHMENE.

Francesconi and Sernagiotto[1] have isolated a terpene from the essential oil of *Crithmum maritimum* distilled from plants grown in Sardinia.

It has the following characters:—

Boiling-point	178° to 180°
Specific gravity	0·8658
Refractive index	1·4806

Crithmene yields an α-nitrosochloride, crystallising in laminæ, and melting at 101° to 102°, and a β-nitrosochloride, $C_{10}H_{16}ONCl$, forming quadratic plates and melting at 103° to 104°. Both are devoid of optical activity. The nitrosite melts at 89° to 90° and the nitrosate at 104° to 105°. A tetrabromide is formed, $C_{10}H_{16}Br_4$, but could not be obtained in the crystalline condition. The isomeric nitrolpiperides, prepared from the nitrosochlorides, melt in both instances at 138°. The benzylamine compound melts at 103° to 104°. If the nitrosochloride be hydrolysed by means of alcoholic alkali and the resulting products distilled in a current of steam, a solid body, forming minute crystals melting at 131°, is left behind. It contains nitrogen. Crithmene yields a dihydrochloride, $C_{10}H_{16}(HCl)_2$, melting at 52°, and apparently identical with that of terpinene. The constitution of crithmene is probably that of a $\Delta^{1\cdot 7-4\cdot 8}$ *para*-menthadiene, as follows:—



CARENE.

This terpene has been isolated by Simonsen[2] from Indian turpentine oil, from *Pinus longifolia*. It is identical with the terpene previously described by Robinson[3] as a terpene yielding sylvestrene hydrochloride when treated with hydrogen chloride. Its characters are as follows:—

Specific gravity at $\frac{30°}{30°}$	0·8586
Refractive index at 30°	1·4690
Optical rotation	+ 7·69°
Boiling point at 705 mm.	168° to 169°
,, ,, ,, 200 ,,	123° ,, 124°

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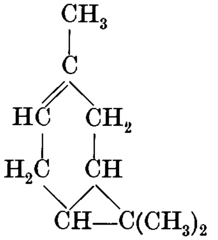
[1] *All. R. Acad. Linc.* **(1913)**, 231, 312.

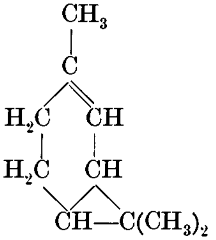
[2] *Jour. Chem. Soc.*, **1920**, 570.

[3] *Proc. Chem. Soc.*, 1911, **27**, 247.

Dextro-carene is a colourless oil with a sweet odour. Its nitrosate, $C_{10}H_{16}O_3N_2$, melts at 141·5°.

On treatment in ethereal solution with hydrogen chloride, it yields a mixture of sylvestrene and dipentene hydrochlorides. Its constitution is probably represented by one of the two following formulæ :—





DACRYDENE.

Baker and Smith[1] have isolated a terpene from the essential oil of the leaves of *Dacrydrium Franklini* (the huon pine of Tasmania) which has the following characters :—

Boiling-point	165° to 166°
Specific gravity at 22°	0·8524
Refractive index at 22°	1·4749
Optical rotation	+ 12·3°

It forms a nitrosochloride melting sharply, but with decomposition, at 120° to 121°. It has been named dacrydene.

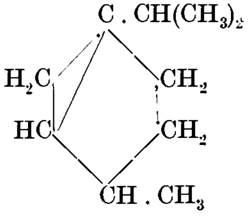
In addition to the above-described terpenes proper, there are a few other hydrocarbons which may be conveniently dealt with here. These are salvene, the so-called olefinic terpenes, myrcene and ocimene, the terpene homologues, cantharene, santene, and a hydrocarbon of the formula $C_{11}H_{18}$ found in sandalwood oil, and the diterpene phyllocladene.

SALVENE.

Salvene is a hydrocarbon of the formula $C_{10}H_{18}$ found in oil of sage[2] by Seyler. It has the following approximate characters —

Specific gravity	0·800 at 20°
Boiling-point	142° to 145°
Refractive index	1·4438
Optical rotation	+ 1° 40'

Its constitution is as follows :—



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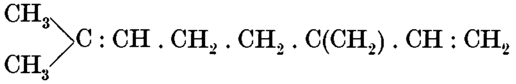
[1] *The Pines of Australia*, 397 (1st edition).

[2] *Berichte*, 35 (1902), 550.

MYRCENE.

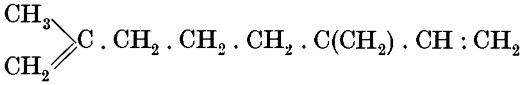
Myrcene is a compound of the formula $C_{10}H_{16}$ which has been found in a number of essential oils, such as bay oil, West Indian lemon-grass oil, the oil of *Lippia citriodora*, etc., etc. It has sufficient resemblance to the terpenes proper to have been classified as an "olefinic" terpene, its constitution being that of an open chain, and not a ring compound.

Myrcene has one of the two following constitutions :—



$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right>C:CH.CH_2.CH_2.C(CH_2).CH:CH_2$$

or



$$\left.\begin{matrix}CH_3\\CH_2\end{matrix}\right>C.CH_2.CH_2.CH_2.C(CH_2).CH:CH_2$$

Myrcene can be obtained, according to Power and Kleber,[1] from oil of bay in the following manner: The oil is first shaken with a 5 per cent. solution of caustic soda to remove phenols, and is then fractionally distilled *in vacuo*. Eventually, by repeated fractionation a colourless liquid results, which distils at 67° to 68° at 20 mm. pressure, and is practically pure myrcene.

Myrcene has the following characters :—

Specific gravity	0·801
Refractive index	1·4700 at 19°
Boiling-point	167°
,, ,, at 20 mm.	67° to 68°

By reduction with sodium alcohol, myrcene yields dihydromyrcene, $C_{10}H_{18}$, a liquid, which yields a tetrabromide melting at 88°, which is a useful compound for the identification of myrcene. The olefinic terpene ocimene (*q.v.*) yields the same body on reduction, so that dihydromyrcene and dihydro-ocimene are identical. By acting upon linalol with sodium alcohol, a hydrocarbon of the formula $C_{10}H_{18}$ is formed by abstraction of the oxygen, which is also identical with dihydromyrcene, although it has been named linalolene. It yields the characteristic tetrabromide melting at 88°. The physical characters of the dihydromyrcenes prepared from these various sources are as follows :—[2]

	Linalolene	Dihydromyrcene	Dihydromyrcene	Dihydro-ocimene	Dihydromyrcene
	(Semmler).		(Enklaar).		(Schimmel & Co.).
B.-p.	165° to 168°	171·5° to 173·5°	166° to 168°	166° to 168°	168°
Sp. gr.	0·7882 (20°)	0·7802 (? °)	0·7852 (15°)	0·7750 (15°)	0·7824 (15°)
Refr.	1·455 (20°)	1·4501	1·4514 (17°)	1·4507 (17°)	1·45251 (15°)

The preparation of dihydromyrcene tetrabromide is often attended by difficulties. The method recommended by Enklaar, and recently also adopted by Semmler, of dissolving the hydrocarbon in glacial acetic acid, has not stood the test of practice, because according to Schimmel & Co.

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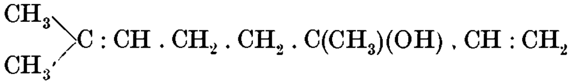
[1] *Pharm. Rund.*, New York, **1895**, 13.
[2] Schimmel & Co., *Report*, Oct. **1911**, 129.

it generally gives rise to oily bromides. Hydrobromic acid appears to be evolved as soon as the bromine is added to the glacial acetic acid solution. The reaction is accomplished more quickly and effectively by dissolving the hydrocarbon in a mixture of 1 part by volume of amyl alcohol and 2 parts by volume of ether. Soon after the addition of the calculated quantity of bromine the tetrabromide separates out.

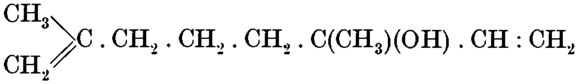
If myrcene be heated with glacial acetic acid to 40° for three to four hours, with the addition of a little sulphuric acid, hydration takes place, and an alcohol, which is termed myrcenol is formed. This body is an oil, of specific gravity 0·9032, refractive index 1·4806 at 15°, and boiling-point 99° at 10 mm. pressure. It yields a phenylurethane melting at 68°.

Myrcenol probably has the constitution :—



$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!\!>\!C : CH . CH_2 . CH_2 . C(CH_3)(OH) . CH : CH_2$$

or



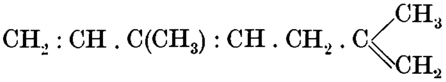
$$\genfrac{}{}{0pt}{}{CH_3}{CH_2}\!\!\gg\!C . CH_2 . CH_2 . CH_2 . C(CH_3)(OH) . CH : CH_2$$

The resemblance of myrcene to the terpenes proper may possibly be connected with the fact that, like geraniol and linalol, they show a marked tendency towards closing the open chain into a six carbon ring. For example, when dihydromyrcene $C_{10}H_{18}$ is treated with acetic and sulphuric acids, an alcohol is formed, together with the isomeric hydrocarbon, $C_{10}H_{18}$, where a six carbon ring has been formed, and which is termed cyclo-dihydromyrcene. This body is an odorous oil having the following characters :—

Boiling-point	169° to 172°
Specific gravity	0·828 at 20°
Refractive index	1·4620 ,, 20°
Molecular refraction	45° to 63°

Myrcene is easily polymerised, and it is probable that this fact accounts for the decrease in solubility of essential oils which contain myrcene, when they have been kept for any length of time.

Koschelew [1] has recently prepared a closely related olefinic terpene, which he has termed β-myrcene, by treating isoprene in a sealed tube to 80° to 90° for five days. This body has the constitution :—



$$CH_2 : CH . C(CH_3) : CH . CH_2 . C\!\!<\!\genfrac{}{}{0pt}{}{CH_3}{CH_2}$$

It is a colourless oil having an odour very similar to that of myrcene, and boiling at 63° at 20 mm.

OCIMENE.

This body is very closely related to myrcene, and has been found in the oil of basil distilled in Java. It has the following constitution :—

$$CH_3 . C(CH_3) : CH . CH_2 . CH : C(CH_3) . CH : CH_2$$

Its characters are as follows :—

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[1] *Chem. Zentral.* (1916), i. 1068, 1136.

Specific gravity	0·803
Refractive index	1·4850
Boiling point	172° at 750 mm.
,, ,,	73° to 74° at 20 mm.

As stated above it yields dihydromyrcene (dihydro-ocimene) when reduced by sodium alcohol. On hydration by means of acetic and sulphuric acids it yields an alcohol, ocimenol, which has the following characters:—

Specific gravity	0·901
Refractive index	1·4900 at 15°
Boiling-point	97° at 10 mm.
Melting-point of phenylurethane	72°

By heat, ocimene is converted into allo-ocimene, which is probably a stereoisomeric compound.

CANTHARENE.

Haworth [1] has described a lower homologue of the terpenes which he obtained by the dehydration of the alcohol cantharenol. Cantharene, C_8H_{12}, was first prepared by Piccard during his classical work on cantharidine, and it so closely resembled the terpenes in character that Piccard regarded it as the first artificially prepared terpene. The close relationship of these bodies, which are dihydroxylenes, to the terpenes, made it of interest to carry out a careful examination of them, and with this object in view a general method has been devised for the preparation of pure hydrocarbons of this group. If methyl-cyclo-hexenone is treated with magnesium methyl iodide the alcohol cantharenol is obtained, which is the "terpineol" of the group. The dehydration of the alcohol leads to the formation of the corresponding hydrocarbon, which, chemically, is 1:2 dimethyl $\Delta^{2 \cdot 6}$ cyclohexadiene. This body boils at 135·5,° and has a specific gravity 0·852 at $\frac{20°}{4°}$, and refractive index 1·4895; and appears to agree in all its characters with Piccard's cantharene. It has a high refractive index, and gives similar colour reactions, and yields orthotoluic acid on oxidation. There are, of course, three isomeric dihydroxylenes, and the other two were also prepared, and have the following characters:—

	Dihydro-o-xylene.	Dihydro-m-xylene.	Dihydro-p-xylene.
Boiling-point	135·5°	135°	135° to 138°
Specific gravity $\frac{20°}{4°}$	0·8521	0·8373	0·830
Refractive index	1·4895	1·4856	1·4797
Molecular refraction	36·62	37·01	36·94

SANTENE.

This hydrocarbon, also known as nor-camphene, is an immediate lower homologue of the terpenes, of the formula C_9H_{14}. It was dis-

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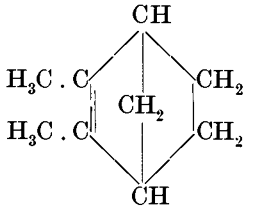
[1] *Jour. Chem. Soc.*, **1913**, 1242; *P. and E.O.R.*, **1913**, 254.

covered in oil of sandalwood by Muller.[1] It is also present in Siberian pine-needle oil, and in several other pine oils.

According to Semmler[2] it has the constitution:—



This constitution is confirmed by the conversion of camphenylone into santene by Komppa and Hintikka.[3]

Santene has also been examined by Aschan.[4] The following are the characters of the purest specimens which have been isolated from sandalwood and Siberian pine oils:—

	Sandalwood.		Siberian Pine.
	Semmler.	Aschan	
Boiling-point	31° to 33° (9 mm.)	140°	140°
Specific gravity . .	0·863 (20°)	0·8708 (15°)	0·8698 (15°)
Refractive index . .	1·46658 (20°)	1·4688 (17·5°)	1·4696 (19°)
Rotation	± 0°	± 0°	± 0°

Santene forms a nitrosochloride, prepared in the usual manner, melting at 109° to 110°, and a nitrosite melting at 125°. It also forms a hydrochloride melting at 80° to 81°. By hydration with sulphuric and acetic acids it yields an alcohol $C_9H_{15}OH$, which is termed santenol (isosantenol, nor-borneol). This body melts at 97° to 98° and boils at 195° to 196°.

Kondakow[5] has carried out an investigation on the haloid derivatives of santene, and finds that mixtures of liquid and solid hydrochlorides and hydrobromides are usually obtained so that the haloid derivatives are unsatisfactory for identification purposes.

Santenyl acetate, $C_9H_{15} . OOC . CH_3$, is a liquid of specific gravity 0·9859 at 20°, refractive index 1·45929, and boils at 85° to 89° at 8 mm.

HYDROCARBONS $C_{11}H_{18}$, FROM SANDALWOOD OIL.

Schimmel & Co.[6] have isolated a hydrocarbon of the formula $C_{11}H_{18}$ from sandalwood oil. This body is completely saturated and is unaffected by potassium permanganate at ordinary temperatures.

Semmler[7] in the course of his researches on the constitution of the

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[1] *Archiv. d Pharm.* **238** (1900), 366.
[2] *Berichte*, **40** (1907), 465, 4594, 4844; **41** (1908), 121, 385.
[3] *Bull. Soc. Chim.* [4], **21**, 13.
[4] *Ibid.*, 4918.
[5] *Jour Russ. phys. Chem. Ges.*, **43** (1911), 1107.
[6] *Report*, October, **1910**, 121.
[7] *Berichte*, **40** (1907), 1124; **43** (1910), 1722.

santalols, obtained from tri*cyclo*eksantalic acid, by splitting off carbon dioxide gas, a hydrocarbon which he termed nor-tri*cyclo*eksantalane. The most recent investigations of Semmler have shown that tri*cyclo*eksantalic acid posseses twelve carbon atoms, from which it would seem that the correct formula of nor-tri*cyclo*eksantalane is $C_{11}H_{18}$, and Semmler's analyses agree with this view.

The following are the characters of the two hydrocarbons:—

	Hydrocarbon from Sandalwood Oil.	Nor-tri*cyclo*eksantalane (according to Semmler).
Boiling-point . . .	183°	183·5°
Specific gravity at 20° .	0·9092	0·885
Rotation	– 23° 55'	– 11°
Refractive index . .	1·4786	1·46856
Molecular refraction . .	46·74	47·15.

It is probable that the tricyclic hydrocarbon from sandalwood oil is identical with, or at least closely allied to, Semmler's nor-tri*cyclo*eksantalane.

PHYLLOCLADENE.

Baker and Smith have isolated from the essential oil of the leaves of *Phyllocladus Rhomboidalis* a diterpene, which they have named phyllocladene It has the formula $C_{20}H_{32}$, and melts at 95°. It is dextro-rotatory, its specific rotation being + 16·06°.

2. SESQUITERPENES.

The sesquiterpenes are compounds of the formula $C_{15}H_{24}$, which are of higher specific gravity, boiling point, and refractive index than the terpenes. They are of complicated constitution, and are less well understood in this respect than the terpenes, although modern research is gradually elucidating many of the problems connected with this interesting group of compounds. Apart from the so-called aliphatic sesquiterpenes, which appear to bear the same relationships to the sesquiterpenes proper as do the aliphatic terpenes to the true terpenes, the sesquiterpenes are classified according to the number of closed rings existing in the molecule, which, where the constitution is not clearly understood, may be deduced from the molecular refraction of the compound. The following figures generally hold good:—

	Molecular Refraction Calculated.	Specific Gravity.
Monocyclic	67·76	0·875 to 0·890
Bicyclic	66·15	0·900 ,, 0·920
Tricyclic	64·45	0·930 ,, 0·940

BISABOLENE.

This sesquiterpene is a monocyclic compound, first isolated from the essential oil of Bisabol myrrh by Tucholka.[1] It was found in oil of limes, and described by Burgess under the name limene. It occurs in several other essential oils. When separated by fractional distillation from lemon oil, Gildemeister and Müller[2] found it to have the following characters:—

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[1] *Arch. der. Pharm.*, **235** (1897), 292.

[2] Schimmel, *Bericht*, October, **1909**. 50.

Boiling-point at 4 mm.	110° to 112°
Specific gravity	0·8813
Optical rotation	– 41° 31′
Refractive index	1·49015

When prepared by regeneration from the trihydrochloride, the sesquiterpene is inactive, a pure specimen having the following characters:—

Boiling-point at 751 mm.	261° to 262°
Optical rotation	0°
Specific gravity	0·8798
Refractive index	1·4901

If a current of hydrochloric acid gas be passed through an ice-cold solution of the sesquiterpene dissolved in ether a crystalline trihydrochloride is obtained, which melts at 79° to 80°, and has the formula $C_{15}H_{24} \cdot 3HCl$.

ZINGIBERENE.

This sesquiterpene was isolated from oil of ginger by Von Soden and Rojahn[1] and has been examined by them and by Schreiner and Kremers.[2] It is obtained by fractional distillation under reduced pressure and is a colourless and nearly odourless oil. Its characters are as follows:—

Boiling-point	270° (with decomposition)
,, ,, at 32 mm.	160° to 161°
,, ,, ,, 14 mm.	134°
Specific gravity	0·873 at 20°
Refractive index	1·49399
Specific rotation	– 73° (approximate).

Zingiberene forms a dihydrochloride, $C_{15}H_{24}$, 2HCl, when its solution in an equal volume of glacial acetic acid is saturated at 0° with dry hydrochloric acid gas. It crystallises from hot alcohol in fine white needles melting at 168° to 169°.

The nitrosochloride, $C_{15}H_{24} \cdot NOCl$, prepared in the usual manner, is a white powder melting with decomposition at 96° to 97°.

The nitrosite, $C_{15}H_{24}N_2O_3$, is formed when zingiberene is dissolved in ten times its volume of petroleum ether, the solution well cooled and treated with a solution of sodium nitrite, and acetic acid added. It crystallises from hot methyl alcohol, and melts at 97° to 98°.

Zingiberene also forms a nitrosate, $C_{15}H_{24} \cdot N_2O_4$, when the sesquiterpene dissolved in an equal volume of glacial acetic acid, is cooled to 0°, and ethyl nitrite, and then nitric acid added. The nitrosate is dissolved in acetic ether and precipitated with alcohol. It forms a yellow powder, melting with decomposition at 86°.

When the dihydrochloride above mentioned is produced, it is probable that molecular rearrangement takes place and that the compound is really the dihydrochloride of a bicyclic *iso*-zingiberene. According to Semmler and Becker[3] when zingiberene is treated with acetic and sulphuric acids, it is converted into *iso*-zingiberene. This sesquiterpene has the following characters:—

Boiling-point at 7 mm.	118°
Specific gravity	0·9118 at 20°
,, rotation	– 51° 36′
Refractive index	1·5062

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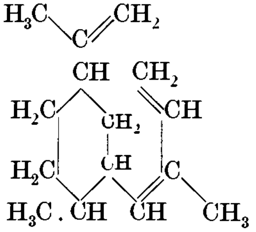
[1] *Pharm. Zeit.*, **45**, 414.

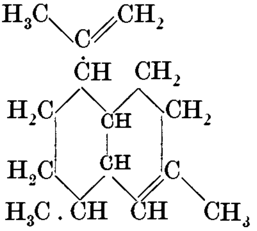
[2] *Pharm. Arch.*, **4**, 141, 161.

[3] *Berichte*, **46** (1913), 1814.

Zingiberene and *iso*-zingiberene probably have the following constitutions:—



Zingiberene.



Iso zingiberene.

CADINENE.

Cadinene owes its name to its occurrence in considerable quantity in oil of cade—which, of course, is not a true essential oil, but the product of destructive distillation. It is found in numerous essential oils, including those of patchouli, savin, galbanum, camphor, cedar wood, West Indian santal, juniper, and many others. Cadinene is best prepared as follows:—

The fraction of oil of cade boiling at 260° to 280° is converted into cadinene dihydrochloride by saturating its solution in dry ether with dry hydrochloric acid gas. The hydrochloride is separated, dried, and recrystallised, and the hydrochloric acid removed by heating it with aniline or with sodium acetate in glacial acetic acid. The liberated cadinene is rectified in a current of steam. Cadinene from oil of cade is highly laevo-rotatory, the dextro-rotatory variety being obtained from Atlas cedar oil and West Indian sandalwood oil.

The purest specimens of cadinene prepared have the following characters:—

Specific gravity	0·9215
Refractive index	1·5065
Optical rotation	− 105° 30′
Boiling point	272° to 275°

Lepeschkine[1] prefers the use of sodium ethylate for the regeneration of the sesquiterpene, and gives the following figures for pure cadinene so produced:—

Specific gravity	0·9183 at 20°
Refractive index	1·5073
Optical rotation	− 111°
Boiling-point	271° to 272°

Cadinene yields a beautiful colour reaction when a few drops are dissolved in chloroform and shaken with a few drops of concentrated sulphuric acid. The liquid turns dark green, passing to blue and becoming red on warming. If acetic acid be used instead of sulphuric acid, the blue colour is more marked.

Cadinene forms a well-defined crystalline dihydrochloride, $C_{15}H_{24}$ 2HCl. In order to prepare it most successfully the fraction of oil of cade boiling between 260° and 280°, as mentioned above, is dissolved in twice its volume of dry ether, and saturated with dry hydrochloric acid gas. The mixture is allowed to stand for several days and

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[1] *Jour. Soc. phys. chim. Russ.*, **40**, 698.

a portion of the ether is distilled off On further evaporation, the dihydrochloride crystallises out The crystals are separated, washed with a little alcohol, and recrystallised from ethyl acetate. Cadinene dihydrochloride melts at 117° to 118° and has a specific rotation (in 5 per cent. chloroform solution) − 37°.

Cadinene dihydrobromide, $C_{15}H_{24} . 2HBr$, is obtained by shaking cadine dissolved in acetic acid with fuming hydrobromic acid. It forms white needles melting at 124° to 125°, and having a specific rotation − 36 13°. The dihydriodide, $C_{15}H_{24}$ 2HI, prepared in a similar manner, melts at 105° to 106° and has a specific rotation − 48°

Cadinene nitrosochloride, $C_{15}H_{24}NOCl$, is prepared by mixing a solution of cadinene in glacial acetic acid, kept in ice, with ethyl nitrite, and then adding a saturated solution of hydrochloric acid gas in acetic acid. It forms crystals melting, with decomposition, at 93° to 94° The nitrosate, $C_{15}H_{24} . N_2O_4$, is prepared by treating a well-cooled mixture of the sesquiterpene dissolved in glacial acetic acid, and ethyl nitrite, with a mixture of nitric acid and acetic acid. This compound melts with decomposition at 105° to 110°.

Cadinene is a bicyclic sesquiterpene, whose constitution is not definitely understood.

CARYOPHYLLENE.

Caryophyllene, as isolated from essential oils, and as usually described in literature is, without the slightest doubt, a mixture of at least two, if not three distinct chemical individuals.

This sesquiterpene, or mixture of sesquiterpenes, is found to a considerable extent in nature, especially in clove oil, pimento oil, pepper oil, cinnamon oil, betel oil, copaiba oil, and numerous other essential oils. As isolated from these oils the sesquiterpene has the following characters —

Boiling point	258° to 261°
Specific gravity	0 905 ,, 0 910
Optical rotation	− 7° ,, − 9°
Refractive index	1·5010

Deussen and Lewinsohn[1] were the first chemists to show conclusively that at least two sesquiterpenes are present in this body. By repeated fractional distillation they separated it into two bodies having the following characters, suggesting that the former might be an optically inactive sesquiterpene, slightly contaminated with the optically active variety —

Boiling-point (16 mm)	132° to 134° C.	Boiling point (17 mm.)	128° to 128·5° C.
Specific gravity at 20°	0 90346	Specific gravity at 17°	0·91034
$[\alpha]_D$	− 4 67°	$[\alpha]_D$	− 23 57°
n_D^{20}	1 49973	n_D^{17}	1 49899

The former of these bodies gave a yield of 20 per cent of a nitrosochloride and 8 2 per cent. of a blue nitrosite The second gives only a very small quantity of nitrosochloride and only 0·5 per cent of nitrosite.

Deussen termed the inactive caryophyllene, as further experiments showed it to be, α-caryophyllene, and the laevo-rotatory compound, β-caryophyllene. A third body was obtained, which yielded no blue nitrosite at all, to which Deussen assigned the name γ-caryophyllene This body

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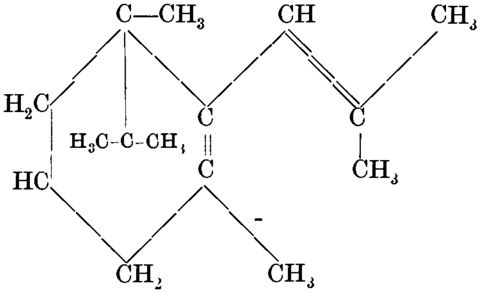
[1] *Annalen*, **356**, 1 , **359**, 245

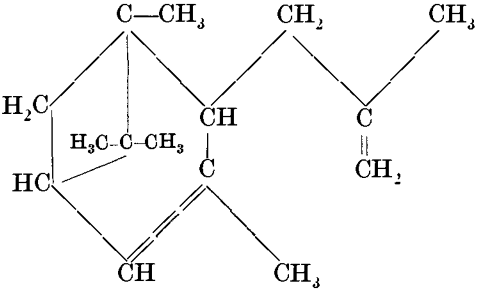
was obtained by heating the alcoholic solution of β-caryophyllene nitrosite. It is identical with the body previously known as isocaryophyllene, and has the following characters —

Boiling point at 14 mm.	124° to 125°
Optical rotation	− 22 22°

Semmler and Mayer[1] have taken up the study of this complicated question, and have agreed with Deussen in the main, but have further complicated the question by introducing fresh nomenclature of a scarcely scientific character. They consider, as Deussen proved, that crude caryophyllene consists of three distinct chemical individuals (1) the inactive α-caryophyllene isolated by Deussen, which is probably identical with the sesquiterpene from oil of hops described as humulene, (2) *terp*-caryophyllene, so called because Semmler considers it to be in some degree related to terpinolene, and (3) *lim*-caryophyllene, so called on account of its believed relationship in some remote manner to limonene. The following formulæ have been suggested for the last named two modifications —



Terp caryophyllene.



Lim-caryophyllene.

Terp-caryophyllene and *lim*-caryophyllene can be converted the one into the other by the preparation of their nitrosites or their nitrosochlorides, and subsequent regeneration of the sesquiterpene. They also both yield the same hydrochloride, melting at 69°.

Schimmel & Co.[2] showed that by treating caryophyllene hydrochloride melting at 69° (68° to 70°) with sodium ethylate, an unsaturated tricyclic sesquiterpene resulted. This body has the following characters —

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[1] *Berichte*, **44**, 3657.

[2] *Report*, October, **1910**, 180

Boiling-point at 738 mm.	257° to 259°
Specific gravity	0·919
Optical rotation	− 35° 37′
Refractive index	1 49586

If milk of lime be used as the regenerating reagent, a different sesquiterpene results, which has the following characters —

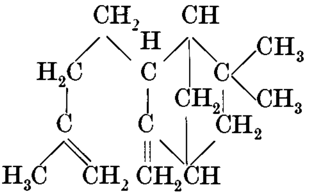
Boiling-point at 738 mm	257° to 258°
Specific gravity	0 9117
Optical rotation	− 35° 28′
Refractive index	1 49941

Semmler and Mayer[1] agree that the reagent used and the conditions of temperature, etc., govern the character of the sesquiterpene, or mixture of sesquiterpenes which result. By using sodium methylate very cautiously, they obtained a caryophyllene having the following characters —

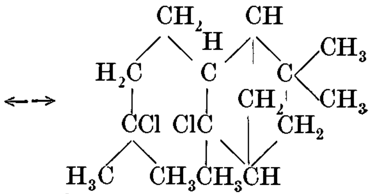
Boiling-point at 12 mm.	121° to 122 5°
Specific gravity at $\frac{20^\circ}{4^\circ}$	0 8996
Optical rotation	+ 19°
Refractive index	1·4990

So that by suitable procedure it is possible to regenerate dextro-caryophyllene from the crystalline hydrochloride.

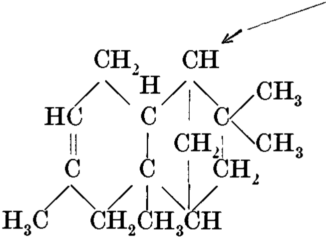
By using pyridine to split off the hydrochloric acid, Semmler and Mayer obtained a caryophyllene substantially identical with that obtained by Schimmel, but of optical rotation − 57°, indicating that Schimmel's body was a mixture of the two compounds. Semmler and Mayer give the following formulæ for the caryophyllenes indicated by the above, together with that of the hydrochloride, to indicate the transpositions which occur:—



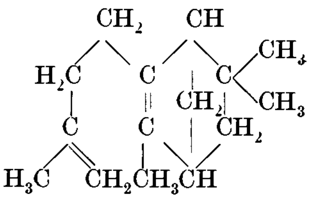
(1) Bicyclic regenerated caryophyllene.



Dihydrochloride



(2) Tricyclic caryophyllene.



(3) The caryophyllene which yields a blue nitrosite.

Formula (1) would thus indicate the natural dextro-caryophyllene of clove stems, formula (2) indicates the highly laevo-rotatory caryophyllene resulting from regeneration by means of pyridine, and (3) may represent the α-caryophyllene of Deussen.

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[1] *Berichte*, **43** (1910), 3451.

If these assumptions be correct, there must be at least four natural sesquiterpenes of the caryophyllene character, namely, those represented by formulæ (1) and (3), and the *terp*-caryophyllene and *lim*-caryophyllene of Semmler The most characteristic derivatives of the caryophyllenes are the following —

Caryophyllene dihydrochloride, $C_{15}H_{24}.2HCl$, may be obtained by saturating a quite dry ethereal solution of the sesquiterpene with dry hydrochloric acid gas, and exposing the mixture to very intense cold. It melts at 69° to 70°.

Caryophyllenic alcohol, $C_{15}H_{26}O$, is the easiest crystalline derivative to obtain for purposes of identification. The fraction of the oil containing caryophyllene is heated for a considerable time on the water-bath, using 25 grams with a mixture of 20 grams of strong sulphuric acid, 40 grams of water, and 1000 c c of glacial acetic acid. When the reaction is complete, the mixture is steam-distilled At first acetic acid and a mobile oil pass over, and then a much less volatile product, which solidifies on cooling. This is collected and purified by crystallisation from alcohol. It is caryophyllenic alcohol, and melts at 94° to 96°. It forms a phenylurethane melting at 136° to 137°. On treatment with dehydrating agents this alcohol yields not any modification of caryophyllene above described, but a sesquiterpene which is known as clovene, but which is probably just as accurately described as an isomeric caryophyllene as any of the other sesquiterpenes in question. It is, however, described below under a separate heading in order to be in conformity with the current, although unsatisfactory, nomenclature.

Caryophyllene nitrosochloride, $(C_{15}H_{24})_2N_2O_2Cl_2$, is obtained when a mixture of the sesquiterpene, alcohol, ethyl acetate, and ethyl nitrite is cooled in a freezing mixture, and then treated with a saturated solution of hydrochloric acid in alcohol The reaction mass is allowed to stand on ice for an hour and is then exposed to sunlight Thus prepared it melts at about 158° to 163°, and can be separated into two compounds, one being that of α-caryophyllene and the other that of β-caryophyllene Deussen's sesquiterpenes of natural caryophyllene from clove oil). α-caryophyllene nitrosochloride melts at 177°, and β-caryophyllene nitrosochloride at 159°. They can be separated by fractional crystallisation. The corresponding α-nitrolbenzylamine melts at 126° to 128°, and the β-nitrolbenzylamine at 172° to 173°. The bimolecular formula given above is probable but not certain.

Nitroso-caryophyllene, $C_{15}H_{23}NO$, is prepared by splitting off hydrochloric acid from the corresponding nitrosochloride, by means of sodium methylate α-Nitrosocaryophyllene melts at 116° and is optically inactive (as is the α-nitrosochloride), and β-nitrosocaryophyllene melts at 120° to 121° and has a specific rotation + 61 77° (as against − 98 07° for the β-nitrosochloride).

Caryophyllene nitrosite is an interesting compound. It has the formula $C_{15}H_{24}N_2O_3$, and was first produced by Schreiner and Kremers.[1] It is formed by treating a mixture of equal volumes of the sesquiterpene and petroleum ether with a concentrated solution of sodium nitrite and glacial acetic acid. It crystallises in fine blue needles, when recrystallised from alcohol it melts at 115° and has a specific rotation + 103°.

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[1] *Pharm Archives*, 2 (1899), 283

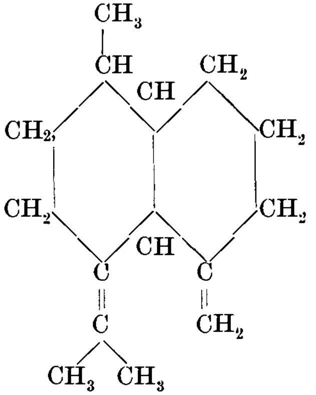
By treating this blue nitrosite, which Deussen calls β-caryophyllene nitrosite, with alcoholic potash at 0°, it is converted to a colourless isomer, melting at 139°, which Deussen terms β-caryophyllene isonitrosite. By treatment with boiling petroleum ether decomposition takes place and a compound melting at 159° is formed, of formula not yet established, and a nitro-compound of the formula $C_{15}H_{22}N_2O_4$, melting at 130·5°.

From the mother liquors of the preparation of the nitrosite from caryophyllene, a sesquiterpene is obtained, which may be the product of inversion by acids, or may be naturally present. It has the following characters:—

Specific gravity	0·8990 at 20°
Refractive index	1·49617
Optical rotation	− 25°

This body has been termed by Deussen isocaryophyllene. It yields two nitrosochlorides, α-isocaryophyllene nitrosochloride melting at 122°, and β-isocaryophyllene nitrosochloride melting at 146°.

A study of the oxidation products and nitroso-derivatives of caryophyllene, leads Deussen to consider that this sesquiterpene is a naphthalene derivative of the formula—



The above considerations indicate the complex nature of the hydrocarbons known as caryophyllene. For practical purposes, however, the compounds indicated are obtained of practically definite melting-points, and, in spite of the complicated isomerism existing amongst most of them, are useful for identification of the sesquiterpene or mixture of sesquiterpenes, occurring naturally and known as "caryophyllene".

HUMULENE.

Humulene is the name assigned by Chapman[1] to the sesquiterpene which he isolated from essential oil of hops. Its characters are as follows:—

Specific gravity	0·9001 at 20°
Boiling-point	263° to 266°

It is probably optically inactive. The following derivatives of humulene were prepared:—

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[1] *Journ. Chem. Soc.*, 67 (1895), 54. 780.

Humulene nitrosochloride, $C_{15}H_{24}NOCl$, melts at 164° to 165°, and yields a nitrolpiperidine, $C_{15}H_{24}NO \,.\, N \,.\, C_5H_{10}$, melting at 153°, and a nitrolbenzylamine, $C_{15}H_{24}NO \,.\, N \,.\, C_7H_7$, melting at 136°.

Humulene nitrosate, $C_{15}H_{24}N_2O_4$, melts at 162° to 163°.

Humulene nitrosite, $C_{15}H_{24}N_2O_3$, was obtained in two modifications, one forming blue crystals melting at 120°, and the other colourless melting at 166° to 168°.

Deussen[1] considers that the nitrosate above described is identical with that of α-caryophyllene, and that the nitrosochloride is identical with that of the same sesquiterpene. He therefore considers that humulene is, at all events in greater part, actually α-caryophyllene.

The similarity between humulene and caryophyllene had not escaped Chapman's notice at the time that he isolated humulene, but as he was unable to prepare a hydrate, which is one of the easiest of the caryophyllene derivatives to obtain in a pure state, he concluded that the sesquiterpene was not identical with caryophyllene. Recent work by Semmler does not tend to establish the identity of the two sesquiterpenes, and unless and until further evidence to the contrary is forthcoming, humulene may be regarded as a definite chemical individual.

SELINENE.

Selinene is a bicyclic sesquiterpene occurring in essential oil of celery. Its presence was first indicated by Ciamician and Silber[2] who announced the isolation of a sesquiterpene boiling at 262° to 269°, but no characteristic derivatives were prepared. Schimmel & Co.[3] examined this sesquiterpene to which they assigned the name selinene. They prepared a solid dihydrochloride melting at 72° to 74° and having a specific rotation + 18°. The pure sesquiterpene, regenerated from the dihydrochloride by means of sodium ethylate had the following characters :—

Boiling-point	268° to 272°
Specific gravity	0·9232
Optical rotation	+ 49° 30′
Refractive index	1·50483
Molecular refraction	65·82

The most recent work, however, on the sesquiterpene is that of Semmler and Risse.[4] From the crude selinene, prepared by fractional distillation, they prepared the crystalline dihydrochloride, $C_{15}H_{24} \,.\, 2HCl$, melting at 72° to 74°, by passing a mixture of 1 part of dry hydrochloric acid gas with 3 parts of air, into the sesquiterpene dissolved in ether. This compound on digestion at very gentle heat, with a solution of caustic potash in methyl alcohol, yields selinene, which the authors conclude is a doubly unsaturated bicyclic compound. The characters of the selinene thus obtained are as follows :—

Boiling-point at 11 mm.	128° to 132°
Specific gravity at 20°	0·919
Refractive index	1·5092
Optical rotation	+ 61° 36′

By reducing selinene with sodium alcohol, tetrahydroselinene was

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[1] *Jour. prakt. Chim.* [2], **83**, 483.

[2] *Berichte*, **30**, 496.

[3] *Report*, April, **1910**, 32.

[4] *Berichte*, **45**, 3301; **46**, 599.

obtained, of the formula $C_{15}H_{28}$. This body has the following characters :—

Boiling-point at 10 mm.	125° to 126°
Specific gravity at 20°	0·888
Optical rotation	+ 1° 12′
Refractive index	1·48375

In a second specimen prepared the optical rotation was + 7°.

Selinol, an alcohol of the formula $C_{15}H_{26}O$, was prepared from the dihydrochloride by shaking it for thirty-six hours at a temperature of 95° with milk of lime. It is a yellow oil, boiling at 155° to 163°. This alcohol yields dihydroselinol, $C_{15}H_{28}O$, when reduced by hydrogen in the presence of finely divided platinum. This body melts, after crystallisation from diluted acetic acid, at 86° to 87°.

They have also carried out the oxidation of selinene by means of ozone and potassium permanganate and have thus been able to establish that the regenerated selinene is not absolutely identical with the natural selinene. They are the first to record the existence of a *hemi-cyclic-sesquiterpene ;* this compound is termed pseudo-(β)-selinene. By passing a current of ozone into a solution of natural selinene (pseudo-(β)-selinene) in acetic acid, there is obtained a *diketone*, $C_{13}H_{20}O_2$, which is purified by treatment with permanganate in acetone solution. Its properties are as follows :—

Boiling-point at 11 mm.	179° to 180°
Specific gravity	1·0644 at 20°
Refractive index	1·49983
Optical rotation	+ 6° 36′

Its *disemicarbazone*, $C_{15}H_{26}N_6O_2$, melts at 228° C. with decomposition. The diketone regenerated by the action of oxalic acid on the disemicarbazone has the following properties :—

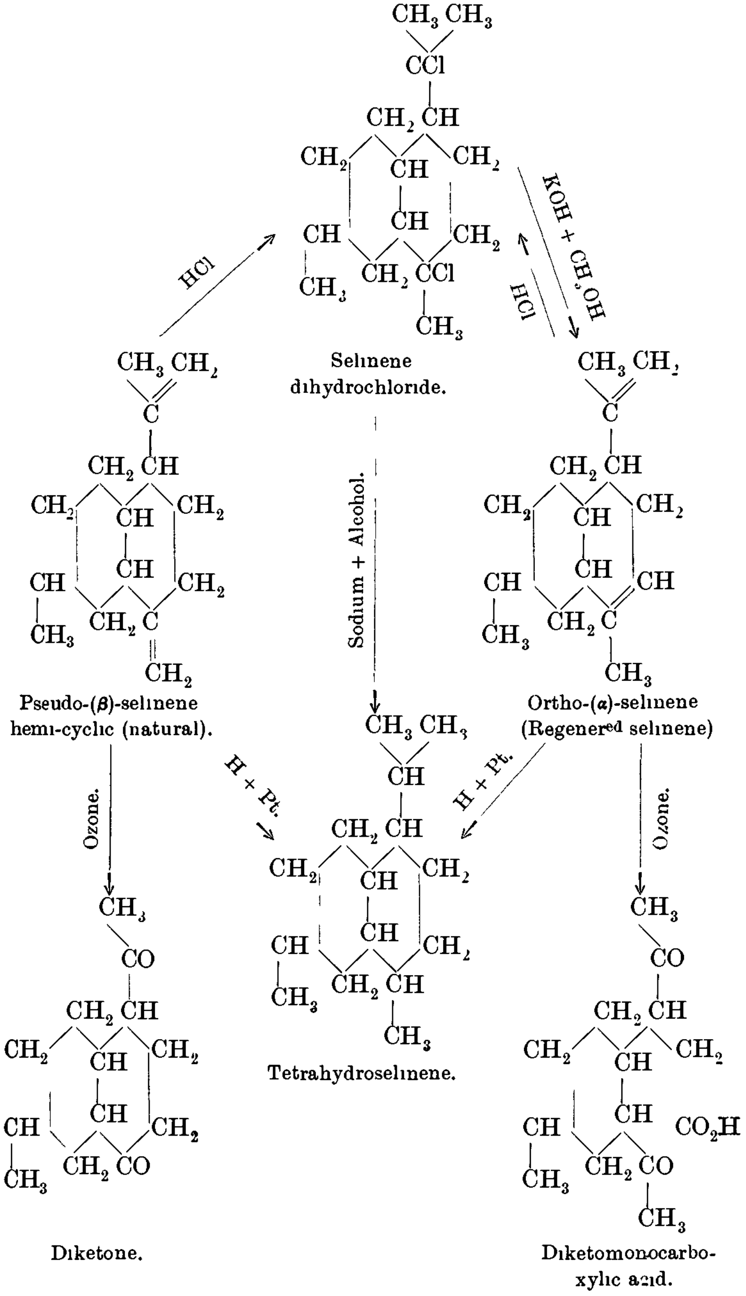
Boiling-point at 11 mm.	178° to 180°
Specific gravity	1·0566 at 20°
Refractive index	1·4994
Optical rotation	+ 15°

The principal oxidation product of the selinene regenerated from the dihydrochloride is a diketocarboxylic acid, of the formula $C_{14}H_{24}O_4$, melting at 226°.

Semmler deduces from these results that natural selinene is composed of a mixture containing principally the hemicyclic pseudo-(β)-selinene, together with a small quantity of ortho-(α)-selinene. By passing through the dihydrochloride it is possible to convert the pseudo-(β)-selinene into the ortho-(α)-selinene or regenerated selinene, which contains only a small proportion of the β form. Both yield the same solid dihydrochloride. Selinene affords a typical example of the possibility of the displacement of the double bond from the side chain into the nucleus.

The following structural formulæ represent, according to Semmler, the constitutions of the two forms of selinene and illustrate how they both yield the same dihydrochloride and the same tetrahydroselinene.

Selinene is still another case of unhappy nomenclature. The natural body is first known as selinene. The regenerated sesquiterpene is termed ortho-α-selinene, and because the natural, originally named selinene does not agree with the artificial body, it is now called “*pseudo*-selinene”.


HCl
KOH + CH₃OH
HCl
Selinene dihydrochloride.
Sodium + Alcohol.
Pseudo-(β)-selinene hemi-cyclic (natural).
Ortho-(α)-selinene (Regenered selinene)
H + Pt.
H + Pt.
Ozone.
Ozone.
Tetrahydroselinene.
Diketone.
Diketomonocarboxylic acid.

THE SANTALENES.

Two distinct sesquiterpenes exist in the essential oil of *Santalum album*, known as α-santalene and β-santalene. β-santalene is probably a bicyclic and α-santalene a tricyclic sesquiterpene. These sesquiterpenes were discovered by Guerbet.[1] From the method of their preparation it is doubtful whether they have been obtained in a state of purity, so that the characters assigned to them must be accepted with some reserve, and as probably being only approximate.

α-santalene has, according to Semmler, the following characters :—

Boiling-point at 9 mm.	118° to 120°
,, ,, ,, 760 mm.	253° ,, 254°
Specific gravity at 20°	0·8984
Refractive index	1·4910
Optical rotation	− 15°

β-santalene has, according to Semmler, the following characters :—

Boiling-point at 9 mm.	125° to 127°
,, ,, ,, 760 mm.	261° ,, 262°
Specific gravity at 20°	0·892
Refractive index	1·4932
Optical rotation	− 35°

α-santalene, according to Schimmel & Co., has the following characters :—

Boiling-point at 7 mm.	118°
,, ,, ,, 753 mm.	252°
Specific gravity at 15°	0·9132
Refractive index at 15°	1·49205
Optical rotation	− 3° 34'

whilst Schimmel's values for β-santalene are as follows :—

Boiling-point at 7 mm.	125° to 126°
Specific gravity at 20°	0·894
Refractive index at 20°	1·4946
Optical rotation	− 41° 3'

β-santalene has been synthesised by Semmler and Jonas by heating *l*-α-phellandrene and isoprene in a sealed tube.

No crystalline hydrochlorides could be obtained from either santalene. α-Santalene forms a liquid dihydrochloride of optical rotation + 6°, when dry hydrochloric acid is passed through its ethereal solution. It also forms a crystalline nitrosochloride melting with decomposition at 122°, and a nitrol-piperidide melting at 108° to 109°. β-santalene forms corresponding compounds, the dihydrochloride having a rotatory power + 8°. It forms, however, two isomeric nitrosochlorides, $C_{15}H_{24}NOCl$. They may be separated by fractional crystallisation from alcohol. One melts at 106°, the other at 152°. The corresponding nitrol-piperidides melt at 105° and 101° respectively.

By the dehydration of the isomeric santalols contained in sandalwood oil, Guerbet obtained two sesquiterpenes, which he designates α-isosantalene and β-isosantalene, according to the santalol from which they are respectively obtained. He assigns to them the following characters :—

	Boiling-point	Optical Rotation.
α-isosantalene	255° to 256°	+ 0·2°
β-isosantalene	259° ,, 260°	+ 6·1°

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[1] *Compt. Rend.*, **130** (1900), 417, 1324.

ATRACTYLENE.

Gadamer and Amenomiya[1] have prepared a well-defined sesquiterpene which they term atractylene, by dehydrating atractylol, a crystalline sesquiterpene alcohol separated from the oil of *Atractylis ovata*. It is an oil with an odour of cedar wood, and is probably bicyclic. It polymerises on keeping and has the following characters:—

Boiling-point at 10 mm.	125° to 126°
Specific gravity	0·9101 at 20°
Refractive index	1·50893

It yields a liquid dihydrochloride, from which, by the action of aniline, hydrochloric acid is split off. The regenerated sesquiterpene, however, differs in character from atractylene.

GUAIENE.

By dehydrating guaiol, the sesquiterpene alcohol present in guaiac wood oil, Wallach and Tuttle[2] obtained a bicyclic sesquiterpene which they called guaiene. It has been obtained by different methods by other observers from guaiol, and its characters are recorded as follows:—

Specific gravity	about 0·910 at 20°
Refractive index	„ 1·5010
Optical rotation	from − 40·35° to − 66·11°
Boiling-point	124° to 128° (at 9 to 13 mm.).

No crystalline derivatives have been prepared.

CAPARRAPENE.

Tapia[3] has prepared this bicyclic sesquiterpene by distilling caparrapiol, the sesquiterpene alcohol present in caparrapi oil, with phosphoric anhydride. It is a colourless oil having the following characters:—

Boiling-point	240° to 250°
Specific gravity	0·902 at 16°
Refractive index	1·4953
Specific rotation	− 2·21°

Its glacial acetic acid solution gives a rose-violet coloration on the addition of a few drops of sulphuric acid.

CYPRESSENE.

Odell[4] has isolated from the wood of *Taxodium distichum* (the so-called southern cypress) a sesquiterpene which he terms cypressene. It has the following characters:—

Boiling-point at 35 mm.	218° to 220°
„ „ „ 778 mm.	295° „ 300°
Specific rotation	+ 6·53°

It yields, on oxidation with nitric acid, an acid having the odour of isovaleric acid. It is probably trycyclic.

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[1] *Arch. der Pharm.*, **241** (1903), 33.

[2] *Annalen*, **279** (1894), 396.

[3] *Bull. Soc. Chim.*, **19** (iii.), 638.

[4] *Jour. Amer. Chem. Soc.*, **33**, 755.

GURJUNENE.

Deussen and Philipp[1] have separated the sesquiterpene fraction of gurjun balsam oil into two distinct sesquiterpenes which they term α-gurjunene and β-gurjunene. The former is a tricyclic and the latter a bicyclic compound. By repeated fractionation they obtained α-gurjunene, boiling at about 119° at 12 mm., and which had an optical rotation of not less than − 61°. They found β-gurjunene to boil at 123° at 12 mm., and to be slightly dextro-rotatory. Semmler and Spornitz[2] have, however, prepared β-gurjunene in a state of purity. By oxidising the mixed sesquiterpenesin acetone solution with potassium permanganate the α-sesquiterpene is readily oxidised, whilst β-gurjunene is attacked only with difficulty. The latter was obtained in a state of purity and had the following characters:—

Boiling-point	113·5° to 114° at 7 mm.
Specific gravity at 20°	0·9329
Refractive index	1·50526
Optical rotation	more than + 19°

When reduced by spongy platinum it yields dihydro-β-gurjunene, $C_{15}H_{26}$, having the following characters:—

Boiling-point	115° to 117° at 7 mm.
Specific gravity at 20°	0·9239
Refractive index	1·4949
Optical rotation	− 37°

Semmler considers β-gurjunene to resemble the tricyclic sesquiterpene, cedrene, so that it is doubtful whether it is bicyclic or tricyclic.

According to Deussen, both α- and β-gurjunene yield, on oxidation, a ketone $C_{15}H_{24}O$, which yields a semicarbazone melting at 234°, and has the following characters:—

Boiling-point at 12 mm.	175° to 178°
Specific gravity	1·0160
Optical rotation	+ 120° to + 130°
Refractive index	1 5303

When rectified gurjun balsam oil, that is, a mixture of α- and β-gurjunene, is saturated in ethereal solution with hydrochloric acid gas, and the mixture is left standing for two days at room temperature, and the hydrochloric acid abstracted by heating with sodium acetate, the regenerated sesquiterpene appears to be a bicyclic compound having the following characters:—

Boiling-point	129·5° to 132° at 12 mm.
Specific gravity	0·9183
Refractive index	1·5057

Deussen and Philipp term this sesquiterpene isogurjunene.

Semmler and Jakubowick[3] have isolated a tricyclic gurjunene from the oil having the following characters:—

Specific gravity	0·9348
Optical rotation	+ 74·5°
Refractive index	1·50275

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[1] *Annalen*, **374** (1910), 105.

[2] *Berichte*, **47** (1914), 1029.

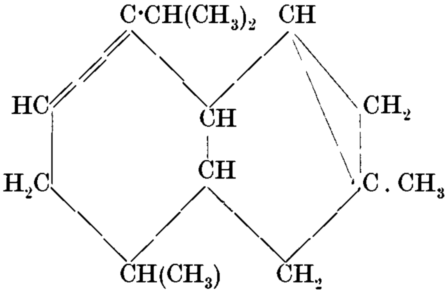
[3] *Ibid.*, 1141.

COPAENE.

Semmler and Stenzel[1] have isolated a sesquiterpene which they term copaene, from African copaiba oil. It is probably a tricyclic compound. Its physical characters are as follows :—

Boiling-point at 10 mm.	119° to 120°
Specific gravity	0·9077 at 17°
„ rotation	– 13° 35′
Refractive index	1·48943

It does not yield a solid nitrosochloride, nor a nitrosite, but it yields a crystalline hydrochloride, melting at 117° to 118°, which is identical with cadinene hydrochloride. Semmler considers copaene to have the formula—



Copaene.

It yields on reduction dihydrocopaene, a compound boiling at 118° to 121° at 12 mm. By oxidation by ozone or by permanganate of potassium it yields a ketonic acid of the formula $C_{15}H_{24}O_3$, which forms a semicarbazone melting at 221°. These derivatives characterise copaene as a new sesquiterpene. Its characters, however, have only been very slightly investigated at present.

SESQUICAMPHENE.

Semmler and Rosenberg[2] have identified a new sesquiterpene in the higher boiling fractions of camphor, oil, to which they have given the name sesquicamphene. This compound has the following characters :—

Boiling-point at 8 mm.	129° to 133°
Specific gravity at 20°	0·9015
Optical rotation	+ 3°
Refractive index	1·50058

It is a doubly unsaturated bicyclic sesquiterpene from which no crystalline derivatives have, so far, been prepared.

CEDRENE.

Cedrene is the naturally occurring sesquiterpene of cedar wood oil of which it forms the principal constituent. It is a tricyclic compound having the following characters :—

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[1] *Berichte*, **47** (1914), 2555.

[2] *Ibid.*, **46** (1913), 768.

Boiling-point at 12 mm.	124° to 126°
,, ,, ,, 760 mm.	262° ,, 263°
Specific gravity	0·9354
Optical rotation	– 55°
Refractive index	1·50233

The above figures are for the purest specimen of natural cedrene which has been prepared.

Semmler and Hoffmann[1] have examined this sesquiterpene in considerable detail. It was dissolved in acetone and oxidised with potassium permanganate, and the indifferent products thus obtained were separated by fractional distillation. Cedrene glycol, $C_{15}H_{26}O_2$, was obtained to the extent of 12 to 15 per cent. ; it crystallises from acetone in prisms, melting at 160°.

In addition to the glycol, a compound, $C_{15}H_{24}O_2$, was formed, which Semmler and Hoffman regard as a keto aldehyde, or a diketone, of specific gravity 1·055.

When cedrene was oxidised with permanganate, there were chiefly formed products of an acid nature, from which a cedrene keto acid, $C_{15}H_{24}O_3$, was isolated, which boiled at 215° to 222° (11 mm. press.). Its semicarbazone melts at 245° and its oxime at 60°.

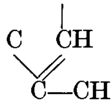
When cedrene is oxidised by chromic acid, in acetic acid solution, a mixture of two ketones is obtained, of which the principal is a body to which the name cedrone has been assigned. Cedrone has the following characters :—

Boiling-point at 9 mm.	147° to 150·5°
Specific gravity	1·0110° at 12·5°
Optical rotation	– 91° 30'
Refractive index	1·51202

It is a yellowish liquid having a strong odour of cedar wood, and forms a semicarbazone, melting at 242° to 243°.

By the reduction of cedrone by means of sodium and alcohol, there is formed *dihydro-isocedrol*, $C_{15}H_{26}O$, boiling at 148° to 151° C. under a pressure of 9·5 mm. When cedrene is heated at 180° to 210° C. with hydriodic acid and red phosphorus, and the product formed is reduced by sodium and alcohol, a body $C_{15}H_{26}$ is obtained, which Semmler describes by the name *dihydro-cedrene* It boils at 116° to 122° C. under 12 mm. pressure ; its specific gravity is 0·9052 at 15° C.

Although the constitution of cedrene is not understood, Semmler and Hoffmann consider that the following complexes are present in the various bodies described :—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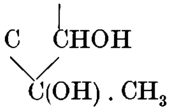
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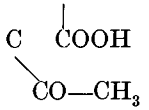
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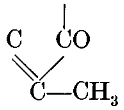
IV

in cedrene (I), cedrene-glycol (II), the ketonic acid (III), and cedrone (IV).

Semmler and Risse[2] have studied the oxidation of cedrene by means of ozone. They obtained the keto-acid, $C_{15}H_{24}O_3$, which on further oxidation either by means of bromine or nitric acid yields a dicarboxylic acid,

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[1] *Berichte*, **40** (1907), 3511.

[2] *Ibid.*, **45** (1912), 355.

$C_{14}H_{22}O_4$, melting at 182·5. The formation of this cedrene-dicarboxylic acid serves for the detection of cedrene in essential oils. It is sufficient if the fraction to be examined be oxidised by permanganate or ozone, and the acid obtained (boiling-point at 10 mm. = 200° to 220° C.) be then oxidised further, either by an alkaline solution of bromine or by nitric acid. Even very small proportions of cedrene have definitely led to the obtaining of this acid melting at 182·5° C.

Semmler and Mayer[1] have isolated from the oil of cedar wood an alcohol, pseudocedrol. There also exists in the oil a sesquiterpene alcohol, cedrol. The latter, on dehydration yields cedrene, which is probably identical with, or very closely allied to, natural cedrene, whilst pseudocedrol yields a mixture, when heated in a sealed tube, of cedrene and dihydrocedrene. Dihydrocedrene is a colourless oil having the following characters :—

Boiling-point at 10 mm.	109° to 112°
Specific gravity at 20°	0·907
Optical rotation	+ 37°
Refractive index	1·4882

By reducing natural cedrene with hydrogen in the presence of spongy platinum, a dihydrocedrene is obtained which has the following characters :—

Boiling-point at 10 mm.	122° to 123°
Specific gravity at 20	0 9204
Optical rotation	+ 2°
Refractive index	1·4929

No crystalline halogen derivatives of cedrene have been prepared, only liquid compounds being obtained when the sesquiterpene is treated by the usual processes.

CLOVENE.

When caryophyllene alcohol is dehydrated by means of zinc chloride or phosphorus pentoxide, a hydrocarbon results, which does not appear to be identical with any of the sesquiterpenes described under the name caryophyllene. It has therefore been named "clovene". Clovene has the following characters :—

Boiling-point	261° to 263°
Specific gravity	0·930 at 18°
Refractive index	1·50066 at 18°
Molecular refraction	64·77

VETIVENE.

A sesquiterpene was isolated from oil of vetivert by Genvresse and Langlois,[2] and was named by them vetivene. This body, or mixture of bodies, has, more recently, been examined by Semmler, Risse, and Schroeter.[3] There is no evidence, however, that the sesquiterpenes described as vetivene were obtained in a state of purity. From a German distilled oil they prepared a tricyclic "vetivene" and a bicyclic vetivene, having the following characters :—

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[1] *Berichte*, **45** (1912), 1384.

[2] *Comptes rend.*, **135**. 1059.

[3] *Berichte*, **45**, 2347

	Tricyclic Vetivene	Bicyclic Vetivene
Boiling-point at 16 mm.	123° to 130°	137° to 140°
Specific gravity at 20°	0·9355	0·9321
Refractive index	1·51126	1·51896
Optical rotation	– 12° 16′	– 10° 12′

The sesquiterpenes obtained from an oil distilled in Bourbon had the following characters:—

	A	B.
Boiling point at 9 mm.	124° to 127°	128° to 132°
Specific gravity at 20°	0·9299	0·9322
Refractive index	1·5130	1·52164
Optical rotation	– 2°	– 12° 36′

The former is considered to contain mostly tricyclic vetivene, and the latter bicyclic vetivene. The great differences in the characters of these sesquiterpenes are strong evidence of their impurity, and the above characters must be accepted with considerable reserve.

Two isomeric alcohols, known as vetivenol, also exist in the oil. By treatment with phosphorus pentachloride this mixture of alcohols is converted into a chloride, or mixture of chlorides, which on reduction yields an artificial vetivene, having the following characters:—

Boiling point at 9 mm.	121° to 127°
Specific gravity at 20°	0·9296
Optical rotation	– 25° 48′
Refractive index	1·51491
Molecular refraction	66·1

In another experiment the resulting sesquiterpene, after treatment with permanganate of potassium, had a dextro-rotation, + 6° 12′.

SUGININE.

The wood of *Cryptomeria japonica*, a Japanese cedar tree, yields an oil which contains a sesquiterpene to which the name suginene has been assigned. It has the following characters:—

Specific gravity	0·918
„ rotation	– 10° 34′

It yields a liquid hydrobromide of specific gravity 0·988 and specific rotation – 11° 15′.

SESQUICITRONELLENE.

Semmler and Spornitz[1] have isolated a sesquiterpene from Java citronella oil, which they have named sesquicitronellene. It has the following characters:—

Specific gravity at 20°	0·8489
Optical rotation	+ 0° 36′
Refractive index	1·5325
Boiling point at 9 mm	138° to 140°

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[1] *Berichte*, **46** (1913), 4025.

CALAMENE.

Semmler and Spornitz[1] have isolated a sesquiterpene from the oil of *Acorus calamus*, which they have termed calamene. This body has the following characters :—

Boiling-point at 10·5 mm.	123° to 126°
Specific gravity at $\frac{20^\circ}{19^\circ}$	0·9224
Optical rotation	+ 5°
Refractive index	1·50572

HERABOLENE.

This body is apparently a tricyclic sesquiterpene. It was isolated from essential oil of Herabol myrrh by Von Friedrichs,[2] who found it to have the following characters :—

Boiling-point at 16 mm.	130° to 136°
Specific gravity at 20°	0·943
Optical rotation	– 14° 12′
Refractive index	1·5125
Molecular refraction	64·98

It yields a dihydrochloride melting at 98° to 99°.

AROMADENDRENE.

Baker and Smith[3] have isolated from a number of eucalyptus oils, a sesquiterpene to which they have given the name aromadendrene. This compound was separated from the oil of *eucalyptus nova-angelica* in the dextrorotatory form, and from the oil of *eucalyptus baileyana* in the laevorotatory form. The two specimens had the following characters :—

	1.	2.
Specific gravity	0·9222	0·924
Boiling-point	260° to 265°	——
,, ,, at 10 mm.	124° to 125°	123° to 125°
Optical rotation	+ 4·7°	– 3·7°
Refractive index at 20°	1·4964	1·4964.

It yields a characteristic reaction with bromine. If a few drops are dissolved in 3 c.c. of glacial acetic acid and a little bromine vapour allowed to pass down the tube, a fine crimson colour forms which rapidly extends to the whole of the liquid and soon changes to violet and then to indigo blue; with phosphoric acid, the acetic acid solution gives a rose madder colour at the junction of the liquids, and when the liquids are mixed, the colour changes to crimson and then slowly to violet. Baker and Smith consider that the sesquiterpene contains one double linkage Semmler considers that it is a mixture of at least two bodies, one a bicyclic and the other a tricyclic sesquiterpene.

LIBROCEDRENE.

A sesquiterpene has been isolated from the oil of the leaves and twigs of the Californian incense cedar tree, *Libocedrus decurrens*, which has been named librocedrene. It has the following characters :—

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[1] *Berichte*, **46** (1913), 3700.
[2] *Arch. der Pharm.*, **245** (1907), 208.
[3] *A Research on the Eucalypts*, 2nd edition, 416.

Specific gravity	0·929 at 20°
Boiling-point	270° (approximate)
Refractive index	1·4994
Optical rotation	+ 6·4°

FERULENE.

Semmler, Jones, and Roenisch[1] have isolated a sesquiterpene from the oil of *Peucedanum ammoniacum*, which they have termed ferulene. This substance has the following characters:—

Boiling point at 10 mm.	126° to 128°
Specific gravity at 20°	0·8687
Optical rotation	+6°
Refractive index at 20°	1·4837

It is possible that it is not an individual compound, but a mixture of two bodies.

COSTENE AND ISOCOSTENE.

Semmler and Feldstein[2] have isolated three isomeric sesquiterpenes from the oil of costus root. These have been named α-costene, β-costene, and isocostene. They have the following characters:—

	α costene	β costene	Isocostene
Boiling-point	122° to 126° at 12 mm	144° to 149° at 19 mm.	130° to 135° at 12 mm.
Specific gravity	0·9014 at 21°	0·8728 at 22°	0·906 at 21°
Refractive index	1·49807	1·4905	1·50246
Optical rotation	− 12°	+ 6°	+ 31°

ELEMENE.

Elemene is a monocyclic sesquiterpene resulting from the reduction of elemol, the sesquiterpene alcohol present in Manila elemi oil.[3] It has the following characters:—

Boiling-point at 10 mm	115° to 117°
Specific gravity at 20°	0·8797
Refractive index	1·4971

It is possibly a mixture of more than one sesquiterpene.

OPOPONAX SESQUITERPENE.

The fraction of opoponax oil boiling at 135° to 137° *in vacuo* contains a sesquiterpene, which has been examined by Schimmel & Co.[4] On fractionation at ordinary pressure, it boiled at about 260° to 270°, and in this impure condition was dissolved in ether and saturated with hydrochloric acid gas. The crystalline hydrochloride which resulted melted at 80°, and was optically inactive. It has the composition $C_{15}H_{24} . 3HCl$.

The sesquiterpene is apparently one containing three double linkages. When regenerated from the hydrochloride by boiling with sodium acetate in glacial acetic acid, it has the following characters:—

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[1] *Berichte*, **50**, 1823.

[2] *Ibid.*, **47** (1914), 2687.

[3] *Ibid.*, **49** (1916), 794.

[4] *Report*, October, **1904**, 68.

Specific gravity	0·8708
Optical rotation	± 0°
Refractive index at 26°	1·48873
Boiling-point at 3 mm.	114° to 115°

PATCHOULENE.

This sesquiterpene has not been found naturally. It is formed by the dehydration of the so-called patchouli camphor, a sesquiterpene alcohol, $C_{15}H_{26}O$, found in oil of patchouli. It has the following characters:—

Boiling-point	255° to 256°
Specific gravity	0·9334
Optical rotation	– 36° 52′

Von Soden and Rojahn[1] have isolated two sesquiterpenes from patchouli oil, which have the following characters:—

	1.	2.
Boiling-point	264° to 265°	273° to 274°
Specific gravity	0·9335	0·930
Optical rotation	– 58° 45′	+ 0° 45′

MAALI SESQUITERPENE.

Schimmel & Co.[2] have isolated a sesquiterpene alcohol from Samoan resin, known as Maali resin, and by dehydrating it by means of formic acid have obtained a sesquiterpene which has not been named other than as Maali sesquiterpene. It has the following characters:—

Specific gravity	0·9190
Optical rotation	+ 121° 20′
Refractive index	1·52252
Boiling-point	271°

CITRONELLA SESQUITERPENE.

Ceylon citronella oil contains an olefinic sesquiterpene having the following characters:—

Specific gravity	0·8643
Refractive index	1·5185 at 15°
Optical rotation	+ 1° 28′
Boiling-point	280°, with decomposition

No crystalline derivatives have been prepared.

CANNABIS SESQUITERPENE.

A sesquiterpene has been isolated from the essential oil of *Cannabis Indica*. This may fairly be considered a definite body, as it has been isolated by many different observers and described by them at different times. Valenta[3] first mentions it. Vignolo[4] describes it as a mobile liquid boiling at 256°, of specific gravity ·897 at 15°, and slightly laevo-rotatory. Wood, Spivey, and Easterfield[5] give the boiling-point as 258° to 259°, the specific gravity as ·898 at 18°, and the rotation as – 8·6°.

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[1] *Berichte*, **37** (1904), 3353.

[2] *Report*, November, **1908**, 137.

[3] *Gazzetta*, **1880**, 540.

[4] *Ibid*, **1895**, 110.

[5] *Jour. Chem. Soc.*, **1896**, 543.

The name *cannibene* may be applied to this hydrocarbon. Personne first gave this name to what is now known to be an impure compound obtained from the oil.

Gonostylene.

This sesquiterpene is obtained by the dehydration of the sesquiterpene alcohol gonostylol. It has the following characters:—

Boiling-point at 17 mm.	137° to 139°
Specific gravity at 17°	0·9183
,, rotation	+ 40° (in alcohol)
Molecular refraction	66·7

Eudesmene.

Eudesmene is a sesquiterpene obtained by the dehydration of eudesmol, the sesquiterpene alcohol found by Baker and Smith in several species of eucalyptus oil. It has the following characters:—

Boiling-point at 10 mm.	129° to 132°
Specific gravity at 20°	0·9204
,, rotation	+ 49°
Refractive index	1·50738

It forms a dihydrochloride melting at 79° to 80°. The sesquiterpene regenerated from the dihydrochloride has slightly different characters, so that a molecular rearrangement is probable; and the regenerated "eudesmene" may contain another sesquiterpene. Its characters are as follows:—

Boiling-point at 7 mm.	122° to 124°
Specific gravity at 20°	0·9196
,, rotation	+ 54° 6′
Refractive index	1·50874

On reduction it yields tetrahydro-eudesmene, $C_{15}H_{30}$, having the following characters:—

Boiling-point at 75 mm.	122° to 125°
Specific gravity at 20°	0·8893
,, rotation	+ 10° 12′
Refractive index	1·48278

Chinese Pine Sesquiterpene.

The essential oil from the oleo-resin of Chinese turpentine[1] (botanical origin unknown) contains a tricyclic sesquiterpene, having the following characters:—

Boiling-point at 2·5 mm.	92° to 93°
Specific gravity	0·9408
Refractive index at 20°	1·5031
Optical rotation	+ 47·3°

It forms a monohydrochloride melting at 58° to 59°.

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[1] *Jour. Chem. Ind. Tokyo*, **23**, 45.

LONGIFOLENE.

Longifolene in its dextrorotatory form is a sesquiterpene isolated by Simonsen[1] from Indian turpentine oil from *Pinus longifolia.* It is a colourless viscous liquid having the following characters :—

Boiling-point at 706 mm.	254° to 256°
" " " 36 mm.	150° to 151°
Specific gravity at $\frac{30^\circ}{30^\circ}$	0·9284
Refractive index at 30°	1·4950
Optical rotation	+ 42·73°

It yields a crystalline hydrochloride melting at 59° to 60° ; a hydrobromide melting at 69° to 70°, and a hydriodide melting at 71°.

AZULENE.

This hydrocarbon is not a sesquiterpene, but may be conveniently dealt with here. It has been thoroughly investigated by Sherndal.[2] In many essential oils, especially those containing sesquiterpenes, a blue coloration is observed, which becomes concentrated in the higher boiling fractions. This is especially marked in oil of chamomiles. The body responsible for this blue colour was separated by taking advantage of its ready solubility in mineral acids. A very blue fraction was shaken out with one-fifth of its weight of 63 per cent. sulphuric acid. After standing the acid layer was separated, diluted with water, and shaken with petroleum ether until no more colour was extracted. The dark blue petroleum was then extracted with phosphoric acid, 85 per cent. The acid extract, diluted with water, was shaken with ether. On evaporating the solvent, azulene was left. It was further purified by steam distillation, and, finally, by distilling *in vacuo.* It is a viscid liquid, with a weak phenolic odour, suggestive of thymol. It is a hydrocarbon, having the formula $C_{15}H_{18}$. Its specific gravity is 0·9738 at 25°. Under normal pressure the boiling-point is 295° to 300° C. with decomposition ; under 25 mm. pressure azulene distils between 185° and 195° C., leaving a brown residue.

When azulene is heated with sulphuric acid and acetic anhydride a sulphonic acid, soluble in water, is formed. This acid forms a fine violet sodium salt. This sodium salt is not very stable ; when kept for three months it decomposes into a mixture of oil and resin. Its aqueous solution gives blue precipitates with calcium and barium salts.

Sherndal considers the formation of a crystalline picrate, melting at 122°, the best method of identifying azulene. On reduction azulene yields a dihydro-sesquiterpene, $C_{15}H_{26}$, and in Sherndal's opinion, it is closely related to α-gurjunene in constitution.

APLOTAXENE.

Semmler and Feldstein[3] have isolated from the oil of costus root a hydrocarbon of the formula $C_{17}H_{28}$, to which they have given the name aplotaxene. Its characters are approximately as follows :—

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[1] *Jour. Chem. Soc.* **1920**, 570.

[2] *Jour. Amer. Chem. Soc.*, **37** (1915), 167, 1537.

[3] *Berichte*, **47** (1914), 2687.

Boiling-point at 11 mm.	153° to 155°
Specific gravity at 21°	0·831
Refractive index	1·4830
Optical rotation	± 0°

Its low specific gravity indicates that it is an open-chain compound, and from its easy reduction by sodium and alcohol, into dihydroaplotaxene, $C_{17}H_{30}$, and by hydrogen and platinum black into normal heptadecane $C_{17}H_{26}$, it is evident that aplotaxene is a tetraolefinic normal chain hydrocarbon.

3. ALCOHOLS.

Bodies of an alcholic nature play a very important part in both natural and synthetic perfumery. They are found to a very large extent in essential oils, both in the free state and also in the form of esters. Some that have not so far been recognised as constituents of essential oils, have been found to be so highly odorous, and so useful as perfume materials, that they are prepared artificially, and enter largely into the composition of the synthetic perfumes which to-day are indispensable to the manufacturer of perfumes. It is obvious that those alcohols which are soluble in water, such as methyl and ethyl alcohols, although they may be original constituents of some essential oils, are removed by the ordinary distillation processes, so that they do not, in fact, appear in the essential oil as found in commerce.

The higher homologues of the methane series of alcohols are found, sometimes in the merest traces only, in certain essential oils, but their value in perfumery has been so well established that a number of them are now manufactured as "synthetics".

The alcohols of the geraniol series and those of the closed-chain series are practically insoluble in water, and, where they occur as natural constituents of essential oils, are present in the distilled oil.

E. Emmet Reid[1] describes a method of separating alcohols from a mixture which may contain primary, secondary, and tertiary alcohols. It consists in esterifying with phthalic anhydride, and converting the acid ester into the sodium salt, which reacts with *p*-nitrobenzyl bromide, forming an ester which serves for identification. Primary alcohols combine with phthalic anhydride below 100°, whilst secondary react rapidly only above 120°. An excess of the alcohol is heated for one hour with 1 gram of phthalic anhydride (a sealed tube being used for the lower alcohols), and the product is transferred to a separating funnel containing 10 c.c. of water. About 15 c.c. of ether and 5 c.c. of normal solution of caustic soda are added, and the whole shaken for five minutes. The water is drawn off and the ether solution washed with a little water. The water solution is again extracted with ether. The aqueous solution is evaporated to dryness, and the sodium salt is transferred to a 100 c.c. flask with 5 c.c. of water and 10 c.c. of 95 per cent. alcohol. To this is added 1 gram of *p*-nitrobenzyl bromide, and the mixture is boiled for one hour on a steam bath under a reflux condenser. The product is then obtained by evaporation of the liquid, and recrystallised from 63 per cent. alcohol. The following are the results obtained :—

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[1] *Jour. Amer. Chem. Soc.* (**1917**), 1249 ; Krogh, *P. and O.E.R.*

Alcohol.	Melting-point of *p*-nitrobenzyl Phthalate.	Strength of Alcohol Solvent.	No of c.c. of Alcohol Required for about 1·3 Grams.
	Degrees.	Per Cent.	
Methyl	105	63	9
Ethyl	80	63	9
Propyl	53	63	27
Isopropyl	74	63	30
Allyl	61·5	71	17
N-butyl	62	76	40
N-octyl	41	70	30
Benzyl	83	76	28
Phenylethyl	84·3	76	21
Borneol	100	80	20
Isoborneol	87	—	—

Isobutyl, isoamyl, and cinnamic alcohols, menthol and geraniol gave *p*-nitrobenzyl phthalates which were oily liquids and could not be crystallised.

METHYL ALCOHOL.

This alcohol, the lowest of the paraffin series, is found in the distillation waters of a number of essential oils, being soluble in all proportions in water. It does not therefore form a constituent of essential oils in the form in which they are found in commerce. In the form of esters, methyl alcohol is found as a constituent of a number of essential oils, such as, for example, oil of wintergreen, which consists almost entirely of methyl salicylate. Methyl alcohol, CH_3OH, is a liquid of specific gravity 0·810, boiling at 64°.

ETHYL ALCOHOL.

Ethyl alcohol, C_2H_5OH, is also a natural constituent of a number of essential oils, but being, like methyl alcohol, soluble in water in all proportions, it is washed away in the distillation waters. It is an inflammable liquid of specific gravity 0·794, and boiling at 78°.

ISOBUTYL ALCOHOL.

This alcohol, of the formula $(CH_3)_2CH.CH_2OH$, is found in the free state in the distillation water of the oil of *Eucalyptus Amygdalina.* It boils at 108·5°, and has a specific gravity 0·8003. It yields a phenyl-urethane melting at 80°.

ISOAMYL ALCOHOL.

Isoamyl alcohol, $(CH_3)_2.CH.CH_2CH_2OH$, has been found in the free state in various eucalyptus oils, and also in geranium, lavender, and peppermint oils. It boils at 131° and yields a phenyl-urethane, melting at 53°.

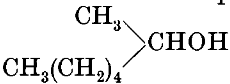
HEXYL ALCOHOLS.

Normal hexyl alcohol, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2OH$, is found, principally in the form of esters, in a few essential oils, especially the oil of *Heracleum giganteum.* It is a liquid of specific gravity 0·824, and boils at 157°.

An isohexyl alcohol, $(C_2H_5)(CH_3).CH.CH_2.CH_2.OH$ (methyl-ethyl-propyl alcohol), is found in the form of esters in Roman chamomile oil. This body is an oil of specific gravity 0·829, optical rotation $[\alpha]_D = + 8{\cdot}2°$, and boiling at 154°.

HEPTYL ALCOHOL.

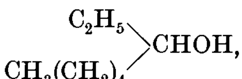
One of the heptyl alcohols, methyl-amyl carbinol, of the formula



$\begin{matrix} CH_3 \\ CH_3(CH_2)_4 \end{matrix}\!\!>\!CHOH$, has been isolated from oil of cloves. It has a specific gravity 0·8244, and boils at 157° to 158°. On oxidation by chromic acid, it yields methyl-amyl-ketone, which gives a semicarbazone, melting at 122° to 123°.

ETHYL-AMYL CARBINOL.

Ethyl-amyl carbinol,



$\begin{matrix} C_2H_5 \\ CH_3(CH_2)_4 \end{matrix}\!\!>\!CHOH$, one of the isomeric octyl alcohols, has been found as a constituent of Japanese peppermint oil. It has been prepared synthetically by Pickard and Kenyon[1] by passing the vapour of a mixture of 145 grams of normal caproic acid and 180 grams of propionic acid through a tube charged with thorium oxide heated to 400°. By this means they obtained 124 grams of ethyl-amyl-ketone. This was reduced in a solution of moist ether with sodium, and the carbinol resulted. It has the following characters :—

Specific gravity at $\frac{20°}{4°}$	0·8247
Boiling-point at 753 mm.	168° to 172°
,, ,, ,, 16 mm.	76°
Optical rotation	+ 6·79°
Refractive index	1·4252
Melting-point of phthalate	66° to 68°
Boiling-point of the ketone	165° ,, 166°
Melting-point of semicarbazone	112°

HIGHER ALIPHATIC ALCOHOLS.

The higher aliphatic alcohols, from octyl alcohol upwards, have recently been introduced as perfume materials with considerable success. Only one or two of them, such as nonyl and undecylenic alcohols, have so far been detected as natural constituents of essential oils, but other members of the series are prepared artificially, and are employed in minute quantities in the preparation of perfumes with characteristic fruity bouquets. These alcohols are greatly diminished in perfume value by traces of impurities. According to H. J. Prins,[2] the first interesting member of the series is octyl alcohol ; it has a very sweet, rose-like odour, and is especially suitable for giving a rose perfume that peculiar sweet smell which distinguishes a *rose* from a *rose perfume.* This feature of the aliphatic alcohols diminishes in the series from C_8 to C_{12}-

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[1] *Jour. Chem. Soc.*, **103** (1913), 1923.

[2] *P. and E.O.R.*, **1917**, 68.

Laurinic or duodecylic alcohol has a soft and not very strong but delicate odour. These alcohols can be used in much greater quantities than the corresponding aldehydes. The latter are only admissible in a perfume base to the extent of from 1 to 2 per cent. The alcohols may be used in quantities up to 5 per cent. Laurinic alcohol is very suitable as a basis for perfumes of the lily type, owing to its delicate odour; it has, moreover, very powerful fixative properties.

Prins (*loc. cit.*) considers that the melting and boiling-points of these alcohols are amongst the best criteria of their purity. He gives the following values for the more important of them :—

	Melting-point.	Boiling-point at 13 mm.
Octyl alcohol	– 22° to – 21°	95°
Nonyl ,,	– 11° ,, – 10°	102°
Decyl ,,	– 10° ,, – 8°	110°
Duodecyl alcohol	13° ,, 15°	142°
Undecylenic ,,	– 12° ,, – 11°	128°

It is strange that only the normal alcohols amongst the higher aliphatic alcohols are of any value as perfumes, the iso-alcohols being useless.

The following are the only members of the series which have, so far, been utilised as perfume materials :—

Octyl Alcohol.—This is the primary normal alcohol of the formula $CH_3(CH_2)_6CH_2OH$. It has an odour recalling that of opoponax, and is useful in the blending of perfumes of this type. It boils at 196° to 197°, and has a specific gravity 0·8278. It yields octyl aldehyde on oxidation, whose naphtho-cinchoninic acid compound melts at 234°.

Nonyl Alcohol.—This is the normal alcohol of the formula

$$CH_3(CH_2)_7CH_2OH.$$

This alcohol has a marked rose odour, resembling that of citronellol, and has also a suggestion of orange in it. It can be extracted from orange oil by saponifying the high boiling constituents and extracting the alcohol in the form of its phthalic acid compound. It has a specific gravity 0·840, and refractive index 1·43582. It boils at 98° to 101° at 12 mm. It can be identified by its phenyl-urethane, melting at 62° to 64°. There is a secondary nonyl alcohol, methyl-heptyl carbinol, which exists in certain essential oils. It is a liquid of specific gravity 0·8273, and boils at 198° to 200°. It is of little use, however, for perfumery purposes.

Decyl Alcohol.—This alcohol, of the formula $CH_3(CH_2)_8CH_2OH$, is often considered to be the most useful of this series. It boils at 110° at 13 mm., and melts at – 10°. Its odour is hardly describable, and although very expensive it is used in such small amounts as to render its cost but small. It is very useful in modifying the bouquet of numerous flower odours, and has been well described by an American perfumer as "an alcohol which the up-to-date manufacturer uses to deceive the copier of odours".

Undecylic Alcohol.—This alcohol, $CH_3(CH_2)_9CH_2OH$, may be described as of the same general characters as decylic alcohol, useful for the same purpose, but giving a slightly different modification to the bouquets. It occurs in Algerian Rue oil and in oil of Trawas. It boils at 231° to 233°.

Undecylenic Alcohol.—This alcohol is an unsaturated 11-carbon alcohol, and therefore not a homologue of ethyl alcohol. It is, however, so closely related to the series, and so similar to the two last described, that its inclusion here is convenient. It boils at 128° at 13 mm. and melts at $-12°$. Its constitution is $CH_2 : CH(CH_2)_8CH_2OH$. It is being used to a fairly considerable extent by the more skilful perfumers in the same way as decyl alcohol.

Duodecylic Alcohol.—This alcohol has the formula $CH_3(CH_2)_{10}CH_2OH$, and is used exactly as are the last three described bodies. It is a liquid boiling at 142° at 13 mm. It crystallises at low temperatures, and melts at 14°.

The above series of alcohols are exceedingly difficult to manufacture, hence their expense. The general method of their preparation would theoretically be by distilling the calcium salts of the corresponding fatty acid with calcium formate, *in vacuo*. This would yield the corresponding aldehyde, which on reduction would yield the corresponding alcohol. In practice, however, many technical difficulties arise, and special processes have to be used which are kept carefully as trade secrets.

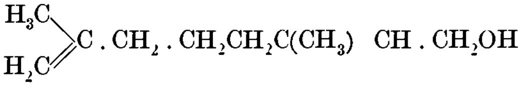
The next group of alcoholic bodies to be studied are those which, although open-chain alcohols, show considerable tendency to easily pass into closed-chain compounds, so that they occupy a definite position of their own, midway between the ordinary aliphatic series and the closed-chain series. The principal members of this important group are geraniol, nerol, linalol, and citronellol, together with the so-called aliphatic sesquiterpene alcohols, farnesol and nerolidol.

GERANIOL.

Geraniol, $C_{10}H_{17}OH$, is a constituent of many essential oils, both in the free state and in the form of esters. It is present to a very large extent in palmarosa oil, ginger-grass oil, and citronella oil, principally in the free state, and in geranium oil, to some extent in the free state, but principally in the form of esters. It is also an important constituent of otto of rose, and is present in numerous other oils belonging to the most distantly related groups.

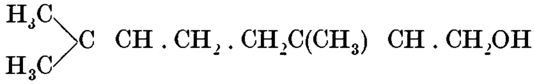
This alcohol is of the highest importance in artificial perfumery, and is manufactured on a very large scale from either palmarosa or citronella oil. It can be separated from essential oils containing it by intimately mixing them with an equal weight of dry powdered calcium chloride, and keeping the mixture in a desiccator at $-4°$ for 16 hours. The soft mass is then rubbed down with dry petroleum ether, and the liquid portion removed by means of a suction filter. The calcium chloride compound of geraniol is then treated with water, which decomposes the compound, and the oil purified by fractional distillation. The geraniol comes over between 228° and 230°. In the case of palmarosa oil the geraniol can be prepared in a state of fair purity by first saponifying the oil and then fractionally distilling it. It can be prepared in a state of absolute purity by treating it with sodium and then with dry ether and phthalic anhydride. The resulting geraniol sodium phthalate is hydrolysed by alcoholic potash, and the pure geraniol precipitated by water.

Geraniol is a colourless liquid of sweet odour, recalling that of the rose, principally, and to a lesser extent the pelargonium. It is an open-chain alcohol, having one of the two following constitutional formulæ :—



$$\begin{matrix}H_3C\\ H_2C\end{matrix}\!\!>\!C\,.\,CH_2\,.\,CH_2CH_2C(CH_3)\ CH\,.\,CH_2OH$$

or



$$\begin{matrix}H_3C\\ H_3C\end{matrix}\!\!>\!C\ CH\,.\,CH_2\,.\,CH_2C(CH_3)\ CH\,.\,CH_2OH$$

Pure geraniol has the following physical characters —

Specific gravity at 15°	0·880 to 0·883
Optical rotation	0°
Refractive index at 20°	1·4766 to 1·4786
Boiling point at 760 mm	228° „ 230°

At 10 mm. it boils at 110° to 111°, and at 18 mm. at 121° This alcohol is, of course, an essential constituent of synthetic otto of rose and all odours of a similar type

The following are the most satisfactory methods of recognising it. It yields, as above described, a characteristic compound with calcium chloride, from which the geraniol may be regenerated and examined as to its physical characters It also yields a characteristic diphenylurethane, $(C_6H_5)_2N\ COOC_{10}H_{17}$, melting sharply at 82°. It may be prepared as follows 1 gram of the oil, 1·5 gram of diphenylcarbamine chloride and 1·3 gram of pyridine are heated in a water-bath for two hours. The reaction product is submitted to a current of steam to remove unaltered products, and the solid residue recrystallised from alcohol If citronellol is present as well as geraniol, it is necessary to recrystallise several times before the product is pure and melts at 82°. The naphthyl-urethane is also characteristic and easily prepared. Equimolecular proportions of naphthyl-isocyanide and geraniol are allowed to stand for twelve hours, when the mass will be found to be solid. Recrystallised from diluted methyl alcohol, the product melts at 47° to 48°. One of the most characteristic derivatives for identification purposes is geranyl-phthalate of silver. This salt is prepared as follows · 90 grams of phthalic anhydride and 90 c c of geraniol are heated in a water-bath for forty-five minutes, 100 c c. of boiling water are then added. The whole is well shaken and the water separated, and the oil washed five or six times in the same manner. 100 c.c of water and 35 c.c. of ammonia are then added. Neutral compounds are then extracted with ether. After separation of the ether, the liquid is diluted with 200 c c. of alcohol, and then 175 c.c. of a normal solution of nitrate of silver added A white crystalline precipitate rapidly settles out. This is washed with alcohol and then with ether, and then dried *in vacuo* The resulting crystals, recrystallised from a mixture of alcohol and benzene, melt at 133° The salt has the formula $C_6H_4(COOC_{10}H_{17})$ $(COOAg)$

The identification of geraniol can be confirmed by its conversion into citral, $C_{10}H_{16}O$, its aldehyde, which has a very characteristic odour and yields well-defined crystalline derivatives. Five parts of the alcohol fraction are shaken with 2·5 parts of chromic acid and four parts of concentrated sulphuric acid dissolved in 100 parts of water. The mixture is warmed in the water-bath for a few minutes, when crude citral separates on the surface of the liquid This is purified by steam distillation and conversion into its sulphonic acid compound in the usual manner and then yields characteristic crystalline compounds, which are described under "citral".

Geraniol is converted into the isomeric alcohol, linalol, by heat, and both alcohols yield the same chloride when treated with dry hydrochloric acid gas. Dupont and Labaune first prepared this chloride, which they considered was linalyl chloride, but Forster and Cardwell[1] have shown that it is geranyl chloride.

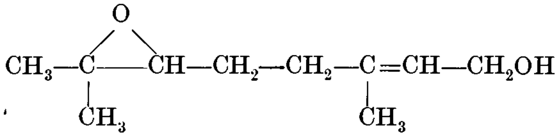
These chemists prepared it by acting upon either geraniol or linalol with thionyl chloride in the presence of pyridine. It is a colourless liquid, having the following characters:—

Boiling-point at 14 mm.	103°
Specific gravity at 25°	0·918
Refractive index	1·4741

By heating geranyl chloride with sodium alcoholate geranyl ethyl ether was obtained. This body, $C_{10}H_{17}.O.C_2H_5$, is an oil with a faint rose odour, having the following characters:—

Specific gravity at 25°	0·864
Boiling-point at 19 mm.	115°
Refractive index	1·4662

Prileshajeff[2] has prepared the oxide and dioxide of geraniol by direct oxidation by means of hydrated benzoyl peroxide. By using the equivalent of 9 grams of active oxygen on 100 grams of geraniol, geraniol monoxide was formed, which has the following constitution:—

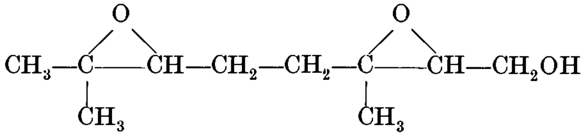


The yield was 55 per cent. It is a viscous mass with feeble odour, and having the following characters:—

Boiling-point at 25 mm.	157° to 158°
Specific gravity at 16°	0·9610
Refractive index at 16°	1·4681

When heated with acetic anhydride at 150° C., this oxide yields the ester $C_{10}H_{17}O_3(COCH_3)_3$, boiling at 208° C., under 25 mm. pressure.

Geraniol dioxide—



is obtained when 50 grams of geraniol are oxidised by means of 8 grams of active oxygen. The dioxide occurs as a colourless mobile liquid having the following characters:—

Boiling-point at 25 mm.	180° to 183°
Specific gravity at 16°	1·0472
Refractive index at 16°	1·4653

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[1] *Journ. Chem. Soc.*, **103**, 1338.

Jour. Soc. Chem. Phys. Russ., **44**, 613.

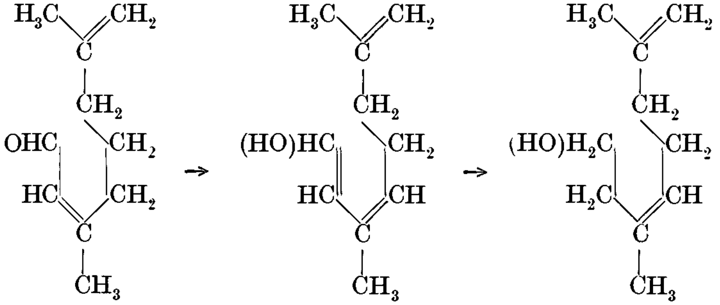
Geraniol, as will be seen below, is the alcohol corresponding to one of the stereoisomeric forms of citral, nerol being the isomeric alcohol, corresponding with the other stereoisomeric citral. Semmler[1] and Schossberjer have recently succeeded in enolising citral, that is, causing a migration of the double linkage towards a CH_2 group, and from the enolic form of citral thus obtained preparing an isomeric alcohol which he terms isogeraniol.

When citral is heated with acetic anhydride, the migration of the double bond takes place towards the CH_2 group and the acetic ester of *enol*-citral is formed. This acetate is resinified by all saponifying agents and therefore does not regenerate citral. By reducing it with sodium amalgam and methyl alcohol slightly acidified with acetic acid, an alcohol was obtained which is not identical with geraniol nor with nerol, and which has therefore been named *isogeraniol.*

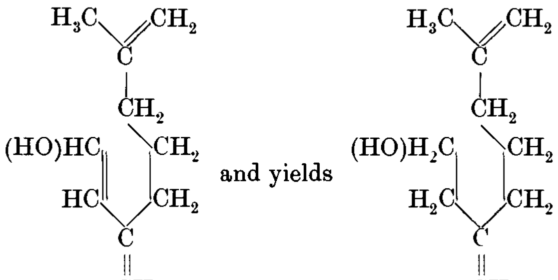
This alcohol possesses a very pleasant odour of roses, and after purification has the following characters :—

Boiling-point at 9 mm.	102° to 103°
Specific gravity at 20°	0·8787
Refractive index	1·47325

The passage from citral to isogeraniol through *enol*-citral may be represented by the following formulæ :—


Citral. Enolic form I. Isogeraniol I.

or possibly—



Enolic form II. Isogeraniol II.

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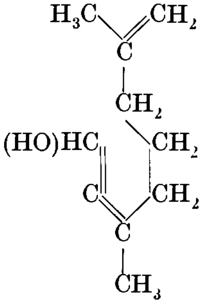
[1] *Berichte*, **44**, 991.

and probably passing in a primary stage through a body of the constitution —



Isogeraniol yields *isogeraniol-diphenylurethane*, $C_{10}H_{17}O \cdot CON(C_6H_5)_2$, melting at 73° C., free from geranyl- and nerylurethanes. By the saponification of this derivative isogeraniol is again liberated.

The properties of isogeraniol, geraniol, and nerol are compared below —

	Geraniol	Nerol	Isogeraniol
Boiling-point	104° to 108° C. (8·5 mm. pressure)	111° C. (11 mm. pressure)	102° to 103° C. (9 mm. pressure)
Specific gravity	0·882 at 15° C.	0·881 at 15° C.	0·879 at 20° C.
Refractive index .	1·477	1·468	1·473
Melting-point of the diphenylurethane .	82·5° C.	52° to 53° C.	73° C.
Melting point of the tetra bromide . .	70° to 71° C.	118° to 119° C.	oily

The tetrabromide and the phenylurethane of isogeraniol have so far only been obtained in the oily condition.

NEROL.

Nerol is an alcohol, isomeric with geraniol, of the formula $C_{10}H_{18}O$. It was discovered by Hesse and Zeitschel in neroli and petit-grain oils, by freeing the oil as far as possible from geraniol and then preparing diphenylurethanes of the residuary mixed alcohols. By fractional crystallisation from a mixture of methyl alcohol and petroleum ether, the nerol compound can be obtained in a state of purity, and the alcohol is obtained by saponification in the usual manner. Nerol has the following characters —

Boiling point . .	226° to 227°
Specific gravity	0·8813
Optical rotation	± 0°
Refractive index at 17°	1·47665

The diphenylurethane melts at 52° to 53° (that of geraniol melts at 81°) and the tetrabromide at 118° to 119°. Nerol is a stereoisomer of geraniol, related to it as shown by the appended formulæ, and their corresponding aldehydes are probably α-citral (= geraniol) and β-citral (= neral) —[1]

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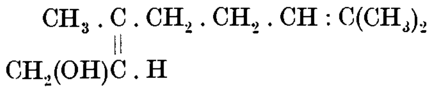
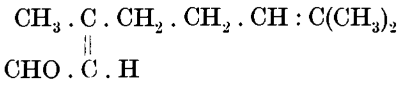
[1] But see also under citral for alternative constitutions.

Geraniol.



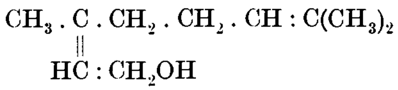
$$\begin{array}{l} \mathrm{\quad\;\; CH_3 . C . CH_2 . CH_2 . CH : C(CH_3)_2} \\ \qquad\quad\;\, \| \\ \mathrm{CH_2(OH)C . H} \end{array}$$

α-Citral.



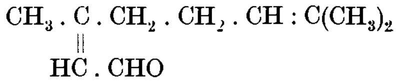
$$\begin{array}{l} \mathrm{\;\; CH_3 . C . CH_2 . CH_2 . CH : C(CH_3)_2} \\ \qquad\quad \| \\ \mathrm{CHO . C . H} \end{array}$$

Nerol.



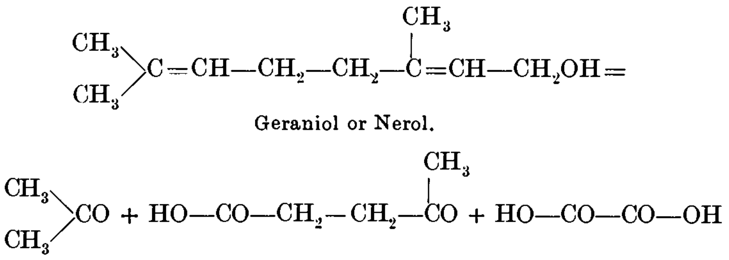
$$\begin{array}{l} \mathrm{CH_3 . C . CH_2 . CH_2 . CH : C(CH_3)_2} \\ \qquad\;\; \| \\ \mathrm{\quad\; HC : CH_2OH} \end{array}$$

β-Citral.



$$\begin{array}{l} \mathrm{CH_3 . C . CH_2 . CH_2 . CH : C(CH_3)_2} \\ \qquad\;\; \| \\ \mathrm{\quad\; HC . CHO} \end{array}$$

Considerable difference of opinion has been expressed as to the relationships of nerol and geraniol, and Soden and Treff have considered the isomerism of a structural nature. The question of this isomerism has, however, been definitely solved by Blumann and Zeitschel,[1] who have applied the degradation-oxidation method of Tiemann and Semmler[2] to both geraniol and nerol. If the two bodies are stereoisomers, there should be obtained under identical experimental conditions, from both compounds, the same products of degradation in the same proportions, according to the following diagrammatic equation :—



Geraniol or Nerol.

Acetone. Lævulinic acid. Oxalic acid.

Blumann and Zeitschel have obtained these degradation products in practically equal amounts from both geraniol and nerol, so that there no longer exists the slightest doubt as to the constitution of nerol.

The nerol used for these experiments was extracted from the oil of *Helichrysum angustifolium*. Its characters were :—

Specific gravity	0·8815
Boiling-point	225° to 226°
Optical rotation	± 0°
Coeff. of sapon. of the acetylated product	286
Tetrabromide, melting-point	118° to 119° C.
Diphenylurethaue, melting-point	52° ,, 53° C.

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[1] *Berichte*, **44**, 2590.

[2] *Ibid.*, **28**, 2130.

The geraniol, purified by means of calcium chloride, had the following characters :—

Specific gravity	0·8824
Boiling-point	230°
Optical rotation	± 0°
Tetrabromide, melting-point	70° to 71° C.
Diphenylurethane, melting-point	82° C.

In regard to the crystallisation of these two derivatives of nerol and geraniol, Blumann and Zeitschel have made a curious observation : one of the bodies corresponding to one of the modifications of the two alcohols is readily obtained in the solid state, whilst the other crystallises with difficulty. Thus, the tetrabromide of nerol solidifies fairly quickly whilst the tetrabromide of geraniol remains oily for a very long time; in the case of the diphenylurethanes these conditions are reversed.

However, nerol and geraniol yield on oxidation exactly the same products.

The identity of the two alcohols from a chemical point of view is shown by the following results, obtained from 25 grams of each of the two bodies :—

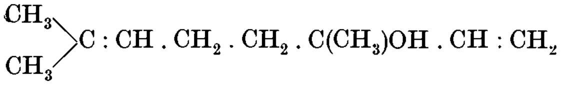
	Geraniol.	Nerol.
Acetone, identified by its *p*-bromophenylhydrazone	m.p. 94° to 95° C.	m.p. 94° to 95° C.
Læevulinic acid, identified by its phenylhydrazone	18 grams = 54 per cent. of theoretical m.p. 108° C.	18·5 grams = 55·5 per cent. of theoretical m.p. 108° C.
λ-isonitrosovaleric acid	m.p. 95° C.	m.p. 95° C.
Lævulinic acid regenerated	m.p. 32° to 33° C.	m.p. 28° to 32° C.
Alcohol regenerated	4·2 grams	4·1 grams.

LINALOL.

Linalol, $C_{10}H_{18}O$, is isomeric with geraniol and nerol, but it is structurally isomeric, and not stereoisomeric, as it is known in both optical forms. It was first isolated by Morin[1] from oil of linaloe. The same body has been isolated from various other essential oils, and has been described under the names licareol, coriandrol, lavendol, etc., all of which have been found to be more or less impure forms of linalol.

Linalol is found very widely distributed in essential oils. It forms the principal constituent, in the free state, of oil of linaloe, and the chief odorous constituent, in the form of esters, in bergamot and lavender oils. It is also found in ylang-ylang, rose, champaca leaf, cinnamon, petit-grain, spike, geranium, lemon, spearmint, and numerous other essential oils.

It is a tertiary open-chain alcohol, probably of the constitution—



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C : CH . CH_2 . CH_2 . C(CH_3)OH . CH : CH_2$$

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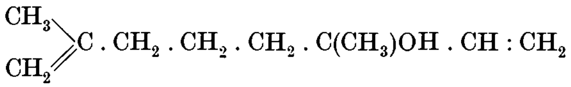
[1] *Ann. Chem. Phys.*, [5], **25**, 427.

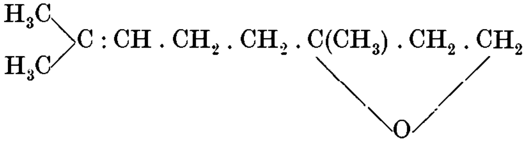
although it is possible that the alternative formula—



$$\begin{matrix} CH_3 \\ CH_2 \end{matrix} \!\!> C\,.\,CH_2\,.\,CH_2\,.\,CH_2\,.\,C(CH_3)OH\,.\,CH : CH_2$$

correctly represents its constitution.

Béhal[1] considers that linalol is not an alcohol but an oxide of the following constitution :—



$$\begin{matrix} H_3C \\ H_3C \end{matrix} \!\!> C : CH\,.\,CH_2\,.\,CH_2\,.\,\underbrace{C(CH_3)\,.\,CH_2\,.\,CH_2}_{O}$$

Linalol is not particularly easy to purify, as it yields practically no crystalline compounds suitable for purification purposes. The characters of the various specimens prepared therefore vary, especially in regard to their optical rotation. The following figures, for example, have been recorded for linalol with a laevo-rotation :—

	From			
	Lavender Oil.	Bergamot Oil.	Linaloe Oil.	Lime Oil.
Boiling-point	197° to 199°	197° to 199°	197° to 200°	198° to 199°
Specific gravity	0·8725	0·8720	0·877	0·870
Refractive index	1·4640	1·4629	1·4630	1·4668
Optical rotation	− 10° 35'	− 16°	− 2°	− 17° 37'

A specimen from lime oil, however, has been isolated with an optical rotation − 20° 7′, and a specimen of dextro-linalol from orange oil, with a rotation of + 19° 18′. The characters of pure linalol, therefore, may be taken approximately as follows :—

Specific gravity	0·872
Refractive index	1·4650
Optical rotation	+ or − 20°
Boiling-point	198° to 199°

Tiemann[2] prepares linalol in a state of approximate purity by the following method. The linalol fraction of the essential oil is heated with sodium, and the liquid heated under reduced pressure so long as sodium continues to be dissolved. After cooling, the unchanged metallic sodium is removed and the sodium compound of linalol is suspended in ether and treated with phthalic anhydride. After standing for several days, the mixture is shaken with water, which dissolves the linalyl sodium phthalate, unchanged linalol and terpenes remaining dissolved in the ether. The aqueous liquid is washed several times with ether, the solution acidified and again extracted with ether. The resulting linalyl acid phthalate is hydrolysed by alcoholic potash, and the pure linalol is extracted with ether.

Optically inactive linalol can be artifically prepared by heating

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[1] *Comptes Rendus.*, 1919, **168**, 945.

[2] *Berichte*, **29**, 901 ; **31**, 837.

geraniol in an autoclave for some time to a temperature of 200°, or it can be obtained by treating geraniol with hydrochloric acid and treating the resulting chlorides with alcoholic potash. The conversion of geraniol into linalol has been very fully studied by Dupont and Labaune, who give the following results of their work :—[1]

The geraniol with which they worked was extracted from palmarosa oil, and purified by means of its phthalic acid ether and finally by means of calcium chloride. Its characters were as follows :—

Boiling-point	230° to 231°
Specific gravity	0·8842
Rotation	0°
Refractive index	1·4763

After reaction with hydrochloric acid, and repeated fractional distillation, a product was obtained which contained 97·3 per cent. of chloride of the formula $C_{10}H_{17}Cl$. This body had the following characters :—

Boiling-point (6 mm.)	94° to 96° C.
Specific gravity at 20°	0·9293
Refractive index	1·4798
Optical rotation	Practically inactive

If the physical properties of this monochlorinated compound be compared with those of the corresponding chloride from linalol, they are found to be practically identical with the latter. The identity of the two bodies derived from distinct chemical individuals is therefore almost certain.

In order to clear up this question it was important to restore the alcoholic group, avoiding as far as possible any chance of a molecular transposition. Since the action of alcoholic potash and of the acetates might leave the matter open to criticism from this point of view, the authors had recourse to an alcoholic solution of silver nitrate. The elimination of the chlorine is instantaneous, it takes place even below 10° C. 50 grams of the chloro derivative are dissolved in 250 grams of 90 per cent. alcohol; to this solution there is added in the cold a solution of 55 grams of silver nitrate in 50 grams of water and 100 grams of alcohol. The liquid becomes acid owing to the liberation of nitric acid. After separating the silver chloride, the liquid is neutralised, the alcohol is evaporated on the water-bath and the residue is rectified *in vacuo*.

With the chloro derivative of linalol the result is extremely sharp. The whole of the product passes over, under a pressure of 6 mm., at a temperature of 82° to 86° C., the residue being insignificant. The constants of this body are as follows :—

Boiling-point (760 mm.)	198° to 199° C.
,, ,, (6 mm.)	82° ,, 86° C.
Specific gravity at 20°	0·8605
,, rotation	+ 0·65°
Refractive index	1·4665

which are approximately those of linalol. It is therefore clear that the ester is the hydrochloric ester of linalol of the formula—

$$(CH_3)_2C : CH . CH_2 . CH_2 . C(CH_3)Cl . CH : CH_2.$$

The corresponding ester obtained from geraniol was not obtained in

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[1] Roure-Bertrand Fils, *Report*, October, **1909**, 24.

a perfectly pure state, and on regenerating the alcohol, a small amount of geraniol was obtained, but the main constituent was pure linalol.

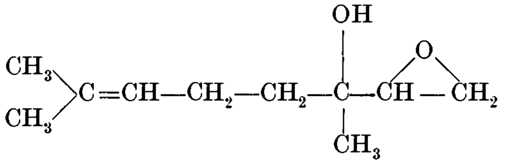
Paolini and Divizia[1] have succeeded in partially resolving inactive linalol into its optically active isomers, but only to the extent of optical rotations of + 1° 70′ and − 1° 60′ respectively. Linalol was converted into its acid phthalate, and an alcoholic solution of this compound was treated with the equivalent quantity of strychnine. By fractional crystallisation the laevo-rotatory salt, yielding dextro-rotatory linalol, separates first, leaving the more soluble dextro-rotatory strychnine salt, which yielded laevo-rotatory linalol in the mother liquor.

Linalol yields a somewhat remarkable compound, by artificial oxidation which appears also to be formed naturally. This body is termed linalol monoxide, and has the formula $C_{10}H_{18}O_2$. It was first found in oil of linaloe by Schimmel & Co., and it is probably to be explained by the oxidation of the essential oil on exposure to the air at the surface of the trunk of the tree. It has been prepared artificially by Prileshajeff[2] by oxidising linalol with hydrated benzoyl peroxide. By further oxidation with the same reagent, he obtained linalol dioxide.

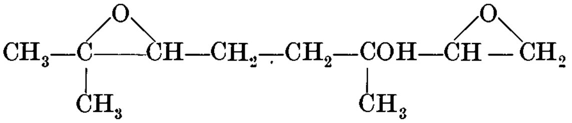
Linalol monoxide has the following characters:—

Boiling-point	193° to 194°
„ „ (at 4 mm.)	63° „ 64°
Specific gravity	0·9442
Optical rotation	− 5° 25′
Refractive index	1·45191
Molecular refraction	48·88

The two oxides have the following formulæ:—

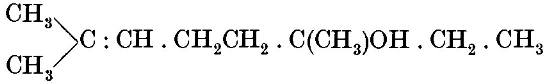


Linalol monoxide.



Linalol dioxide.

By the hydration of dihydromyrcene, Schimmel & Co. obtained dihydrolinalol. This body has the constitution—



or possibly the similar constitution related to the alternative formula for linalol given above. Dihydrolinalol was also prepared by the action of magnesium methyl-iodide on methyl-heptenone. The only difference observed between the bodies thus produced was that the latter was less easy to convert into a phenyl-urethane. This is probably due to the fact that in the case of dihydrolinalol produced from methyl-heptenone,

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[1] *Chem. Zentral.*, **1915**, 1, 603.

[2] *Jour. Soc. Chim. Phys. Russ.*, **44**, 613.

the isomerism of the original citral is reproduced in the dihydrolinalol, which may consist of two stereoisomeric forms, whilst in the case of hydration of dihydromyrcene, no stereoisomerism results. The following figures are recorded for dihydrolinalol prepared from various sources:—

Prepared from.	Boiling-point.	$d_{15°}$.	$n_{D_{15°}}$.	Molecular Refraction.	
				Found.	Calculated.
Dihydromyrcene . .	92° to 92·5° (12 to 13 mm.)	0·8570	1·45531	49·47	49·438
Methyl-heptenone from citral (by oxidation) .	77° to 78° (7 mm.)	0·8588	1·45641	49·46	49·438
Methyl-heptenone from lemon-grass oil . .	66° to 66·5° (4 mm.)	0·8575	1·45661	49·558	49·438
Methyl-heptenone from citral (by boiling with solution of carbonate of potassium) . .	67·5° (4 mm.)	0·8590	1·45611	49·424	49·438

Linalol may be characterised by the following methods:—

1. By oxidation to citral (*q.v.*).

2. By converting it into geraniol. This is effected by boiling linalol with acetic anhydride for two hours and then saponifying the resulting ester. Pure geraniol can be obtained by fractionating the regenerated alcohol, and the geraniol so obtained can be identified by the usual method.

3. Preparation of the urethane, $C_6H_5 . NH . COOC_{10}H_{17}$. A mixture of 2 or 3 grams of the alcohol is mixed with rather more than the theoretical amount of phenyl-isocyanate, and allowed to stand in a stoppered flask for a week. It is then mixed with water, and a current of steam passed through the mixture, in order to remove the unaltered linalol. The crystalline mass which remains is collected, dried on a porous plate, and extracted with ether, which dissolves the phenyl-urethane. The ethereal solution is allowed to evaporate spontaneously when crystals of the urethane separate, which melt at 65°.

4. Preparation of the naphthyl-urethane. This compound is prepared in a similar method to that just described, using α-naphthyl-isocyanate. The naphthyl-urethane melts at 53°.

CITRONELLOL.

Citronellol, $C_{10}H_{20}O$, is an alcohol which was first obtained by Dodge,[1] by reducing the aldehyde citronellal, $C_{10}H_{18}O$, by means of sodium amalgam and acetic acid. It was then found to be a constituent of rose, geranium, and other essential oils. The citronellol question has given rise to a somewhat acrimonious and prolonged controversy, as Barbier and Bouveault claimed that the body which they termed rhodinol was a chemical individual differing from citronellol, whilst Tiemann and Schmidt and other German chemists maintained that rhodinol was nothing more than a mixture of geraniol and citronellol, and not a chemical individual at all. The controversy developed, as indicated in the previous edition of this work (p. 51) on the following lines:—

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[1] *Jour. Amer. Chem. Soc.*, 1889, **xi**. 463.

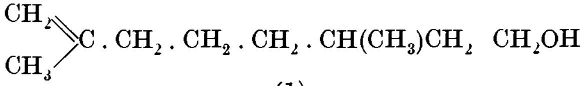
Rhodinol was announced by Eckart to be an essential ingredient of Bulgarian and German rose oils He regarded it as an unsaturated open-chain alcohol. Markovnikoff thereupon urged that roseol, $C_{10}H_{20}O$, was the chief ingredient of rose oil Bertram, in 1894, claimed that it was in reality merely geraniol, but in 1896 Tiemann and Schmidt showed that the alcohols of rose oil consisted of a mixture of geraniol and citronellol, $C_{10}H_{20}O$, which latter body, they claimed, had evidently been mistaken for the so-called "rhodinol" and "roseol".

The names geraniol and citronellol therefore appeared to be those most entitled to remain in chemical literature. Poleck, however, complained that the name geraniol had been substituted for the earlier rhodinol, overlooking the fact that the old rhodinol was apparently a mixture. Erdmann further complicated this matter by insisting on treating geraniol of commerce as a more or less impure body of which the principal constituent, $C_{10}H_{17}OH$, is called rhodinol, claiming that geraniol (pure) and rhodinol are identical, and that the former name should be expugned from chemical literature.

The last of these bodies announced as being alcoholic constituents of rose and geranium oils was reuniol, found in various geranium oils (Réunion, African, and Spanish) by A Hesse This had previously been announced as a probable chemical individual by Barbier, but he stated that he had not obtained it pure Erdmann and Huth claimed that it was more or less pure rhodinol

Up till about three years ago, there appeared to be little reason to doubt that rhodinol was in fact an impure form of citronellol, the reduction product of citronellal being dextro-citronellol, whilst the natural alcohol, which the French chemists had termed rhodinol was considered to be laevo-citronellol.

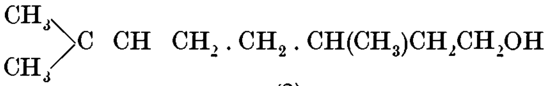
Citronellol was considered to have one of the two following alternative formulæ —



$$\begin{matrix} CH_2 \\ CH_3 \end{matrix}\!\!>\!C\,.\,CH_2\,.\,CH_2\,.\,CH_2\,.\,CH(CH_3)CH_2\quad CH_2OH$$

(1)

or



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\quad CH\quad CH_2\,.\,CH_2\,.\,CH(CH_3)CH_2CH_2OH$$

(2)

There seems, however, to-day, to be overwhelming evidence that the French chemists were correct and that citronellol and rhodinol are two very similar, but chemically different, compounds, citronellol being represented by the formula (1) and rhodinol by formula (2) Considerable evidence of this is to be found in the work of Barbier and Locquin[1]

Starting from the acetic esters of ordinary *d*-citronellol and rhodinol from oil of geranium or rose, they attached hydrogen chloride to the double bond, and obtained the same additive product according to the equations —

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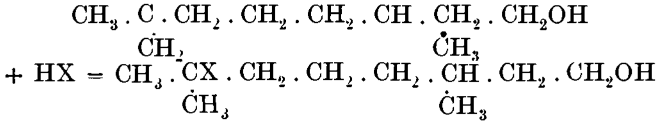
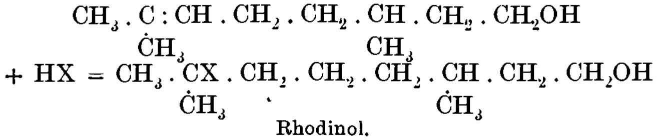
[1] *Comptes Rendus*, **157**, 1114.



$$CH_3 . \underset{CH_2}{C} . CH_2 . CH_2 . CH_2 . \underset{CH_3}{CH} . CH_2 . CH_2OH$$
$$+ HX = CH_3 . \underset{CH_3}{CX} . CH_2 . CH_2 . CH_2 . \underset{CH_3}{CH} . CH_2 . CH_2OH$$

Citronellol.



$$CH_3 . \underset{CH_3}{C} : CH . CH_2 . CH_2 . \underset{CH_3}{CH} . CH_2 . CH_2OH$$
$$+ HX = CH_3 . \underset{CH_3}{CX} . CH_2 . CH_2 . CH_2 . \underset{CH_3}{CH} . CH_2 . CH_2OH$$

Rhodinol.

The authors found that on elimination of the halogen acid from this compound, rhodinol, and not citronellol, is regenerated, dextro-rhodinol from dextro-citronellol, and laevo-rhodinol from the laevo-rotatory alcohol from oil of roses or geranium, the two bodies, in the latter case being identical.

Further, *d*-citronellal, the corresponding aldehyde, may be converted into citronellic acid through its oxime and nitrile. Citronellic acid, when treated with thionyl chloride in benzene solution, yields a chloride of a chlorinated acid which is converted by the action of alcohol into the hydrochloride of ethyl citronellate, or hydrochloride of ethyl rhodinate,

$$(CH_3)_2CCl—CH_2—CH_2—CH_2—CH(CH_3)—CH_2—CO_2C_2H_5.$$

This ester loses hydrogen chloride by the action of sodium acetate giving ethyl rhodinate which when reduced by sodium and absolute alcohol yields rhodinol.

Citronellal can thus be converted into rhodinol without being first reduced to citronellol.

A third method of converting citronellol into rhodinol is by hydrating citronellol by means of 30 per cent. sulphuric acid. This yields the glycol 3-7-dimethyl octanediol-1-7, of the formula—

$$(CH_3)_2 . C(OH) . CH_2 . CH_2 . CH_2 . CH(CH_3) . CH_2 . CHOH$$

which is dehydrated by boiling with 5 per cent. sulphuric acid, yielding rhodinol.

The three optical varieties of rhodinol have thus been obtained, namely, laevo-rhodinol, the natural constituent of rose and geranium oils; dextro-rhodinol by conversion of dextro-citronellol obtained by reduction of citronellal, and inactive rhodinol by the reduction of synthetic ethyl rhodinate.

Further evidence of the difference between rhodinol and citronellol is forthcoming, in that the former yields on oxidation an aldehyde, rhodinal, whose oxime does not yield citronellic acid nitrile when treated with acetic anhydride, nor citronellic acid when the nitrile is treated with alkalis, wheras citronellal, the aldehyde of citronellol, does yield the nitrile and citronellic acid.

Harries and Comberg[1] have also supplied much evidence, which, taken with the above-mentioned researches, places the chemical isomerism of citronellol and rhodinol practically beyond dispute. By ozonisation experiments decomposition products were obtained, which proved that natural "citronellal," obtained from citronella oil, is a mixture of about

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[1] *Annalen*, 1915, **410**, 1.

40 per cent. of true citronellal and 60 per cent. of rhodinal. It is true that only one semicarbazone can be obtained by crystallisation, but this can be ozonised, and the ozonide decomposed by boiling water, yielding two semicarbazones, one of which is a derivative of citronellal, and the other of rhodinal. It is obvious therefore that the semicarbazones of natural "citronellal" is either a very difficultly separable mixture of two bodies, or an individual substance in which a shifting of the double bond occurs by ozonisation.

H. J. Prins[1] has now isolated the two isomeric citronellals from Java citronella oil (see under citronellal).

The physical characters, therefore, of the bodies which have hitherto been described as citronellol or rhodinol must therefore be understood to apply to the respective bodies in as pure a state as their separation has rendered possible. At all events, it is clear that the two alcohols are very similar in their general characters. These characters are approximately as follows:—

From Rose Oil.

Boiling-point at 15 mm.	113° to 114°
Specific gravity at 20°	0·8612
Refractive index	1·45789
Optical rotation	− 4° 20′

From Geranium Oil.

Boiling-point at 764 mm	225° to 226°
Specific gravity at 15°	0·862
Refractive index at 22°	1·45611
Optical rotation	− 1° 40′

From Citronella Oil.

Boiling-point at 7 mm.	109°
Specific gravity	0·862
Refractive index at 22°	1·45671
Optical rotation	+ 2° 32′

From Barosma Pulchella Oil.

Boiling-point at 5 to 6 mm.	93° to 95°
Specific gravity	0·8723
Refractive index	1·46288
Optical rotation	+ 2° 14′

By Reduction of Citronellal

Boiling-point at 17 mm.	117° to 118°
Specific gravity at 17·5°	0·8565
Refractive index at 17·5°	1·45659
Optical rotation	+ 4°

Citronellol can be characterised by conversion into citronellyl-phthalate of silver, which is prepared in an exactly similar manner to the corresponding geranyl compound, and melts at 125° to 126°. It can also be oxidised in the same manner as geraniol, yielding the aldehyde citronellal, which can be identified as described later (*vide* citronellal).

Citronellol and rhodinol have faint but sweet rose odours.

Citronellol occurs so frequently associated with geraniol, and is absolutely necessary as an ingredient of artificial otto of rose and similar synthetic perfumes, that it is sometimes a matter of importance to separate the two bodies quantitatively. This can be done in the following manner: To a mixture of 100 grams of phosphorus trichloride and 100 grams of ether, 100 grams of the mixed alcohols, dissolved in an equal amount of ether, are added, so that, by keeping the liquids in a freezing mixture, the temperature does not rise above 0°. The mixture is then allowed to stand at the ordinary temperature, and is then several times washed with iced water. The oily layer is shaken with dilute soda solution, and the citronellyl-phosphoric acid is dissolved out, leaving the geranyl chloride undissolved. The citronellyl-phosphoric acid may be hydrolised by boiling with alcoholic potash and then distilled in a current of steam.

Another separation of a mixture of alcohols is often necessary, namely, that of geraniol, citronellol, and phenyl-ethyl-alcohol, all of which occur in admixture in artificial otto of rose. In this case advantage may be taken of the fact that phenyl-ethyl alcohol is easily soluble in 30 per cent. alcohol, which is not the case with geraniol or citronellol.

For further details on the separation of geraniol and citronellol the chapter on the analysis of essential oils should be consulted.

MENTHO-CITRONELLOL.

Mentho-citronellol or menthonyl alcohol, $C_{10}H_{20}O$, is an alcohol of delicate rose odour, and is synthetically prepared as follows:—

Laevo-menthone is converted into its oxime by means of hydroxylamine. This is treated with strong sulphuric acid, and so inverted to isomenthone oxime. This is treated with phosphorus trichloride in chloroform solution, when hydrochloric acid is given off, and menthonitrile is formed. The last named is reduced by sodium into menthonylamine, and the oxalic acid compound of this is warmed with sodium nitrite solution when menthonyl alcohol is formed. This body has the following characters:—

Specific gravity	0·8315
Refractive index	1·4471
Optical rotation	+ 2°
Boiling-point at 7 mm.	95° to 105°

METHYL-HEPTENOL.

Methyl-heptenol is an alcohol with a delicate rose odour, of the formula $C_8H_{16}O$. It occurs in Mexican and Cayeme linaloe oil, and is prepared by reducing methyl-heptenone, and has the following characters:—

Specific gravity	0·8579
Refractive index	1·4495
Boiling-point	178° to 180°
Optical rotation	− 1° 34′

METHYL-HEPTYLENE CARBINOL.

Methyl-heptylene carbinol, $C_9H_{18}O$, has been obtained by the reduction of methyl-heptylene ketone by means of sodium and alcohol. It is an oil with an odour recalling those of rose and linaloe, and has the following characters:—

Specific gravity	0·848 at 20°
Optical rotation	± 0°
Refractive index	1·4458
Boiling point	185° to 187°

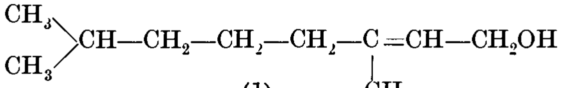
BUPLEUROL.

This alcohol, of the formula $C_{10}H_{20}O$, occurs in the essential oil *Bupleurum fruticosum*, from which it was isolated by Francesconi and Sernagiotto.[1] It was separated by means of its phthalic acid ester, and is an oil of faint rose odour, having the following characters —

Boiling-point at 762 mm	209° to 210°
Specific gravity at 17°	0·849
Optical rotation	0°
Refractive index	1·4508

It yields a phenyl-urethane, melting at 45°. On oxidation it yields an aldehyde having an odour of lemons, which yields a semicarbazone, melting at 135°.

Bupleurol is a primary alcohol, which according to the authors must have one of the three alternative constitutions —



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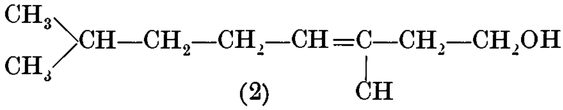

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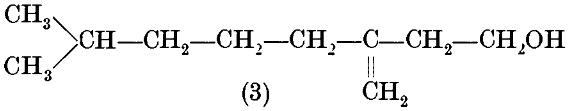

(3)

ANDROL.

This alcohol, $C_{10}H_{20}O$, is, like bupleurol, isomeric with citronellol and rhodinol. It is present in the oil of water fennel (*Phellandrium aquaticum*), and has an odour characteristic of the plant. It has the following characters —

Boiling point	197° to 198°
Specific gravity	0·858
Optical rotation	– 7° 10'
Refractive index	1·44991

It yields a phenyl-urethane melting at 42° to 43°.

No aldehyde or ketone has been obtained from it by oxidation. Its constitution is probably allied to those of citronellol and rhodinol, but, since it contains an asymmetric carbon atom, as shown by its optical activity, the three formulæ given under bupleurol obviously cannot represent androl.

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[1] *Gazz. chim. Ital.*, 43, 1, 153.

UNCINEOL.

Baker and Smith[1] have isolated an alcohol of the formula $C_{10}H_{18}O$ from the "cajuput" oil, distilled from the leaves of *Melaleuca uncinata*. The alcohol, which is probably an open-chain compound, forms snow-white crystals, melting at 72·5°, and having a specific rotation + 36·99°.

FARNESOL.

Farnesol, $C_{15}H_{26}O$, is an aliphatic sesquiterpene alcohol, which occurs in ambrette seed oil, and flower oils of the type of acacia, lime flowers, mignonette, and lilac flowers.

This alcohol is almost invariably present in those essential oils which contain aliphatic terpene alcohols, but in most of these it is present in very small amount, and it is only from ambrette seed oil that any quantity has been prepared. Ambrette seeds contain about 0·1 per cent. of this alcohol, which, when freed from decylic alcohol which is also present, has the following characters:—

Boiling-point at 10 mm.	160°
Specific gravity at 18°	0·885
Optical rotation	± 0°
Refractive index	1·4881
Molecular refraction	72·27

This alcohol appears to be almost odourless, but when a dilute solution in alcohol is allowed to evaporate slowly, a very fine lily-of-the-valley odour is developed, together with the suggestion of cedar-wood oil.

Oxidation of farnesol with chromic acid mixture gives rise to the aldehyde farnesal, which has the following characters:—

Boiling-point at 14 mm.	172° to 174°
Specific gravity at 18°	0·893
Refractive index	1·4995

Farnesal forms a semi-carbazone, which crystallises from acetic ether in fine flakes, which melt at 133° to 135°. This body is particularly useful for the identification of farnesol.

Farnesol forms an acetate, farnesyl acetate, which is a nearly odourless oil, boiling at 169° to 170° at 10 mm.

When dehydrated with potassium hydrogen sulpnate, farnesol yields a sesquiterpene, which has been named farnesene, and is a colourless oil having the following characters:—

Boiling-point at 12 mm.	129° to 132°
Specific gravity at 18°	0·887
Refractive index	1·49951

Kerschbaum[2] has carried out a series of experiments in order to determine the constitution of farnesol.

In order to establish the primary character of farnesol, farnesenic acid was prepared from farnesal oxime and the corresponding nitrile. Saponification of the farnesene-nitrile with caustic soda solution yields farnesenic acid and acetic acid, and also a ketone which was identified as a dihydro*pseudo*ionone. The semi-carbazone melts between 95° and 96°. The dihydro*pseudo*ionone from farnesene nitrile proved to be

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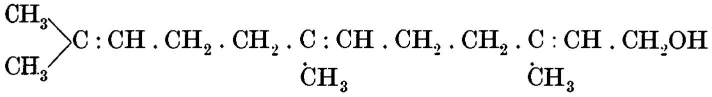
[1] *Jour. and Proc. Royal Soc.*, N.S.W., **41** (1907), 196.

[2] *Ber.chte*, **46** (1913), 1732.

identical with the synthetic product which has been obtained from geranyl chloride and sodium acetic ester. Farnesol was prepared synthetically from hydroxydihydrofarnesenic ester which was prepared from magnesium bromoacetic ester and dihydro*pseudo*ionone. When heated with acetic anhydride and sodium acetate this ester afforded farnesenic methylester. Synthetic farnesenic acids boils at 203° at 14 mm.

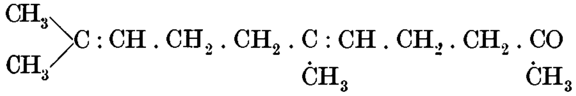
It is evident from these reactions that farnesol has the constitution of an aliphatic sesquiterpene alcohol with three double bonds, and that its formula is—



$$\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C:CH.CH_2.CH_2.\underset{CH_3}{C}:CH.CH_2.CH_2.\underset{CH_3}{C}:CH.CH_2OH$$

Farnesol.

that of dihydro*pseudo*ionone being as follows :—



$$\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C:CH.CH_2.CH_2.\underset{CH_3}{C}:CH.CH_2.CH_2.\underset{CH_3}{CO}$$

Dihydro*pseudo*ionone.

The above constitution of farnesol has been confirmed by the oxidation experiments of Harries and Haarmann.[1]

NEROLIDOL.

Nerolidol is an aliphatic sesquiterpene alcohol of the formula $C_{15}H_{26}O$, which has been isolated from the higher boiling fractions of orange-flower oil. It has the following characters :—

Specific gravity	0·880
Optical rotation	+ 13° 32'
Boiling-point at 6 mm.	128° to 129°
,, ,, ,, 760 mm.	276° ,, 277°

It is an oil with a slight but sweeet odour.

In 1899 Thoms isolated an alcohol from Peru balsam oil, which he termed peruviol. This body was stated to have powerful antiseptic properties, but has not been further investigated until Schimmel & Co. took up the subject. The oil after saponification was fractionated, and after benzyl alcohol had distilled over, a light oil with characteristic balsamic odour passed over. It boiled at 125° to 127° at 4 mm., and had a specific gravity 0·8987, optical rotation + 12° 22', and refractive index 1·48982. This body appeared to be identical with Hesse's nerolidol, whilst in physical and chemical properties it closely resembles peruviol. The characters of the various preparations were as follows :—

	Boiling-point.	Specific Gravity.	Rotation.	Refractive Index.
Peruviol (Thoms) . . .	140° (7 mm.)	0·886	+ 13°	—
Schimmel's body (1) . .	133° ,,	0·882	+ 14°	—
,, ,, (2) . .	127° (4 mm.)	0·899	+ 12°	1·4898
Nerolidol (Hesse) . . .	129° (6 mm.)	0·880	+ 14°	—
,, (Schimmel) . .	127° (5 mm.)	0·880	+ 13°	1·4802

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[1] *Berichte*, **46** (1913), 1737.

It appeared that the impure alcohol isolated from balsam of Peru was, in fact, identical with nerolidol. When allowed to stand for three to four weeks with phenyl-isocyanate both alcohols yielded a phenylurethane, melting at 37° to 38°. A mixture of the two bodies suffered no depression in melting-point. The alcohols have the formula $C_{15}H_{26}O$. The alcohol from balsam of Peru is therefore mixed with a small quantity of an alcohol of higher specific gravity, the nature of which is still undetermined. Traces of benzyl alcohol were found in it, but not in sufficient quantity to account for the differences observed. Oxidation experiments did not throw any light on the question. It may therefore be safely assumed that the peruviol of Thoms consisted in the main of nerolidol, but contaminated with a substance of the same boiling-point to such an extent that its combustion figures pointed to the formula $C_{13}H_{22}O$ instead of $C_{15}H_{26}O$.

CLOSED CHAIN ALCOHOLS.

The next series of alcohols to be examined is that in which the members retain the benzene nucleus in a more or less substituted condition, as distinguished from those in which the benzene nucleus has been so altered as to bring the alcohols within the series known as the "terpene alcohols". A certain number of these alcohols are found in nature, but some of them are prepared synthetically, and, although not yet found naturally, are exceedingly useful in the preparation of perfumes.

BENZYL ALCOHOL.

Benzyl alcohol, $C_6H_5 . CH_2OH$, is the lowest member of the normal series of aromatic alcohols containing the benzene nucleus. It exists to a certain extent in the free state, but more often in the form of esters, principally of acetic, benzoic, and cinnamic acids, in a number of essential oils, such as those of jasmin, tuberose, cassie flowers, and ylang-ylang.

It is prepared artificially, for use as a synthetic perfume, by several methods, for example, by heating benzyl chloride with oxide of lead to 100°, or by heating benzyl chloride with potassium acetate and saponifying the benzyl acetate so formed, with caustic potash.

Benzyl alcohol is an oil with a slight but very sweet floral odour, and has the following characters:—

Boiling-point	205° to 207°
Specific gravity	1·0435
Optical rotation	± 0°
Refractive index	1·53804

It is fairly soluble in dilute alcohol, and in about 35 parts of water. It can therefore be fairly easily separated from less soluble constituents by shaking with 5 or 10 per cent. alcohol. Apart from its actual perfume value, benzyl alcohol is of considerable value to the perfumer, since it acts as a very valuable fixative, and is, moreover, one of the best-known solvents for artificial musk.

Benzyl alcohol forms a solid compound with calcium chloride, and also a phthalic acid compound. The latter is obtained by heating 2 grams of the alcohol with 2 grams of phthalic anhydride and 1 gram of benzene. Caustic soda solution is then added, and the solution washed with ether. The benzyl acid phthalate is precipitated by sulphuric acid, and can be recrystallised from benzene. It then melts at 106° to 107°. It also yields a phenyl-urethane, melting at 77° to 78°. Its esters are agreeably-smelling liquids, which will be described later.

PHENYL-ETHYL ALCOHOL.

Phenyl-ethyl alcohol, $C_6H_5 . CH_2 . CH_2OH$, is the next highest homologue of the benzyl alcohol series. It is found naturally in rose and neroli oils; but as it is very soluble in water, it practically disappears from the distilled otto of rose and is dissolved in the rose water. Hence otto of rose with its beautiful perfume does not truly represent the odour of the rose. By the use of various isolated and synthetic bodies an artificial otto can be prepared which more closely resembles the rose odour than does the natural otto itself. But it is doubtful whether any really good artificial otto of rose can be prepared without some natural otto as its basis.

Phenyl-ethyl alcohol, or benzyl carbinol, has been known for many years, but its powerful rose odour has been entirely overlooked, its discovery having been made by an ordinary research chemist and not a perfumery expert. Its preparation was described in the *Berichte* (9, 373) in 1876, but the product there noted was evidently impure, as its boiling-point is recorded as 212°. Commercial specimens vary greatly in both their odour and their keeping properties, some samples deteriorating in odour very rapidly. It is, therefore, very important to obtain it in a state of the highest purity. It has the following characters:—

Specific gravity	1·0242
Refractive index	1·53212
Boiling-point	220° to 222° at 740 mm.
,, ,,	104° at 12 mm.
Optical rotation	±0°

It yields a diphenyl-urethane, which melts at 99° to 100°, and is very useful for identification purposes. The phenyl-urethane, melting at 80° is less useful for this purpose, since its melting-point is almost identical with those of benzyl and nonyl alcohols. It combines with phthalic acid to form a phthalic acid ester, melting at 188° to 189°.

Phenyl-ethyl alcohol can be prepared by numerous methods, several of which are the subject-matter of patents. It may be prepared, for example, by the conversion of phenyl-bromo-lactic acid into phenyl-acetaldehyde, and then reducing this body with sodium. Or it may be prepared by reducing phenyl-acetic esters with sodium and absolute alcohol in the following manner:—

It is obtained by allowing a solution of one molecule of phenol-acetic ester in three to four times its weight of absolute alcohol, to fall in drops on a quantity of sodium calculated for six atoms. It is then heated for several hours on an oil-bath, until the sodium has disappeared, if necessary adding more alcohol. After cooling, water is added, and the ester which is not attacked is saponified. The alcohol and phenyl-ethyl alcohol are then distilled off with steam, when the latter is at once obtained in the pure state.

It is a colourless, heavy oil, with a typical rose and "honey" odour. It is easily soluble in all organic solvents, and to a considerable extent in water It is soluble in 2 volumes of 50 per cent. alcohol, in 18 volumes of 30 per cent alcohol, and in 60 volumes of water. Its identification is, therefore, best effected by extracting the mixture of alcohols in which it occurs, by means of dilute alcohol, which dissolves the phenyl-ethyl alcohol but not much of the other alcohols.

It is suitable, not only for rose odours, but also for blending with almost any flower oil. Phenyl-ethyl alcohol forms a solid compound with chloride of calcium, which is very useful for its purification On oxidation it is converted into a mixture of phenyl-acetaldehyde and phenyl-acetic acid The last-named body forms an ethyl ester melting at 28°, which serves for its identification.

There is an isomeric and closely associated alcohol, phenyl-methyl carbinol, $C_6H_5CH(OH)CH_3$, known to chemists This is a liquid of different odour, but which is not used very much in synthetic perfumery. It is an oil boiling at 203°, and forms an acetate which is found naturally in essential oil of gardenia This ester is of use in blending perfumes of this type of flower

PHENYL-PROPYL ALCOHOL

Phenyl-propyl alcohol, $C_6H_5\,CH_2 . CH_2\,CH_2\,OH$, is the next highest homologue of phenyl-ethyl alcohol, and is also known as hydrocinnamyl alcohol Like the last described bodies it has been known for many years, its first preparation being described in the *Annalen* (188, 202). It occurs as a cinnamic acid ester in storax, and as an acetic ester in cassia oil It is prepared synthetically by the reduction of cinnamyl alcohol with sodium amalgam and water, or by the reduction of cinnamic or benzyl acetic esters with sodium and absolute alcohol It has the following characters —

Specific gravity	1 007
Boiling point at 12 mm	119°
,, ,, ,, 760 mm . .	235°

It can be characterised by its phenyl-urethane, melting at 47° to 48°, or by oxidising its acetic acid solution by means of chromic acid, when it yields hydrocinnamic acid, melting at 49°.

It is a colourless, thick oil, with an odour recalling that of cinnamic alcohol and hyacinths It is useful in synthetic perfumery in the preparation of bouquets, and it is extremely useful in odours of the type of hyacinth, narcissus, jonquil, and the like

There exist three isomers of phenyl-propyl alcohol, all of which have been prepared and described, and, although not yet introduced into commerce, may eventually be so. These are as follows. Benzyl-methyl-carbinol, $C_6H_5\,CH_2\,CH(OH)CH_3$, boiling at 215°, phenyl-ethyl-carbinol, $C_6H_5 . CH(OH)CH_2\,CH_3$, boiling at 221°, and benzyl-dimethyl-carbinol, $C_6H_5 . C(OH)(CH_3)_2$, melting at 21° and boiling at 225°.

HIGHER HOMOLOGUES OF PHENYL-ETHYL ALCOHOL.

Braun[1] has shown that alcohols of the type of phenyl-ethyl alcohol, containing an aliphatic and an aromatic radicle, can be prepared by the reduction of nitriles of the general formula X . CN with the corresponding

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[1] *Berichte*, **44**, 2867

bases $X.CH_2NH_2$ These are then benzoylated and the benzoyl compound heated with phosphorus pentachloride, when the chlorides $X.CH_2Cl$ are formed. These, of course, are directly convertible into the corresponding alcohols. The following alcohols so prepared are of considerable interest as being homologues of the well-known rose alcohol, phenyl-ethyl alcohol —

Delta-phenyl-butyl alcohol	(boiling-point	140° at 14 mm).
phenyl-amyl	,, ,, ,,	155° ,, 20 ,,
6-phenyl-hexyl	,, ,, ,,	160° ,, 13 ,,
7-phenyl-heptyl	,, ,, ,,	170° to 172° at 15 mm.).

Of these phenyl-amyl alcohol has a pleasant, but somewhat evanescent lemon-like odour; phenyl-hexyl alcohol has a very similar odour to this; and phenyl-heptyl alcohol has a slight, but extremely agreeable odour of roses.

CINNAMIC ALCOHOL

Cinnamic alcohol, $C_6H_5 . CH . CH . CH_2OH$, or γ-phenyl-allyl alcohol, is found in the form of esters, principally of either acetic or cinnamic acid in storax, balsam of Peru, and in hyacinth and other essential oils. It may be prepared synthetically by reducing cinnamic aldehyde diacetate, and saponifying the resulting cinnamyl esters. Cinnamic alcohol is a crystalline body, although commercial specimens frequently contain traces of impurities which prevent crystallisation. It has the following characters —

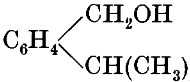
Melting point	33°
Boiling-point	258° at 760 mm.
,, ,,	117° at 5 mm.
Specific gravity at 35°	about 1·020
Refractive index	1·03024

Commercial samples of good quality have a specific gravity between 1·010 and 1 030.

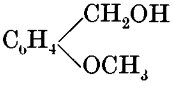
Cinnamic alcohol forms a phenyl-urethane, melting at 90° to 91°, and a diphenyl-urethane, melting at 97° to 98°. On oxidation it yields cinnamic acid, melting at 133°, and by more thorough oxidation, benzoic acid, melting at 120°.

Cinnamic alcohol has an odour, not very powerful, but exceedingly delicate, recalling roses and hyacinths, in which types of perfume it is exceedingly useful. It is fairly soluble in dilute alcohol, and can to some extent be separated from alcohols of the geraniol type by means of 30 per cent. alcohol.

CUMINIC ALCOHOL.

Cuminic alcohol,  $C_6H_4\left\langle\begin{matrix}CH_2OH\\CH(CH_3)_2\end{matrix}\right.$, has been found in the essential oil of cumin. On oxidation it yields cuminic acid, melting at 112° to 113°.

ANISIC ALCOHOL.

Anisic alcohol,  $C_6H_4\left\langle\begin{matrix}CH_2OH\\OCH_3\end{matrix}\right.$ has been isolated from the volatile constituents of Tahiti vanillas. It boils at 117° to 118° at 5 mm., and yields a phenyl-urethane, melting at 93°.

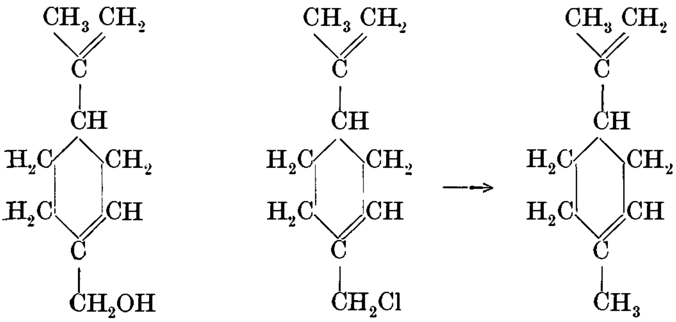
PERILLIC ALCOHOL.

An alcohol of the formula $C_{10}H_{16}O$ was isolated from oil of ginger-grass by Schimmel & Co.,[1] and described by them as dihydrocuminic alcohol. It has, however, now been shown by Semmler and Zaar [2] not to have the constitution assigned to it by Schimmel & Co., but to be identical with the alcohol obtained by reducing perillic aldehyde, $C_{10}H_{14}O$, the aldehyde characteristic of the essential oil of *Perilla nankinensis.*

It was separated from geraniol, which accompanies it in ginger-grass oil by treatment with concentrated formic acid, which destroys the geraniol, but does not attack the perillic alcohol. It has the following characters ;—

Boiling point	119° to 121° at 11 mm.
Specific gravity	0·969 at 20°
Refractive index	1·4996
Specific rotation	− 68·5°

Its constitution is closely related to that of limonene, since its chloride passes at once, on reduction, into this terpene as shown in the following formulæ :—



Perillic alcohol. Chloride. Limonene.

By oxidation this alcohol yields perillic aldehyde which forms a semi-carbazone, melting at 199° to 200°, and perillic acid, melting at 130° to 131°. It also yields a naphthyl-urethane, melting at 146° to 147°.

Terpene Alcohols.

TERPINEOL.

Terpineol, $C_{10}H_{17}.OH$, is an alcohol of the greatest interest from a scientific point of view, and of the highest practical importance from the perfumer's point of view. Three well-defined modifications of the substance known as terpineol are recognised, but as their chemical constitutions are different in each case, it is not a question of so close a relationship as might be expected from the clumsy and slip-shod nomenclature univer-

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[1] *Berichte*, April, **1904**, 53; October, **1904**, 41.

[2] *Ibid.*, **44**, 460.

sally employed for them. These "terpineols" are known as α-terpineol, β-terpineol, and γ-terpineol.

Terpineol of commerce is, in the main, a mixture of the isomers, in which α-terpineol largely predominates.

Terpineol is an alcohol which is used to an enormous extent in synthetic perfumery, and is the basis of all the perfumes of the type of lily of the valley, lilac, and similar odours. It blends so well with numerous other bodies that it is easy to produce a large number of different odours, all with the main perfume of terpineol. Muguet, for example, is terpineol with small quantities of modifying substances. Syringol, lilacine, and artificial gardenia are all based on terpineol. Geranium oil and heliotropine are excellent substances to round off this odour, and on account of its stability it is most useful in soap perfumery, as neither heat, acids, nor alkalis have any appreciable effect on it. Ylang-ylang, sandalwood, and rose are also excellent odours to blend with it.

These alcohols have long been a puzzle to chemists. Terpineol was first prepared by Tilden by the action of dilute acids on terpin hydrate. Wallach first prepared it in really good yield, by acting on terpin hydrate with dilute phosphoric acid. He stated that it was a monatomic alcohol, boiling at 215° to 218°, and described it as a liquid. Bouchardat and Tardy prepared it by the action of very dilute sulphuric acid on terpin hydrate, and found that it solidified on cooling and then melted at 30° to 32°, easily remaining in a state of superfusion. A closer examination by Wallach and Baeyer showed that the true melting-point of the principal terpineol is 35°. A study of the two bodies, the "liquid" and the "solid" terpineol, and of their oxidation products, has revealed that there are at least twelve definite isomeric terpineols, capable of being synthesised. The liquid terpineol of commerce consists of a mixture of at least two of these, those melting at 35° and at 32° to 33°, with either some trace of impurity, or else a third isomeric liquid form. The terpineols all appear to possess an odour recalling hyacinths, hawthorn, and lilac. They are, when prepared artificially, optically inactive, but Semmler has recently prepared optically active terpineols, by replacing the chlorine in the two limonene monohydrochlorides by the hydroxyl group. The resulting terpineol is optically active in the same direction as the limonene from which it is produced. Baeyer has, in addition, synthesised an *isomeric* terpineol, melting at 69° to 70°.

Terpineol (that is α-terpineol) has been prepared synthetically by Perkin and his pupils, his method being described under the synthesis of limonene.

α-terpineol is a solid compound, melting at 35°. It occurs in the dextro-rotatory form in numerous essential oils, including those of petitgrain, neroli, orange, and linaloe; whilst it is found in the laevo-rotatory condition in camphor oil, certain pine oils, and in Mexican linaloe oil. It also occurs in the optically inactive variety in cajuput oil. The artificially prepared α-terpineol, which is a constituent of commercial terpineol, is, of course, inactive.

Synthetic α-terpineol has the following characters:—

Melting-point	35°
Boiling-point	217° to 218°
„ „ at 10 mm	104° „ 105°
Specific gravity	0·935 „ 0·940
Refractive index	1·48084

Natural terpineol has an optical rotation of about ± 100°.

The average characters of the commercial mixture known as terpineol are as follows:—

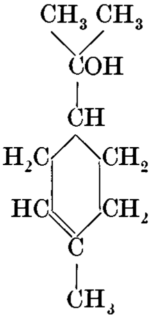
Specific gravity	0.933 to 0.941
Boiling point	217° ,, 220°
Refractive index	1.4800 ,, 1.4840
Optical activity	± 0° or slightly active

It is soluble in two volumes of 70 per cent. alcohol.

Messrs. Schimmel & Co. give the following characters for the active and inactive varieties of α-terpineol:—

	Inactive Varieties	Active Varieties
Melting point	35°	37° to 38°
,, ,, of nitrosochloride	112° to 113°	107° ,, 108°
,, ,, nitrol piperidine	159° ,, 160°	151° ,, 152°
,, ,, ,, methoethyl heptanonolide	64°	46° ,, 47°

α-terpineol has the following constitution:—



α-terpineol is characterised by being converted into dipentene dihydriodide, $C_{10}H_{18}I_2$, melting at 77° to 78°, by being shaken with concentrated hydriodic acid.

It yields a well-defined phenyl-urethane, melting at 113°. It requires considerable care to obtain this compound, which should be prepared as follows: terpineol mixed with the theoretical amount of phenylisocyanate is left for four days at the ordinary room temperature. Crystals separate which are diphenyl urea, and are removed by treating the product with anhydrous ether, in which the diphenyl urea is insoluble. If the liquid be very carefully and slowly evaporated fine needles of terpinyl-phenyl urethane separate. This compound has the formula $C_6H_5.NH.COOC_{10}H_{17}$. The corresponding naphthyl-urethane melts at 147° to 148°.

Terpineol nitrosochloride, $C_{10}H_{17}OH.NOCl$, is, perhaps, the most suitable derivative to prepare for the identification of terpineol. To a solution of 15 grams of terpineol in 15 c.c. of glacial acetic acid, 11 c.c. of ethyl nitrite are added. The mixture is cooled in ice, and 6 c.c. of hydrochloric acid mixed with 6 c.c. of glacial acetic acid are added drop by drop, with continual shaking. Care must be taken to avoid a rise in temperature. When the reaction is complete, water is added to precipitate the nitrosochloride. The oily liquid soon solidifies and may be recrystallised from boiling acetic ether or from methyl alcohol. Terpineol nitrosochloride melts at 112° to 113° in the case of the optically inactive form, or at 107° to 108° in the case of the optically active variety.

As in the case of pinene, the nitrosochloride forms a nitrol-piperidine, $C_{10}H_{17}(OH)NO . N . C_5H_{10}$, melting at 159° to 160° in the case of optically inactive terpineol, or at 151° to 152° in the case of the optically active variety.

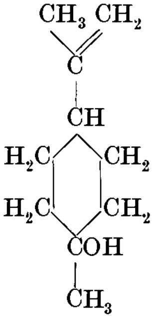
β-terpineol is found with α-terpineol amongst the reaction products of dilute acids on terpin hydrate, so that it is a constituent of commercial terpineol.

It is, when pure, a crystalline compound melting at 32° to 33°, and has the following characters:—

Specific gravity	0·923 (at 15°, superfused)
Refractive index	1·4747
Boiling-point at 752 mm. . . .	209° to 210°

It yields the following crystalline derivatives, which are suitable for its identification: nitrosochloride melting at 103°, nitrol-piperidine melting at 108°, nitrol-anilide melting at 110°, and phenyl-urethane melting at 85°.

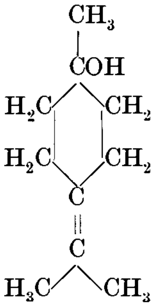
β-terpineol has the following constitution:—



γ-terpineol has not been found in nature. It has been prepared by Baeyer[1] by the reduction of tribrom—1 . 4 . 8—terpene, resulting from the bromination of dipentene dihydrobromide. It also results from the action of dilute phosphoric, or oxalic acid, on terpin hydrate.

It forms prisms melting at 69° to 70°. To identify this body it may be converted into its acetate, which then yields a nitrosochloride in the usual manner, which melts at 82°.

γ-terpineol has the following constitution:—



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[1] *Berichte*, **27** (1894), 443.

A useful method for the production of terpineol for use in perfumery on a commercial scale is the following, due to Bertram and Walbaum:—

Two kilograms of acetic acid are mixed with 50 grams of sulphuric acid and 50 grams of water. Into the mixture, which should not be allowed to rise above 50°, 1 kilogram of rectified oil of turpentine is poured, in portions of 200 grams at a time. After cooling and standing, the liquid is diluted with water and shaken with soda solution. The product consists of terpinene and terpineol esters, which are separated by fractional distillation. The esters, on treatment with alcoholic potash, yield terpineol.

THUJYL ALCOHOL.

Thujyl alcohol, $C_{10}H_{17}OH$, occurs in the oils of wormwood and thuja leaves, etc., and also results from the reduction of its ketone, thujone, by means of sodium. It is identical with the body originally described by Semmler under the name tanacetyl alcohol.

It has, according to Semmler, the following characters:—

Boiling-point	210° to 212°
,, ,, at 13 mm.	92·5°
Specific gravity at 20°	0·925 to 0·926
Refractive index	1·4635

It yields a chloride, thujyl chloride, $C_{10}H_{17}Cl$, by the action of phosphorus pentachloride, which on treatment with aniline yields up HCl, with the formation of the terpene thujene.

Paolini[1] has separated from the reduction products of thujone the acid phthalate of β-thujyl alcohol, $HOOC \cdot C_6H_4 \cdot COO \cdot C_{10}H_{17}$, melting at 120°, and having a specific rotation + 91·27°. This body yields a silver salt which melts at 85° to 86°, and a strychnine salt melting at 177° to 178°. On saponifying the phthalate β-thujyl alcohol results, which has the following characters:—

Boiling-point	206°
Specific gravity	0·9229
Refractive index at 16°	1·4625
Specific rotation	+ 114·7°

Tschujaeff and Fromm[2] have shown that by the recrystallisation of the cinchonine salt of the phthalic acid ester, and hydrolysis of the crystalline salt, *d*-thujyl alcohol can be obtained of specific rotation + 116·9°, and specific gravity 0·9187 at $\frac{20°}{4°}$, thus agreeing with Paolini's results. The more soluble cinchonine salt remaining in the mother liquors, gave a laevo-rotatory thujyl alcohol, but the highest rotation obtained was - 9·12°.

Thujyl alcohol has the constitution:—

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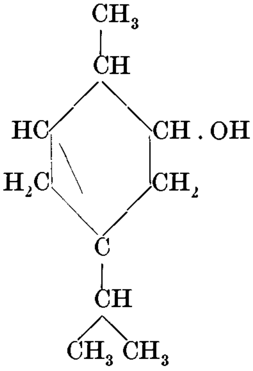
[1] *Atti. R. Accad. dei Lincei*, (v.), **20**, i. 765.

[2] *Berichte*, **45** (1912), 1293.



It can be identified by oxidation with chromic acid, when its ketone, thujone, results. This can then be characterised by its oxime, melting at 54°

SABINOL.

Sabinol, $C_{10}H_{15}.OH$, is a secondary alcohol, existing in the oils of savin, cypress and eucalyptus, either in the free state or in the form of its acetic ester. Somewhat discordant values have been published for this alcohol, its characters, according to Schimmel[1] and Semmler[2] being as follows —

Boiling point	210° to 213°
,, ,, at 20 mm	105° ,, 107°
Specific gravity at 20°	0·9432
Refractive index	1·4880
Molecular refraction	46·5

Paolini and Rebern[3] have, however, prepared sabinol in a pure condition by means of its hydrogen phthalate, in the hope of separating it into its stereoisomeric forms. The hydrogen phthalate of sabinol which they prepared, $COOH.C_6H_4.CO_2\ C_{10}H_{15}$, crystallised in white silky needles melting at 95°, and having a specific rotation, in methyl alcohol, − 14·6°. On hydrolysis, this yielded sabinol having the following characters:—

Boiling point	208°
Specific gravity	0·9518
Refractive index at 18°	1·4895
Specific rotation	+ 7° 56′

No isomer appeared to be present in savin oil, since no separation could be effected by conversion of the hydrogen phthalate into its strychnine salt, and fractional crystallisation thereof. The strychnine salt, $C_{39}H_{40}O_6N_2$, melts at 200° to 201°

Sabinol probably has the constitution —

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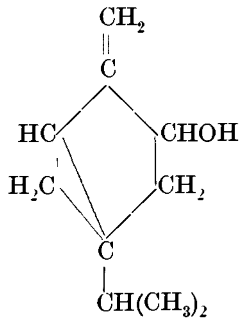
[1] *Berichte*, October (1895), 40. [2] *Ibid*, **33** (1900), 1459

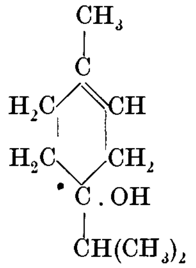
[3] *Atti R Accad dei Lincei*, 1916 (v), **25**, ii 377.



On oxidation with permanganate of potassium it yields sabinol-glycerine, $C_{10}H_{15}(OH)_3$, melting at 152° to 153°, and by further oxidation, tanacetogene-dicarboxylic acid, $C_9H_{14}O_3$, melting at 140°. On reduction with sodium and amyl alcohol, sabinol yields thujyl alcohol, $C_{10}H_{17}OH$.

TERPINENOL.

Terpinenol, $C_{10}H_{18}O$, is found in the oils of marjoram, cardamoms, cypress, and nutmeg, as well as in several others to a small extent. It has the following constitution :—



It can be obtained artificially by treating sabinene or thujene with dilute sulphuric acid, when the resulting alcohol is optically inactive. The natural alcohol, isolated from juniper berry oil, has the following characters :—

Boiling-point at 8 mm.	93° to 95°
Specific gravity	0·940
Optical rotation	+ 13·06°

This was probably an impure preparation, and probably Wallach's preparation[1] was in a much purer condition. This had the following characters :—

Boiling-point	209° to 212°
Specific gravity at 19°	0·9265
Refractive index at 19°	1·4785
Optical rotation	+ 25° 4'

whilst for the inactive variety Wallach gives the following figures :—

Boiling-point	212° to 214°
Specific gravity	0·9290
Refractive index	1·4803

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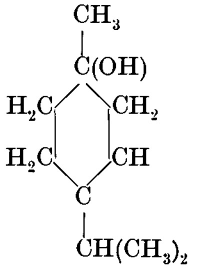
[1] *Annalen*, **356** (1907), 215.

By oxidation with potassium permanganate, terpinenol yields trioxyterpane, $C_{10}H_{17}(OH)_3$, melting at 114° to 116°, and by boiling with dilute sulphuric acid carvenone results. This body yields a semi-carbazone, melting at 202°.

The above-described compound is known as terpinenol-4 in accordance with recognised nomenclature. A body known as terpinenol-1 is present to a small extent in the artificially prepared commercial terpinenol. This body has the following characters:—

Boiling-point	208° to 210°
Specific gravity	0·9265 at 18°
Refractive index	1·4781

It has been prepared synthetically by Wallach[1] from isopropylhexenone. It has the constitution:—



TERPINE HYDRATE.

Terpine hydrate, $C_{10}H_{18}(OH)_2 + H_2O$, is a crystalline alcohol resulting from the action of dilute mineral acids on either pinene or limonene. It can be prepared by several different methods, of which the following is typical: A mixture of 8 parts of oil or turpentine, 2 parts of alcohol, and 2 parts of nitric acid of specific gravity 1·255 is allowed to stand for several days in a flat basin. After standing for a few days the mother liquor is poured off from the crystals of terpine hydrate, and neutralised with an alkali, after which a second crop of crystals is obtained.

Terpine hydrate crystallises in well-defined monoclinic prisms, melting at 116° to 117°. On distillation, or on exposure to sulphuric acid, terpine hydrate gives off the water of crystallisation and yields the anhydrous alcohol terpine. It is probable that terpine exists in the space isomeric forms, known as *cis*-terpine and *trans*-terpine. The product resulting from the dehydration of terpine hydrate is that known as *cis*-terpine. It melts at 39°. *Trans*-terpine melts at 64° and is prepared by dissolving dipentene dihydrobromide in 10 times its amount of glacial acetic acid and gradually adding silver acetate to the ice-cooled solution. The product is filtered after standing for some time and the filtrate is neutralised with soda and extracted with ether. The ethereal solution is treated with alcoholic potash to saponify the acetyl compound and the reaction product is distilled with steam, to remove hydrocarbons and terpineol. *Trans*terpine remains in the residue after this treatment. Terpine has the following constitution:—

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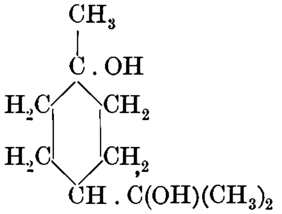
[1] *Annalen*, **362** (1908), 280.



PINOCARVEOL.

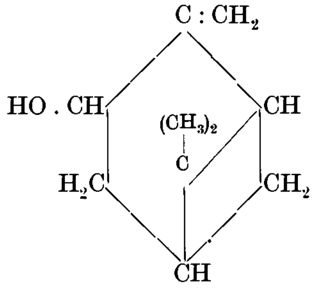
Pinocarveol, $C_{10}H_{16}O$, is a bicyclic alcohol, which has been found in oil of *Eucalyptus globulus*, and is apparently identical with the alcohol obtained by the reduction of nitrosopinene. It can be prepared artificially in the following manner:—

Seventy grams of pinylamine nitrate are treated with a solution of 10 grams of sodium nitrite in 100 c.c. of water for some time. The yellowish oil which separates is distilled with steam, and the distillate is shaken with an oxalic acid solution in order to remove basic compounds, and again distilled with steam. Pinocarveol has the following characters:—

Boiling-point	215° to 218°
,, ,, at 12 mm.	92°
Specific gravity	0·9745 at 20°
Refractive index	1·4963
Specific rotation	− 52° 45′

It forms a phenylurethane which appears to consist of two isomers melting at 82° to 84° and at 94° to 95° respectively. The formation of these two phenylurethanes makes it probable that pinocarveol is itself a mixture of two isomeric compounds. On oxidation with chromic acid pinocarveol yields a compound $C_{10}H_{14}O$ which forms two semi-carbazones, melting at 210° and 320° respectively.

Pinocarveol has the following constitution (probably):—



PINENOL.

This body has been described in detail by Genvresse,[1] but its chemical individuality cannot be regarded as established. Its formula is said to be $C_{10}H_{15}OH$ and it has the following characters:—

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[1] *Comptes rendus*, **130**, 918.

Boiling-point	225° at 740 mm.
„ „	143° „ 88 mm.
Specific gravity	0·9952 at 0°
Refractive index	1·4970°
Specific rotation	– 14·66°

It is prepared by passing nitrous fumes into ice-cold pinene. It forms an acetate, $C_{10}H_{15}O . COCH_3$, which has a marked lavender odour.

DIHYDROCARVEOL.

Dihydrocarveol, $C_{10}H_{18}O$, is a natural constituent of caraway oil, and is also obtained by the reduction of carvone.

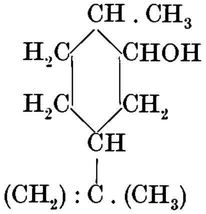
To prepare it artificially, 20 grams of carvone are dissolved in 200 c.c. of absolute alcohol and 24 grams of sodium are added. Towards the end of the reaction water is added, and the product is then distilled with steam.

Dihydrocarveol is an oil of agreeable odour, and having the following characters:—

Boiling-point at 760 mm.	224° to 225°
„ „ „ 7 mm.	100° „ 102°
Specific gravity	0·9368
Optical rotation	– 6° 14′
Refractive index	1·48364

The above values apply to natural dihydrocarveol from caraway oil. A specimen prepared by the reduction of carvone had a specific gravity 0·927 at 20° and refractive index 1·48168.

Dihydrocarveol is obtained from both optical forms of carvone, and is optically active in the same sense as the original carvone. It has the following constitution:—



On oxidation with chromic acid in acetic acid solution, dihydrocarveol yields dihydrocarvone, which has a specific gravity 0·928 at 19°, and refractive index 1·47174. The dihydrocarvone from *laevo*-dihydrocarveol is dextro-rotatory, and *vice versa*. Its oxime melts at 88° to 89° for the optically active variety, and at 115° to 116° for the optically inactive form.

Dihydrocarveol yields a phenylurethane, $C_6H_5NH . CO . OC_{10}H_{17}$, melting at 87° for the optically active variety, and 93° for the optically inactive form.

TERESANTALOL.

Teresantalol is an alcohol of the formula $C_{10}H_{16}O$, which was isolated from sandalwood oil by Schimmel & Co. It has been prepared artificially by Semmler and Bartelt,[1] by reducing teresantalic acid with sodium.

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[1] *Berichte* (1907), 3321.

It is a solid body melting at 112° to 114°, forming exceedingly fine prismatic crystals. It forms a compound with phthalic acid, melting at 140°.

FENCHYL ALCOHOL

The chemistry of fenchyl alcohol, $C_{10}H_{18}O$, must be regarded as in a somewhat unsettled state, as questions of isomerism arise which are as yet unsolved. It was originally prepared by Wallach by reducing the ketone fenchone, a natural constituent of several essential oils, by means of sodium. Later[1] he obtained it in fairly large quantities as a by-product in the preparation of fenchone-carboxylic acid, by passing a current of CO_2 through an ethereal solution of fenchone in the presence of sodium. Fenchyl alcohol has, so far, been found in one essential oil only, namely, that of the root wood of *Pinus palustris*.

Wallach gives the following characters for the laevo-rotatory fenchyl alcohol:—

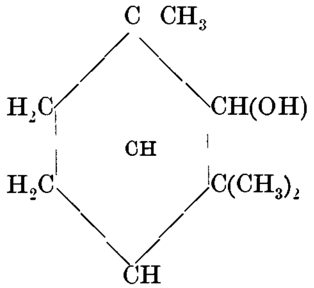
Boiling point	201°
Specific gravity at 50°	0.933
,, rotation	− 10° 35
Melting-point	45°

The naturally occurring fenchyl alcohol is optically inactive and melts at 33° to 35°, which agrees with the observations of Wallach, a mixture of the two optically active forms, each of which melted at 45°, melting at 33° to 35°.

Pickard, Lewcock and Yates[2] have prepared fenchyl alcohol by the reduction of *d*-fenchone; they found it to be laevo-rotatory. On conversion into its hydrogen phthalate and fractionally crystallising the magnesium and cinchonine salts, they obtained a fraction, which on saponification yielded *laevo*-fenchyl alcohol, having a specific rotation of − 15.5°, which is probably the correct value for this figure.

Fenchyl alcohol yields a phenylurethane melting at 88° when prepared from the optically inactive alcohol, and at 82.5° when prepared from the optically active form. It yields fenchone on oxidation, which can be identified by its crystalline combinations (*vide* fenchone).

Fenchyl alcohol has, according to Semmler, the following constitution:—



Fenchyl alcohol yields an acetate, $C_{10}H_{17}O\cdot COCH_3$, boiling at 87° to 88° at 10 mm., and having a specific gravity 0.9748, and specific rotation − 58°.

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[1] *Annalen* (1895), 324.

[2] *Jour Chem Soc*, **29** (1913), 127.

According to Schimmel & Co.,[1] if fenchene be treated with a mixture of acetic and sulphuric acids, it is hydrated with the formation of isofenchyl alcohol, $C_{10}H_{18}O$. This alcohol is a solid body, crystallising in needles melting at 61° to 62°. On oxidation it gives rise to a ketone, $C_{10}H_{16}O$, which is isomeric with fenchone, but which on reduction does not yield either fenchyl or isofenchyl alcohols, but a third isomeric alcohol. Isofenchyl alcohol forms a phenylurethane melting at 106° to 107°. The characters of the isomeric alcohols are compared in the following table:—

	Fenchyl Alcohol	Isofenchyl Alcohol
Melting-point	45°	61° to 62°
,, ,, of phenylurethane	82°	106° ,, 107°
,, ,, ,, hydrogen phthalate	145°	149° ,, 150°
Boiling-point	91° to 92° (11 mm.)	97° to 98° (13 mm.)
Acetic ester, boiling-point	88° (10 mm.)	98° ,, 99° (14 mm.)
Boiling-point of ketone formed	191° to 192°	193° to 194°
Melting point ,, ,, ,,	6°	liquid
,, ,, ,, oxime of ketone	164° to 165°	82°

ISOPULEGOL.

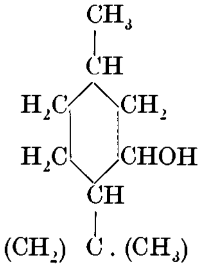
Isopulegol, $C_{10}H_{18}O$, does not appear to exist in essential oils, but it results from the action of acids on citronellal. The last-named body, for example, when boiled with acetic anhydride yields isopulegyl acetate, from which the alcohol is obtained by hydrolysis.

Isopulegol is an oil having an odour resembling that of menthol. Its characters are as follows:—

Boiling-point	91° at 13 mm.
Specific gravity	0.9154 at 17.5°
Refractive index	1.47292

Its optical rotation has usually been recorded as from − 2° to − 3°, but recently Pickard, Lewcock, and Yates[2] have prepared *l*-isopulegol by fractional crystallisation of the magnesium and cinchonine salts of the hydrogen phthalate, and found its specific rotation to be − 22.2°.

Isopulegol has the following constitution:—



On oxidation isopulegol yields isopulegone, which can be characterised by its oxime, which melts at 121° for the active, and about 140° for the inactive variety, or its semi-carbazone, which melts at 172° to 173° for the active, and 182° to 183° for the inactive variety.

Isopulegyl hydrogen phthalate melts at 106° and has a specific rotation − 18.7°, and its magnesium salt melts at 115°.

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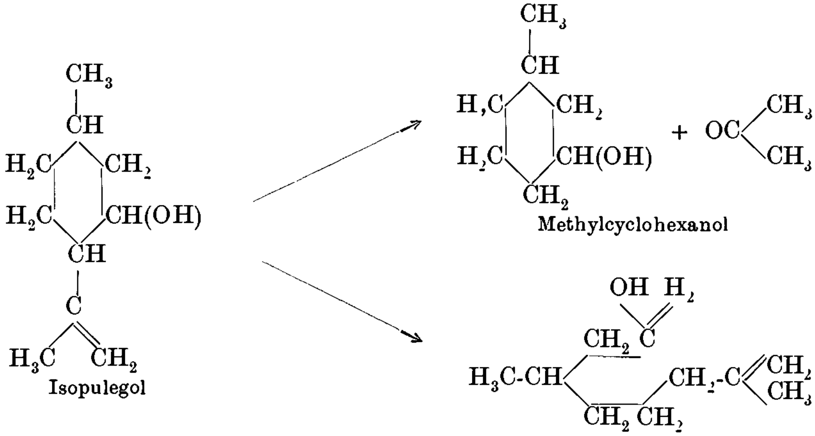
[1] *Report*, October, **1898**, 49; April, **1900**, 55 and 60.

[2] *Jour. Chem. Soc.*, **29** (1913), 127.

Pulegone, on reduction, yields an alcohol, $C_{10}H_{18}O$, which is known as pulegol It is a viscous liquid, having the odour of terpineol, and boiling at 215°. Its specific gravity is 0 912 It is difficult to obtain it in a state of purity.

Schimmel & Co[1] treated isopulegol with aqueous and alcoholic solutions of alkalis to try and convert isopulegol into pulegol By the action of sodium ethylate, instead of pulegol which might have been expected to be produced, two totally different reactions took place, on the one hand there was rupture of the unsaturated side chain with the formation of methylcyclohexanol, on the other hand there was opening of the hexagonal nucleus between the carbon atoms 3 and 4, with formation of citronellol, according to the following scheme —



Isopulegol

Methylcyclohexanol

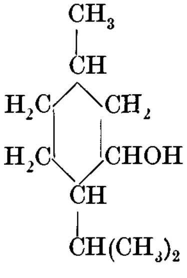
Citronellol

It is probable that the isopulegol was first changed to pulegol and this to methylcyclohexanol.

MENTHOL

Menthol, $C_{10}H_{19}OH$, is the characteristic alcohol of oil of peppermint, from which it separates in fine crystals on cooling It also results from the reduction of the corresponding ketone, menthone, $C_{10}H_{18}O$, and also of pulegone, $C_{10}H_{16}O$

Natural menthol is laevo-rotatory The reduction of both laevo-menthone and dextro-menthone yields a mixture in which laevo-menthol predominates The constitution of menthol is as follows —



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[1] *Report*, October, **1913**, 91

Its physical characters are as follows :—

Melting-point	43° to 44·5°
Boiling-point at 760°	215° ,, 216°
Specific gravity $\frac{45^\circ}{4^\circ}$	0·881
,, rotation	$-$ 49° to $-$ 50°

Various melting-points have been recorded for menthol, and the recent work of F. E. Wright[1] throws some light upon these differences. Wright describes the crystallisation of menthol in four different forms, which he terms *a*, *b*, *c*, and *d*. Three of these appear to bear monotropic relations to the stable *a* form. On crystallisation, all forms of menthol show a pronounced tendency to the development of radial spherulites; these are roughly spherical in shape in the case of crystallisation from the melt, but noticeably ellipsoidal on inversion of one crystal form into a second. The four forms are readily distinguishable under the petrographic microscope. *a*-menthol shows dextro-rotatory polarisation, while the melt is lævo-rotatory. In the formation of the different monotropic forms the initial temperature of crystallisation appears to be the determinative factor. The *a* form is stable between zero and its melting temperature, 42·5° C. The other forms have lower melting temperatures, namely, 35·5° (*b*), 33·5° (*c*), 31·5° (*d*), all of which invert finally into the stable *a* form on standing; the *d* form may invert first into the *b* and then into the *a* form. At a given temperature the rate of growth of crystals of a given form from the undercooled melt is constant; also the rate of growth on inversion of an unstable form into one more stable. The refractive index of melted menthol at 25° is approximately 1·458 for sodium light, whilst that of the crystals is greater. The specific rotation of melted menthol at 15° is $-$ 59·6°, corresponding to a laevo-rotation of $-$ 0·53° per mm. depth of liquid, whilst the crystals are dextro-rotatory, the rotatory power of the stable *a* form being over five times as great when measured for the D line. The melting-points were observed in polarised light, the crystals being melted between two strips of thin cover glass; the slide was immersed in a beaker of water placed on the microscope stage and kept at a definite temperature by means of a small electric resistance heating coil of fine enamelled constantan wire. Melted menthol shows undercooling to a pronounced degree, and does not crystallise within reasonable time until after a temperature of 32° or lower has been reached. Crystals of the *a* form grow at an appreciable rate at 42°. On crystallisation from the melt at the higher temperature needles are commonly formed; these show a tendency toward radial arrangement. At lower temperatures radial spherulites are almost invariably formed.

Menthol forms an acetate, menthyl acetate, $C_{10}H_{19}O \, . \, COCH_3$, a thick highly refractive liquid boiling at 224°, and of specific rotation $-$ 114°.

It forms a characteristic benzoic ester, $C_{10}H_{19}O \, . \, CO \, . \, C_6H_5$, melting at 54°. This is a useful compound for identifying menthol and may be obtained by heating menthol with the theoretical amount of benzoic acid, in a sealed tube to 170°; excess of acid is removed by shaking with a boiling solution of sodium carbonate, and the ester is crystallised from alcohol. Menthol forms a phenylurethane, melting at 111° to 112°.

Boedtker[2] has prepared a number of the homologues of menthol in

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[1] *Jour. Amer. Chem. Soc.*, **39**, 1515, through *P. and E.O.R.*

[2] *Bull. Soc. Chim.*, iv. **17** (1915), 360.

the following manner Sodamide was allowed to react with menthone dissolved in ether. The resulting sodium-menthone was treated with the various alkyl iodides, with the formation of the corresponding alkyl-menthones. These were reduced with sodium and yielded the corresponding menthol homologues The alkyl-menthols so prepared had the following characters —

	Boiling point	Specific Gravity at $\frac{18^\circ}{4^\circ}$	Rotation	Refractive Index
Methylmenthol .	129° to 130° (32 mm)	0 9124	$[\alpha]_{D_{21^\circ}} - 2^\circ 26$	1 4692
Methylmenthylacetate .	125° (17 mm.)	0 9313	$[\alpha]_{D_{22^\circ}} - 18^\circ 7$	1 4578
Ethylmenthol . .	124° (13 „)	0 9246	$[\alpha]_{22^\circ} + 4^\circ 55$	1 4769
Ethylmenthylacetate	131° to 132° (14 mm.)	0·9366	$[\alpha]_{D_{21^\circ}} - 6^\circ 6'$	1·4636
n-Propylmenthol . .	141° „ 145° (27 „)	0 9075	$[\alpha]_{D_{22^\circ}} + 29^\circ 7$	1 4675
n-Propylmenthylacetate	152° (30 mm.)	0 9515	$[\alpha]_{D_{--^\circ}} - 8^\circ 58'$	1 4741 (19°)
Isoamylmenthol .	150° (23 „)	0 8985	$[\alpha]_{D_{22^\circ}} + 33^\circ 44'$	1·4661
Benzylmenthol . .	203° to 205° (24 mm) $d\frac{20^\circ}{4^\circ}$	0 9819	$[\alpha]_{D_{20^\circ}} - 43^\circ 19'$	1·5257

Standnikow[1] has prepared several of the esters of menthol by heating magnesium iodo-mentholate with the esters of ethyl alcohol. For example, with ethyl acetate, propionate, and benzoate the corresponding menthyl esters were obtained. These bodies have the following boiling-points —

Menthyl acetate . .	113° at 19 mm.
„ propionate .	122° to 123° at 19 mm.
„ benzoate .	191° „ 192° „ 18 „

Menthyl benzoate melts at 54·5° to 55°.

Numerous isomeric menthols have been described, many of which are certainly not chemical individuals.

When menthone is reduced there is found, in addition to menthol, a certain amount of isomenthol. This body melts at 78° to 81° and is slightly dextro-rotatory, its specific rotation being + 2°.

The most reliable work on the isomeric menthols is that of Pickard and Littlebury.[2] Starting from the mixture of alcohols which Brunel[3] had obtained by the reduction of thymol, and which he had described under the name of thymomenthol, they isolated from it about 60 per cent. of isomeric menthols, 30 per cent of menthones, and several other compounds They prepared the phthalic acid esters and converted them into their magnesium and zinc salts, which were then fractionally crystallised.

Two distinct bodies were thus obtained, which, on hydrolysis yielded the corresponding menthols, of which one is inactive menthol (melting-point 34° C., boiling-point, 16 mm., 103° to 105° C., acid phthalic ester, melting-point 129° to 131° C.), the other, neomenthol crystallising from petroleum spirit in prismatic tables melting at 51° C.; boiling-point,

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[1] *Journ Russ. phys Chem. Ges*, **47** (1915), 1113.

[2] *Jour. Chem Soc.*, **101**, 109.

[3] *Comptes rendus*, **137**, 1288; and Roure-Bertrand Fils, *Bulletin*.

16 mm., 103° to 105° C.; phenylurethane, melting-point 114° C.; acid succinic ester, melting-point 67° to 68° C.; acid phthalic ester, melting-point 175° to 177° C.

The same menthol and neomenthol have also been obtained by the reduction of inactive menthone by means of hydrogen, in presence of nickel at 180° C.

The inactive menthol melting at 34° C. just described is probably identical with the β-thymomenthol described by Brunel; the inactive neomenthol is probably identical with the isomenthol described above.

Natural laevo-menthol is clearly a homogeneous compound. On the other hand, the inactive menthol melting at 34° C. may be split up, by passing through the form of the brucine salts of the phthalic ester, into laevo-menthol (melting-point 42° C.; $[\alpha]_D - 48 \cdot 76°$) and dextro-menthol (melting-point 40° C.; $[\alpha]_D + 48 \cdot 15°$). Similarly, the inactive neomenthol may be decomposed into dextro-neomenthol ($[\alpha]_D + 19 \cdot 69°$) and laevo-neomenthol ($[\alpha]_D - 19 \cdot 62°$). These active modifications are both liquids; the former having a boiling-point of 98° at a pressure of 16 mm. and the latter boiling at 105° at 21 mm. Dextro-neomenthol has been shown to exist in very small quantity in Japanese peppermint oil.

BORNEOL.

Borneol, $C_{10}H_{17}OH$, the alcohol corresponding to the ketone camphor, occurs naturally, in both optically active modifications; as dextro-borneol in the wood of *Dryobalanops camphora* (Borneo camphor), and as laevo-borneol in *Blumea balsamifera* (Ngai camphor). It also occurs in the optically inactive modification. It is found in numerous essential oils, such as those of the pine-needle type, in the form of its acetic ester, and also in spike, rosemary, and numerous other oils. It forms crystalline masses, or, when recrystallised from petroleum ether, fine tablets which, when quite pure, melt at 204°. Its boiling-point is only a few degrees higher, *viz.* 212°. According to Bouchardat the melting-point is lower than that given, but this is undoubtedly due to the fact that his specimen of borneol probably contained some impurity. Traces of isoborneol, strangely, raise the melting-point to 206° to 208°. Borneol can be prepared artificially by reducing its ketone (camphor) with sodium. Fifty grams of pure camphor are dissolved in 500 c.c. of nearly absolute alcohol, and treated with 60 grams of sodium. After the reaction is complete the whole is poured into a large volume of water, and the resulting borneol is collected, washed, pressed, and recrystallised from petroleum ether. This method of preparation, however, yields a mixture of borneol and isoborneol. The chemically pure body is best prepared by the saponification of its acetate. On oxidation, the converse reaction takes place, with the formation of camphor. Borneol forms a series of esters with the organic acids, of which bornyl acetate is most frequently found in nature. This body melts at 29°, and has a specific gravity of ·991 at 15°. It is optically active. In common with a large number of alcoholic bodies borneol forms a crystalline phenylurethane. This can be prepared by the interaction of phenylisocyanate and borneol. It melts at 138°. Bornyl chloride, prepared by the action of phosphorus pentachloride on borneol, melts at 157°.

Borneol forms crystalline compounds with chloral and bromal, the former melting at 55° and the latter at 104° to 105°.

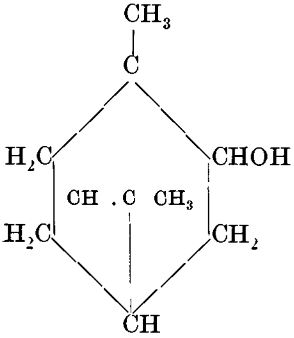
Bertram and Walbaum give the following as the characters of several of the borneol esters —

	Boiling point at 10 mm	Optical Rotation	Specific Gravity	Refractive Index at 15°
Formate	90°	+ 31°	1 013	1 47078
Acetate	98°	− 38° 20′	0·991	1·46635
Propionate	110°	+ 24°	0 978	1·46435
Butyrate	121°	+ 22°	0·966	1·46380
Valerianate	128° to 130°	+ 20°	0 956	1·46280

It also forms a phthalic acid compound melting at 164°. Pure borneol has the following characters —

Melting-point	203° to 204°
Boiling-point	212°
Specific gravity	1·011 to 1·020
„ rotation (in alcohol)	± 37·6° to 39 5°

Borneol has the following constitution —



Henderson and Heilbron[1] recommend the following method for differentiating between borneol and isoborneol (*q.v.*). The alcohol is dissolved in ten to fifteen times its weight of pyridine, and the calculated amount of *para*-nitrobenzoyl chloride added, and the mixture heated on the water-bath for several hours. The pyridine is removed by extraction with ice-cold dilute sulphuric acid, and the resulting *para*-nitrobenzoate of the alcohol, after washing with dilute sulphuric acid again, is separated, dried, and recrystallised from alcohol. Bornyl-*p*-nitrobenzoate melts at 137°, whilst the corresponding isoborneol derivative melts at 129°. It is possible that the usually accepted melting-points of both borneol and isoborneol may require revision, as Henderson and Heilbron find the borneol regenerated from the crystalline nitrobenzoate melts at 208°, and isoborneol obtained in the same way at 217°.

Pickard and Littlebury[2] have carried out a series of investigations on the separation of the optically active borneols and isoborneols, which is of particular interest, as the method of separation can probably be applied to various other similar bodies. This method depends on the

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[1] *Proc. Chem. Soc*, **29** (1913), 381

[2] *Ibid*, **23**, 262, *Jour Chem. Soc*, **91**, 1973.

different solubilities of the crystalline compounds of the acid phthalates of the alcohols, with alkaloids such as cinchonine, or with *laevo*-menthylamine. The specific rotations which these chemists consider accurate for borneol are very concordant for the two optical varieties The values obtained are —

Dextro-borneol $[\alpha]_D$ = + 37·08° (in alcohol)
Laevo-borneol $[\alpha]_D$ = − 37·61° „ „

The corresponding figures for isoborneol are as follows —

Dextro-isoborneol $[\alpha]_D$ = + 34·02° (in alcohol)
Laevo-isoborneol $[\alpha]_D$ = − 34 34° „ „

ISOBORNEOL.

Isoborneol, $C_{10}H_{17}OH$, is an alcohol stereoisomeric with borneol, which it closely resembles in general characters It is obtained, together with borneol, by reducing camphor with sodium, or it may be prepared by hydrating the terpene camphene by means of acetic and sulphuric acids. The following[1] is the best method for the preparation of this alcohol. One hundred grams of camphene are heated with 250 grams of glacial acetic acid and 10 grams of 50 per cent. sulphuric acid to 60° for four hours and the mixture continually shaken. When the reaction is complete, excess of water is added, and the ester, isobornyl acetate, separates as an oily mass. Free acid is removed by shaking the oil in a separator with water until the water is neutral The ester is then saponified by boiling with alcoholic potash under a reflux condenser. The greater part of the alcohol is distilled off, and the residue is poured into a large quantity of water Isoborneol is precipitated as a solid mass, which is filtered off, washed with water, dried on a porous plate and recrystallised from petroleum ether. Prepared in this manner, isoborneol melts at 212° (but see Henderson's and Heilbron's results, *supra*). It is moreover, so volatile that the determination of its melting-point must be made in sealed tubes

Its specific rotation is ± 34°

Isoborneol yields camphor on oxidation, but it yields camphene on dehydration much more readily than borneol does If a solution of isoborneol in benzene be heated with chloride of zinc for an hour, an almost quantitative yield of camphene is obtained Pure borneol under the same conditions is practically unchanged

Isoborneol forms a phenylurethane, $C_6H_5NH . CO \; O \; C_{10}H_{17}$, melting at 138° to 139°, which is identical with the melting-point of borneol phenylurethane

Isobornyl formate is a liquid of specific gravity 1·017, and boils at 100° at 14 mm., isobornyl acetate has a specific gravity 0 9905, and boils at 107° at 13 mm

The following table exhibits the principal difference between borneol and isoborneol —

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[1] *Jour prakt. Chem*, New Series, **49**, 1.

	Borneol.	Isoborneol.
Crystalline form	– double refraction	+ double refraction
Melting-point	204° (208° ?)	212° (217°
Boiling-point	212°	
Solubility in benzene at 0°	1 in 7	1 in 3
„ „ petroleum ether at 0°	1 in 10 to 11	1 in 4 to 4·5
Melting-point of phenylurethane	138°	138°
„ „ „ chloral compound	55° to 56°	liquid
„ „ „ bromal „	104° „ 105°	72°
„ „ „ acetic ester	29°	liquid
With zinc chloride	unchanged	forms camphene
Specific rotation	37°	34°

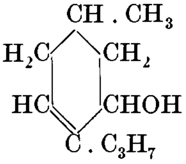
PIPERITOL.

Piperitol is a secondary alcohol, corresponding with the ketone, piperitone, occurring in several of the so-called peppermint group of eucalyptus oils.[1]

It is a liquid of the formula $C_{10}H_{18}O$, having the following characters —

Specific gravity at 22°	0·923
Optical rotation	– 34·1°
Refractive index at 22°	1·4760

Its constitution is probably —



CAMPHENE HYDRATE.

Aschan[2] has recently prepared a new alcohol from camphene, which is not identical with isoborneol. He obtained it by digesting camphene monohydrochloride with a solution of calcium hydroxide for about eighteen hours with continual agitation. The camphene hydrate so formed is a crystalline compound, highly refractive, and melting at 150° to 151°. It boils at 205°. It differs very markedly from borneol and isoborneol by yielding camphene on dehydration with the greatest ease, even when the mildest dehydrating agents are used.

Camphene hydrate is a tertiary alcohol, and a study of its characters and method of preparation caused Aschan to consider that it is improbable that borneol and isoborneol are stereoisomeric, but that they probably have different constitutional formulæ.

MYRTENOL.

Myrtenol, $C_{10}H_{16}O$, is a primary cyclic alcohol, which was isolated from essential oil of myrtle, in which it occurs principally in the form of its acetic ester, by von Soden and Elze[3] It is separated from geraniol, with which it is found, by fractional distillation, and by the crystallisa-

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[1] Baker and Smith, *A Research on the Eucalyptus*, 2nd edition, p. 373.

[2] *Berichte*, **41**, 1092.

[3] *Chem. Zeit.*, **29** (1905), 1031.

tion of its acid phthalate, which melts at 116°. Myrtenol has an odour of myrtle, and possesses the following characters:—

Boiling-point at 760 mm.	222° to 224°
,, ,, ,, 9 mm.	102° ,, 105°
Specific gravity at 20°	0·9763
Optical rotation	+ 45° 45′
Refractive index	1·49668

The above figures are those of Semmler and Bartelt,[1] those of von Soden and Elze being as follows:—

Boiling-point at 751 mm.	220° to 221°
,, ,, ,, 3·5 mm.	79·5° ,, 80°
Specific gravity at 15°	0·985
Optical rotation	+ 49° 25′

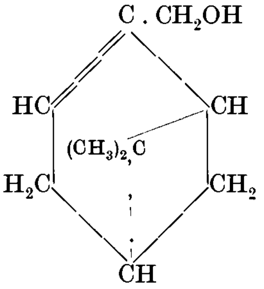
Myrtenol forms an acetic ester, quantitatively, so that it can be determined by acetylisation.

With phosphorus pentachloride it yields myrtenyl chloride, $C_{10}H_{15}Cl$, which by reduction with sodium and alcohol yields pinene.

On oxidation with chromic acid in acetic acid solution, myrtenol yields a corresponding aldehyde, which has been termed myrtenal. This body has the following characters:—

Formula	$C_{10}H_{14}O$
Boiling-point at 10 mm.	87° to 90°
Specific gravity at 20°	0·9876
Refractive index	1·5042
Melting-point of semi-carbazone	230°
,, ,, ,, oxime	71° to 72°

Myrtenol, according to Semmler and Bartelt, has the following constitution:—



SANTELOL.

There exists in East Indian sandalwood oil an alcohol, of the formula $C_9H_{16}O$, which has been named santelol, or santenone alcohol. It is closely allied to, and much resembles, the alcohol obtained by the hydration of the hydrocarbon, santene (*q.v.*), and is probably stereoisomeric with it. There is some difference of opinion as to the proper nomenclature of the two alcohols. According to Charabot,[2] the naturally occurring alcohol, also obtainable by the reduction of santenone, is analogous to borneol, and should therefore be termed, if that analogy is

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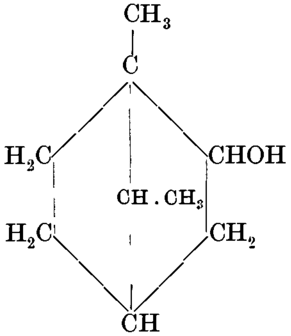
[1] *Berichte*, 40 (1907), 1363.

[2] *Les Principes Odorants des Vegetaux*, p. 100.

to be used in the nomenclature, π-nor-borneol, whilst the name π-nor-isoborneol should be reserved for the isosantelol, which results from the hydration of santene. The two alcohols are probably stereoisomeric, and the names assigned to them are exactly reversed by Semmler and Schimmel, who term the alcohol obtained by the hydration of santene, santelol or π-nor-borneol. Both alcohols are probably of the following constitution :—



Santelol can be purified by conversion into its phthalic acid ester, which is liquid, but which forms a silver salt which does not melt even at 230°.

It is a solid body melting at 58° to 62°, and boiling at 196° to 198°.

π-Nor-isoborneol, obtained by the hydration of santene, or by boiling teresantalic acid with formic acid, has the following characters :—

Boiling-point	87° to 88° at 9 mm.
Melting-point	68° to 70°
Optical rotation	0°

It forms an acetate having the following characters :—

Formula	$C_{11}H_{18}O_2$
Boiling-point	89° to 90·5° at 9 mm.
Specific gravity at 20°	0·987
Refractive index	1·45962
Molecular refraction	50·47

The above figures are given for the alcohols based on the nomenclature advocated by Charabot as mentioned above.

APOPINOL.

Apopinol, $C_{10}H_{18}O$, is an alcohol, which has been identified in a Japanese essential oil by Keimaza.[1] It yields citral on oxidation, and it is not certain that it is in fact a chemical individual, being, possibly, an impure form of linalol.

KESSYL ALCOHOL.

Kessyl alcohol, $C_{14}H_{24}O_2$, has been isolated from Japanese valerian, or *Kesso*, oil. It is a solid compound forming fine rhombic crystals and having the following characters :—

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[1] *Jour. Pharm. Soc.*, Japan (1903), August.

Melting-point	85°
Boiling-point at 11 mm.	155° to 156°
,, ,, ,, 760 ,,	300° ,, 302°

It forms an acetic ester, which boils at 178° to 179° at 16 mm., and has an optical rotation – 70° 6'. Its formula is $C_{14}H_{23}O_2 . OC . CH_3$.

SANTALOL.

There exist in sandalwood oil (from *Santalum album*) two isomeric sesquiterpene alcohols, of the formula $C_{15}H_{24}O$. They are both primary unsaturated alcohols, one being bicyclic, the other tricyclic. These two alcohols are termed α-santalol and β-santalol.

α-santalol has the following characters:—

Boiling-point	300° to 301°
,, ,, at 8 mm.	155°
Specific gravity	0·979
Refractive index	1·4990 at 19°
Specific rotation	+ 1° 6'

The specific gravity, refractive index, and specific rotation given above are those recorded by Paolini and Divizia[1] and are probably accurate since the α-santalol was prepared by regeneration from its strychnine phthalate. The values recorded for commercial santalol, prepared by fractional distillation, are as follows, and are the average values for the mixed santalols as they occur in sandalwood oil:—

	Semmler.	v. Soden.	Schimmel.
Specific gravity	0·973 at 20°	0·976 to 0·978	0·973 to 0·982
Optical rotation	– 21°	– 16° 30' to – 20°	– 14° ,, – 24°
Refractive index	1·50974	—	1·5040 ,, 1·5090

Schimmel gives the following figures for α-santalol, but those of Paolini and Divizia are probably more accurate:—

Specific gravity	0·9854 at 0°
Optical rotation	– 1·2°
Boiling-point	300° to 301°

β-santalol has the following characters:—

Boiling-point at 760 mm.	309° to 310°
,, ,, ,, 10 ,,	168° ,, 169°
Specific gravity	0·9729
Refractive index	1·5092
Specific rotation	– 42°

These values, except the boiling-point at 760°, are those of Paolini and Divizia. Schimmel gives the following figures:—

Boiling-point at 760 mm.	309° to 310°
,, ,, ,, 14 ,,	170° ,, 171°
Specific gravity	0·9868 at 0°
Optical rotation	– 56°

According to Paolini and Divizia (*loc. cit.*), the two santalols can be separated in the following manner: They are first separated as far as possible by careful fractional distillation, and the impure fractions converted in the usual manner into the hydrogen phthalate and this again

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[1] *Atti. R. Accad. Lincei*, 1914 (v.), **28**, ii. 226.

into the strychnine salt. By repeated recrystallisation the strychnine salt can be purified until the melting-point and rotatory power are constant. When this point is reached, saponification yields the pure alcohol. The strychnine phthalate has the following formula —

$$C_6H_4(CO_2 . C_{15}H_{23}) (CO_2H . C_{21}H_{22}O_2N_2).$$

By oxidation of the santalols, an aldehyde, or mixture of aldehydes, is obtained, which has been termed santalal. It has the formula $C_{15}H_{22}O$, and the following are its physical characters —

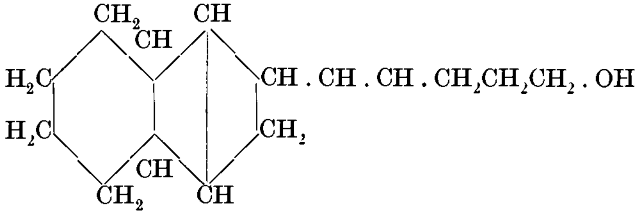
Boiling-point at 10 mm.	152° to 155°
Specific gravity at 20°	0·995
Optical rotation	+ 13° to + 14°
Refractive index	1·51066
Melting-point of oxime	104° to 105°
,, ,, ,, semi-carbazone	230°

Semmler regards the body nor-tricyclo-ecsantalane, $C_{10}H_{16}$, as the parent substance of all the santalol derivatives. It is obtained by decomposing the ozonide of santalol *in vacuo*.

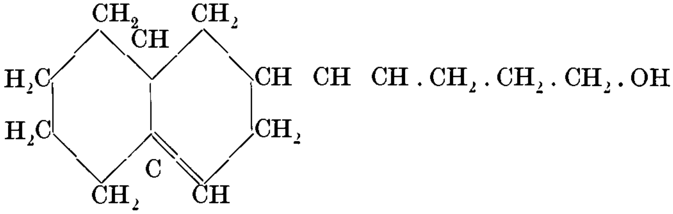
The acetic esters of the two santalols have been prepared, but their absolute purity has not been substantiated.

α-santalyl acetate boils at 308° to 312°, and β-santalyl acetate at 316° to 317°.

The formulæ suggested by Semmler for the two santalols are as follows —



α Santalol.



β Santalol

Amyrol

The alcohols of the so-called West Indian sandalwood oil, which is distilled from a species of *Amyris*, are known under the name of amyrol. It is, in all probability a mixture of two alcohols of the formulæ $C_{15}H_{24}O$ and $C_{15}H_{26}O$ Its characters are as follows —

Specific gravity	0·980 to 0·982
Optical rotation	+ 27°
Boiling point	299° to 301° at 748 mm.
,, ,,	151° ,, 152° ,, 11 ,,

Amyrol has been partially separated into its constituents—of which the higher boiling is probably of the formula $C_{15}H_{26}O$, and has a specific gravity 0·987, optical rotation + 36°, and boiling-point 299°. The lower boiling alcohol appears to have the formula $C_{15}H_{24}O$, and to be optically inactive.

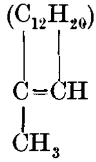
CEDROL AND PSEUDOCEDROL.

Cedrol, $C_{15}H_{26}O$, is a true sesquiterpene alcohol occurring in cedar-wood oil (*Juniperus virginiana*) and several allied essential oils.

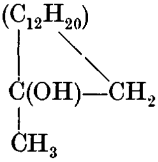
It is a crystalline substance having the following characters:—

Melting-point	86° to 87°
Boiling-point	291° „ 294°
„ „ at 8 mm.	157° „ 160°
Specific rotation (in chloroform)	+ 9° 31′

It yields a phenylurethane if it is heated almost to boiling-point with phenyl-isocyanate. This compound melts at 106° to 107°. On dehydration with phosphoric acid it yields the sesquiterpene cedrene. The relationship between cedrene and cedrol is probably as follows:—



Cedrene.



Cedrol.

Semmler and Mayer[1] have isolated a physical isomer of cedrol from the same oil, which they have named pseudocedrol. This alcohol was obtained by systematic fractionation of the oil, and was found to accumulate in the fraction which distils between 147° and 152° at 9 mm. pressure. Pseudocedrol is a saturated tertiary alcohol having the following characters:—

Specific gravity at 20°	0·9964
Optical rotation	+ 21° 30′
Refractive index	1·5131

When pseudocedrol is heated in a sealed tube at 235° it yields a mixture of dihydrocedrene, $C_{15}H_{26}$, and cedrene, $C_{15}H_{24}$.

According to Semmler and Mayer, cedrol and pseudocedrol are of the same chemical constitution, the two bodies being physical isomers.

CEDRENOL.

In addition to cedrol and pseudocedrol, cedar-wood oil contains a third alcohol, of the formula $C_{15}H_{24}O$, which has been named cedrenol. This alcohol was isolated by Semmler and Mayer,[2] who found it to exist to the extent of about 3 per cent. in the oil. It is a tricyclic unsaturated alcohol, closely related in constitution to the sesquiterpene cedrene, as shown by the following formulæ:—

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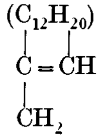
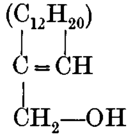
[1] *Berichte*, **45**, 1384.

[2] *Ibid.*. **45**, 786.



$$\begin{array}{l}(C_{12}H_{20})\\ |\quad\;\;|\\ C=CH\\ |\\ CH_2\end{array}$$

Cedrene.



$$\begin{array}{l}(C_{12}H_{20})\\ |\quad\;\;|\\ C=CH\\ |\\ CH_2{-}OH\end{array}$$

Cedrenol.

Cedrenol has been isolated in a state of purity by means of its phthalic acid ester.

It is a viscous, colourless liquid, having the following characters:—

Boiling-point at 10 mm.	161° to 170°
Specific gravity at 20°	1·0098
Optical rotation	+ 1°
Refractive index	1·5230

It was, however, probably not quite pure, when obtained in this manner. It forms an acetic ester, having the following characters —

Boiling-point at 10 mm	165° to 169°
Specific gravity at 20°	1·0168
Refractive index	1 5021
Optical rotation	− 2°

When regenerated by saponification of the acetic ester, cedrenol was found to have the following characters ·—

Boiling-point at 9·5 mm.	166° to 169°
Specific gravity at 20°	1·0083
Refractive index	1·5212
Optical rotation	± 0°

By the action of phosphorus pentachloride, cedrenol yields cedrenyl chloride, $C_{15}H_{23}Cl$, which, when reduced by sodium and alcohol yields cedrene.

CADINOL.

Semmler and Jonas[1] have isolated a sesquiterpene alcohol, $C_{15}H_{26}O$, from oil of galbanum. It yields a hydrochloride melting at 117° to 118°.

VETIVENOL.

Genvresse and Langlois[2] isolated an alcohol of the sesquiterpene group of the formula $C_{15}H_{24}O$ from oil of vetiver, which they named vetivenol. This alcohol has been examined by Semmler, Risso, and Schroeter.[3] From the fraction boiling at 260° to 298° at 13 mm. they obtained an ester of vetivenol, $C_{15}H_{24}O$, with an acid of the formula $C_{15}H_{22}O_2$. On hydrolysis the alcohol was obtained, which had the following characters.—

Boiling-point at 13 mm	170° to 174°
Specific gravity at 20°	1·0209
Refractive index	1 52437
Optical rotation	+ 34° 30'
Molecular refraction	65·94

This alcohol possesses only one double bond, and must be tricyclic. It is a primary alcohol, yielding a phthalic acid ester. On reduction

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[1] *Berichte*, **47** (1914), 2068.

[2] *Comptes rendus*, **135**, 1059.

[3] *Berichte*, **45**, 2347.

with hydrogen and spongy platinum, it yields dihydrovetivenol, $C_{15}H_{26}O$, a true sesquiterpene alcohol, having the following characters:—

Boiling-point at 17 mm.	176° to 179°
Specific gravity at 20°	1·0055
Refractive index	1·51354
Optical rotation	+ 31°

Dihydrovetivenol forms an acetic ester, whose characters are as follows:—

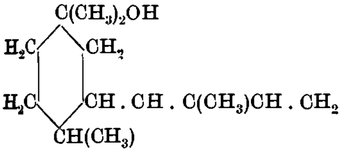
Boiling-point at 19 mm.	180° to 184°
Specific gravity at 20°.	1·0218
Refractive index	1·50433
Optical rotation	+ 25° 48'

There was also obtained from the oil a second alcohol, $C_{15}H_{24}O$, which contains two double bonds, and is bicyclic. It is also a primary alcohol, but its characters have not been ascertained with accuracy. A mixture of bicyclic and tricyclic vetivenol isolated by means of phthalic acid had the following characters, from which those of bicyclic vetivenol may, to some extent, be deduced:—

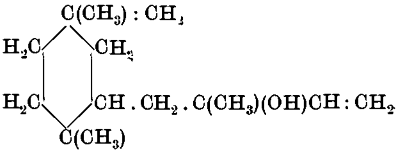
Boiling-point at 14 mm.	168° to 170°
Specific gravity at 20°	1·0095
Refractive index	1·52058
Optical rotation	+ 25°

ZINGIBEROL.

Brooks[1] has isolated from the fraction of oil of ginger boiling at 154° to 157° at 15 mm. an alcohol which he finds to be a sesquiterpene alcohol, $C_{15}H_{26}O$, corresponding to the sesquiterpene zingiberene. It has the fragrant odour of ginger, and probably possesses one of the following constitutions:—



or



GUAIOL.

Guaiol, $C_{15}H_{26}O$, is an odourless sesquiterpene alcohol found in the essential oil of the wood of *Bulnesia Sarmienti*, known as guaiac wood oil.

It is obtained by extracting the wood with ether, and several times recrystallising the pasty mass so obtained from alcohol.

Guaiol is a tertiary bicyclic alcohol, with one double linkage, having the following characters:—

Melting-point	91°
Boiling-point at 9 mm.	147° to 149°
Specific gravity $\frac{20°}{4°}$	0·9714
Refractive index	1·5100
Specific rotation	− 29·8°

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[1] *Jour. Amer. Chem. Soc.*, **38** (1916), 430.

By acting on guaiol with potassium in alcohol, and adding methyl iodide, guaiol methyl ether is formed, which has the following characters:—

Boiling-point at 9 mm.	141° to 143°
Specific gravity at $\frac{25^\circ}{4^\circ}$	0·9332
,, rotation	− 31·8°
Refractive index at 18·5°	1·48963

If guaiol be shaken in aqueous acetone with potassium permanganate a glycerol results, which is the first body of its type known in the sesquiterpene series. This body, guaiol glycerol, $C_{15}H_{28}O_2$, forms colourless tablets, melting at 210° to 211°, and is suitable for the identification of guaiol.

CLOVE SESQUITERPENE ALCOHOL.

Semmler and Mayer[1] have isolated a sesquiterpene alcohol, $C_{15}H_{26}O$, from the high boiling fractions of oil of cloves. It was probably not obtained in an absolutely pure condition, but had the following characters, which must be regarded as approximate only:—

Boiling-point at 8 mm.	138° to 148°
Specific gravity at 20°	0·9681
Optical rotation	− 17°
Refractive index	1·5070

It yields a chloride, $C_{15}H_{25}Cl$, of specific gravity 0·990 at 20°. It is a bicyclic sesquiterpene alcohol, with one double bond.

LEDUM CAMPHOR.

Ledum camphor, $C_{15}H_{26}O$, is a solid sesquiterpene alcohol present in the essential oil of *Ledum palustre*. It forms long, colourless needles having the following characters:—

Melting-point	104°
Boiling-point	281°
Specific gravity at $\frac{20^\circ}{4^\circ}$	0·9814
Refractive index	1·5072

On dehydration it yields the sesquiterpene ledene, which has scarcely been investigated.

COSTOL.

Semmler and Feldstein[2] have isolated a sesquiterpene alcohol, $C_{15}H_{24}O$, from the oil of costus root, to which they have given the name costol. It was purified by conversion into its acid phthalate, which, on hydrolysis yields the pure alcohol, having the following characters:—

Boiling-point at 11 mm.	169° to 171°
Specific gravity at 21°	0·983
Refractive index	1·5200
Optical rotation	+ 13°

---

[1] *Berichte*, **45** (1912), 1390.

Ibid., **47** (1914), 2687.

Costol is a diolefinic bicyclic sesquiterpene alcohol, which, on oxidation by chromic acid in acetic acid yields an aldehyde, $C_{15}H_{22}O$, which yields a semi-carbazone, melting at 217° to 218°. This aldehyde, which is triolefinic has the following characters:—

Boiling-point at 15 mm.	164° to 165°
Specific gravity at 22°	0·9541
Refractive index	1·50645
Optical rotation	+ 24°

Costol forms an acetic ester, having a specific gravity 0·9889 at 21° and optical rotation + 19°.

ELEMOL.

Semmler and Liao[1] have examined the solid body isolated from Manila elemi oil by Schimmel & Co. This was found to be a sesquiterpene alcohol, $C_{15}H_{26}O$, which has been named elemol. It was purified by converting it into its benzoic acid ester, from which the alcohol was prepared in a pure state by hydrolysis. It has the following characters:—

Boiling-point at 17 mm.	152° to 156°
Specific gravity at 20°	0·9411
Refractive index	1·5030
Optical rotation	– 5°

Its benzoic ester has the following characters:—

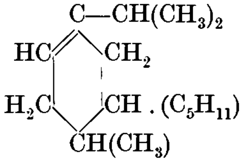
Boiling-point at 10 mm.	214° to 218°
Specific gravity at 20°	1·0287
Refractive index	1·5378
Optical rotation	– 6°

On reduction elemol yields tetrahydroelemol, $C_{15}H_{30}O$. Elemol is a monocyclic sesquiterpene alcohol, and on dehydration yields the sesquiterpene elemene.

According to Semmler and Liao[2] tetrahydroelemol has the following characters:—

Melting-point	35·5°
Boiling-point	138° to 142° at 13 mm.
Specific gravity at 20°	0·9080
Refractive index	1·4807
Optical rotation	– 2°

By treatment with formic acid, it yields tetrahydroelemene. The constitution of this body, which throws some light on that of elemol, is probably as follows:—



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[1] *Berichte*, **49** (1916), 794.

[2] *Ibid.*, **50** (1917), 1286.

JUNIPEROL.

Ramsay[1] has isolated a crystalline sesquiterpene alcohol from the essential oil distilled from the bark of the juniper tree. It forms optically inactive triclinic crystals, melting at 107°, and having the formula $C_{15}H_{24}O$.

EUDESMOL.

Eudesmol is a sesquiterpene alcohol, isolated from several species of eucalyptus oil by Baker and Smith, who regarded it as an oxide of the formula $C_{10}H_{16}O$. Semmler and Tobias[2] have, however, shown that it is a tricyclic, unsaturated alcohol. It has the following characters :—

Melting-point	79° to 80°
Boiling point at 10 mm.	156°
Specific gravity at 20°	0·9884
,, rotation (in chloroform)	+ 38° to 43°
Refractive index	1·5160
Molecular refraction	67·85.

It forms an acetate, which boils at 165° to 170° at 11 mm. By reduction with hydrogen and spongy platinum, it yields dihydroeudesmol, an alcohol melting at 82°. On dehydration it yields a sesquiterpene, eudesmene. Eudesmol appears to have a tendency to liquefy by keeping. Whether the liquid body is an isomer or not is unsettled.

GLOBULOL.

This sesquiterpene alcohol was discovered by Schimmel & Co. in oil of *Eucalyptus globulus*. It is found in the last fractions of the distillate, separating out in crystalline condition. On recrystallisation from 70 per cent. alcohol, it was obtained in the form of brilliant, almost odourless needles, having the following characters :—

Melting-point . . .	88·5°
Boiling-point at 755 mm. .	283°
Specific rotation	− 35° 29′ (12 per cent. chloroform solution)

Its formula is $C_{15}H_{26}O$.

Schimmel & Co.[3] attempted to acetylise the alcohol by means of acetic anhydride, but the reaction product only showed 5 per cent. of ester, which was not submitted to further examination. The bulk of the alcohol had been converted into a hydrocarbon, with loss of water. Ninety per cent. formic acid is most suitable for splitting off water. One hundred grams of the sesquiterpene alcohol were heated to boiling-point with three times the quantity of formic acid, well shaken, and, after cooling, mixed with water. The layer of oil removed from the liquid was freed from resinous impurities by steam-distillation, and then fractionated at atmospheric pressure. It was then found to consist of a mixture of dextro-rotatory and laevo-rotatory hydrocarbons. By repeated fractional distillation, partly *in vacuo*, partly at ordinary pressure, it was possible to separate two isomeric sesquiterpenes, which, after treatment with aqueous alkali, and distillation over metallic sodium, showed the following physical constants :—

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[1] *Zeit. f. Kristallogr.*, **46**, 281.

[2] *Berichte*, **46** (1913), 2026.

[3] *Report*, April, **1904**. 52.

	1.	2.
Boiling-point	247° to 248°	266°
Optical rotation	– 55° 48′	+ 58° 40′
Refractive index	1·4929	1·5060
Specific gravity	0·8956	0·9236

Semmler and Tobias[1] consider that eudesmol and globulol are related in the same manner as borneol and isoborneol.

PATCHOULI CAMPHOR.

Patchouli camphor, $C_{15}H_{26}O$, is a solid alcohol found in oil of patchouli. It is a crystalline body having the following characters —

Melting-point	56°
Specific rotation	– 118° (in fused state)
„ „	– 97° 42′ (in chloroform)

On dehydration it yields patchoulene, a sesquiterpene which has not been investigated.

CUBEB CAMPHOR.

Cubeb camphor, $C_{15}H_{26}O$, is a sesquiterpene alcohol which is found in oil of cubebs, especially in old samples of the oil. It is laevo-rotatory, melts at 68° to 70°, and boils at 248° with decomposition. Nothing is known of its constitution.

MATICO CAMPHOR.

This sesquiterpene alcohol is found in old samples of Matico leaf oil. It is a crystalline body, of the formula, $C_{15}H_{26}O$, melting at 94°, and of specific rotation – 28·73°, in chloroform solution.

GONOSTYLOL

This body, $C_{15}H_{26}O$, exists in the oil of *Gonystilus Miquelianus*. It has the following characters —

Melting point	82°
Boiling-point at 17 mm.	164° to 166°
Specific rotation	+ 30° (in alcohol)

On dehydration it yields the sesquiterpene, gonostylene.

BETULOL.

Betulol is a sesquiterpene alcohol of the formula $C_{15}H_{24}O$, found in oil of birch buds. It can be isolated as a hydrogen phthalate, by warming a solution of betulol in benzene, with phthalic anhydride. It has according to Soden and Elze, the following characters —

Boiling-point at 743 mm	284° to 288°
„ „ „ 4 mm.	138° „ 140°
Specific gravity	0 975
Optical rotation	– 35°
Refractive index	1·50179

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[1] *Berichte*, **46** (1913), 2030.

It forms an acetic ester boiling at 142° to 144° at 4 mm. pressure, of specific gravity 0·986.

This alcohol has, however, been quite recently reinvestigated by Semmler, Jonas, and Richter.[1] They consider that it is a bicyclic sesquiterpene alcohol whose characters are as follows:—

Boiling-point	157° to 158° at 13 mm.
Specific gravity at 16°	0·9777
Refractive index at 16°	1·5150
Optical rotation	– 26·5°

By the action of phosphorus pentachloride it yields betulyl chloride, a partial molecular rearrangement having apparently taken place, since, on hydrolysis, it yields a tricyclic betulol which is of particular interest in that it is the first tricyclic sesquiterpene alcohol of a crystalline character to be discovered. Its characters are as follows:—

Melting-point	147° to 148°
Boiling-point	160° to 166° at 13 mm.

ATRACTYLOL.

Atractylol, $C_{15}H_{26}O$, is a sesquiterpene alcohol which forms the principal constituent of the oil of *Atractylis ovata.* It is a tertiary tricyclic alcohol, having the following characters:—

Melting-point	59°
Boiling-point	290° to 292°
,, ,, at 15 mm.	162°
Optical rotation	± 0°
Refractive index	1·5103

CAPARRAPIOL.

Caparrapiol, $C_{15}H_{26}O$, is a sesquiterpene alcohol found in the oil of *Nectandra Caparrapi.* It has the following characters:—

Boiling-point	260° at 757 mm.
Specific gravity	0·9146
Optical rotation	– 18° 58'
Refractive index	1·4843

GALIPOL.

Galipol is a sesquiterpene alcohol of the formula $C_{15}H_{26}O$, found in oil of Angostura. It has the following characters:—

Specific gravity at 20°	0·927
Boiling-point	260° to 270°

It is a very unstable compound.

MAALI SESQUITERPENE ALCOHOL.

There exists in the essential oil of Maali resin a sesquiterpene alcohol, $C_{15}H_{26}O$, corresponding with the sesquiterpene which has already been described. It has the following characters:—

Melting-point	105°
Boiling-point	260°
Specific rotation	+ 18° 33'

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[1] *Berichte,* **51** (1918), 417.

OPOPONAX SESQUITERPENE ALCOHOL.

A sesquiterpene alcohol, $C_{15}H_{26}O$, has been extracted by means of phthalic anhydride from oil of opoponax resin. It distils at 135° to 137° *in vacuo* (2 mm.), and yields a crystalline phenylurethane. But as, in spite of repeated crystallisations, it could not be obtained of constant melting-point, it is probable that the substance is a mixture of two or more alcohols.

4. ESTERS.

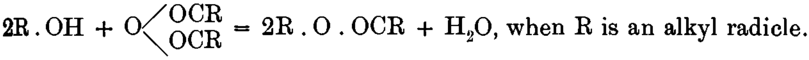
It will now be convenient to pass on to that very important group of compounds, the esters.[1] An ester is a combination of an alcohol with an acid, the combination being associated with the elimination of water. For example, ordinary ethyl alcohol combines with acetic acid to form the ester, ethyl acetate, according to the following equation:—

$$\underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Acetic Acid.}}{HOOC\,.\,CH_3} = \underset{\text{Ethyl Acetate.}}{C_2H_5OOC\,.\,CH_3} + \underset{\text{Water.}}{H_2O}$$

The esters play a most important part in the economy of plant life, and are highly important constituents of numerous essential oils. Indeed, in many cases they are the dominating constituent, and the oil may be said to owe its perfume value largely, or in some cases almost entirely, to the esters it contains.

In dealing with natural perfumes it must be remembered that when one speaks of, for example, lavender oil containing 35 per cent. of linalyl acetate, or geranium oil containing 30 per cent. of geranyl tiglate, these are merely convenient forms of expression, and give a conventional method of expressing the ester value. For the esters are really merely calculated from analytical results to a given formula; whereas, in fact, in nearly every essential oil containing esters there is a predominating ester associated with several others in smaller quantities which are impossible to separate, and are all expressed in terms of the predominating ester. The recognition of these subsidiary esters is of the highest importance, since it enables the scientist to prepare the various synthetic esters and blend them in minute quantities so as to give a long scale of modified odours. Indeed, the synthetic esters form one of the most important portions of the price list of the synthetic perfume manufacturer. The following are the general methods for the artificial preparation of esters:—

1. By the interaction of the alcohols and acids at an elevated temperature; the reaction is assisted by the use of some catalytic agent, or one which absorbs the water formed, such as dry sodium acetate. The reaction is rarely complete, however, and may be rendered more nearly quantitative by using the acid anhydride in place of the acid itself. The reaction is:—



$$2R\,.\,OH + O\Big\langle{}^{OCR}_{OCR} = 2R\,.\,O\,.\,OCR + H_2O, \text{ when R is an alkyl radicle.}$$

2. By the interaction of the silver salt of the acid with the halogen derivatives of the alcohol, when the reaction is as follows:—

$$AgNO_3 + C_2H_5I = C_2H_5NO_3 + AgI.$$

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[1] The section on the esters, is, in the main, reproduced from a monograph by the author in the *Perfumery and Essential Oil Record*, July, 1913.

3. By acting on the alcohols with acid chlorides, as, for example :—

$$C_2H_5OH + C_6H_5COCl = C_2H_5OOC . C_6H_5 + HCl.$$

To decide whether an ester is present in a mixture of compounds, such as a compound synthetic perfume, is a matter of no great difficulty. A weighed quantity, from 2 to 5 grams, according to the probable amount of ester present, is dissolved in a very small quantity of alcohol and a few drops of phenolphthalein solution added. An alcoholic solution of caustic potash is added drop by drop from a burette until all free acid is neutralised, as indicated by the liquid assuming an intense red colour. A measured quantity of the alcoholic potash solution is then run into the flask, 25 c.c. of semi-normal alkali usually being sufficient, and an exactly equal volume run into another flask. The contents of the two flasks are then boiled for an hour under a reflux condenser, and after an hour are cooled and the amounts of alkali present determined by means of semi-normal acid. If the amount of alkali left in the flask containing the sample is less than that in the "blank" flask, the difference has been absorbed in saponifying the esters present, breaking them down into the respective alcohols and acids. So that this consumed alkali is a measure of the amount of esters present. If an investigation into the nature of the esters present is necessary, it must be remembered that after the saponification the alcohol resulting is almost invariably an insoluble oil, so that by diluting the reaction mass with water the resulting alcohol, together with the other compounds of the sample, will float as an oily layer on the surface of the liquid, and this oily layer must be investigated in the usual manner. The acid, however, formed by the decomposition of the ester is usually soluble in the aqueous liquid, which can be separated from the oil, and the acid distilled off if volatile, or precipitated as a silver salt if non-volatile.

Some oils consist almost entirely of esters; for example, those of *Gaultheria procumbens* and *Betula lenta* contain about 99 per cent. of methyl salicylate. Bergamot and lavender owe the greater part of their perfume value to esters of linalol, of which the acetate predominates. Geranium oil owes its fragrance chiefly to geranyl esters, of which the tiglate is the chief. On the other hand, oils such as spike lavender, sandalwood, lemon-grass, and citronella contain but small quantities of esters, and owe their perfume value to entirely different types of compounds.

ESTERS OF METHYL ALCOHOL.

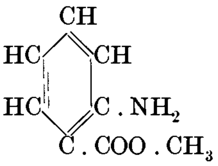
Methyl alcohol, CH_3OH, is the lowest member of the paraffin alcohols, and although it occurs to a small extent in the free state in a few essential oils it is not a perfume material at all, and, being very soluble in water, is entirely washed out of the oil by the distillation waters. There are, however, a number of highly odorous esters of methyl alcohol which are indispensable in synthetic perfumery. These are as follows :—

Fatty Acid Esters of Methyl Alcohol.—The following esters of methyl alcohol are commercial products, and all have fruity odours, and are very suitable for blending with flower oils to impart distinctive secondary odours to them. They are, generally speaking, very expensive, some of them costing as much as £12 per lb., but, as only minute quantities are used, the actual cost is not very material. They may be identified by the melting-point of the fatty acid yielded on saponification :—

	Melting-point of Fatty Acids.
Methyl caprinate, $CH_3(CH_2)_8CO_2CH_3$	31° to 32°
„ caprylate, $CH_3(CH_2)_6CO_2CH_3$	16° „ 17°
„ heptoate, $CH_3(CH_2)_5CO_2CH_3$	– 10°
„ laurinate, $CH_3(CH_2)_{10}CO_2CH_3$	43° to 44°
„ nonylate, $CH_3(CH_2)_7CO_2CH_3$	12° „ 13°

Methyl Anisate.—Methyl alcohol forms an ester with anisic acid, having the formula $C_6H_4(OCH_3)(COOCH_3)$. It is a crystalline body with a fine chervil odour.

Methyl Anthranilate.—This ester is one of extreme importance, and to it is largely due the possibility of manufacturing artificial neroli oils. It was discovered as a constituent of neroli oil in 1895 by Walbaum, and has since been identified in numerous other flower oils, such as tuberose, ylang-ylang, jasmin, and gardenia. Its value in synthetic perfumery is therefore obvious. Its constitution is that of a methyl ester or ortho-amido-benzoic acid, of the formula here shown :—



It is prepared artificially in various ways, most of which depend on the preliminary synthesis of the acid, which is then converted into its methyl ester. Anthranilic acid is prepared by the reduction of *ortho*-nitro-benzoic acid, with tin and hydrochloric acid ; or from phthalimide by treatment with bromine and caustic potash. The ester is prepared directly from isatoic acid (anthranil-carbonic acid), $C_6H_4(CO)(NCO_2H)$, by treatment with methyl alcohol and hydrochloric acid. Methyl anthranilate is a crystalline substance melting at 24° to 25°, whose solutions have a beautiful blue-violet fluorescence, which is apparent in all oils containing it. It boils at 132° at 14 mm., and has a specific gravity 1·168. It possesses a powerful odour similar to that of oil of neroli and similar flower oils. Its identification is easy, since on saponification it yields anthranilic acid, melting at 144° to 145°. It also yields a picrate, melting at 104°. It can be estimated quantitatively by the method proposed by Hesse and Zeitschel. About 25 to 30 grams of the sample are dissolved in two to three times its volume of dry ether. It is cooled in a freezing mixture, and then a mixture of 1 volume of sulphuric acid and 5 volumes ot ether are added slowly, drop by drop, until no further precipitation takes place. The whole of the methyl anthranilate is thus precipitated as sulphate. This is collected and washed with ether and weighed, or it may be titrated with semi-normal potash solution. If p be the weight of oil employed and n the number of c.c. of semi-normal alkali used, then the percentage of methyl anthranilate is $\frac{3·775 \times n}{p}$.

Minute quantities of the ester may be quantitatively determined by diazotising the ester and observing its colour reaction with either β-naphthol or dimethylaniline, against a standard solution of the ester.[1]

Methyl Benzoate.—This highly odorous ester has the composition $CH_3OOC . C_6H_5$. It is present in the oils of ylang-ylang, tuberose, and cloves, etc., and is also known in commerce as Niobe oil. It is a colourless, optically inactive liquid of fragrant odour, and is a necessary constituent of odours of the ylang-ylang type. It is a favourite ingredient in the perfume known as Peau d'Espagne, and blends well with santal, musk, geranium, or rose. It can be prepared by passing a current of dry hydrochloric acid gas into a solution of benzoic acid in methyl alcohol. The mixture is heated to 100° for several hours. and the resulting ester then precipitated with water. Pure methyl benzoate has the following characters: It boils at 199° at 760 mm., has a specific gravity 1·1026, and refractive index 1·5170. It should be free from chlorine, which may be tested for in the manner described under benzaldehyde. Methyl benzoate may be characterised by its forming a crystalline compound with phosphoric acid, which the benzoic esters of homologous alcohols do not.

Methyl Cinnamate.—This ester, which occurs in various balsamic products, has the constitution $C_6H_5 . CH : CH . COOCH_3$. It is an oily body with a penetrating fruity odour, and is of great value in the preparation of perfumes for such articles as toilet vinegars, smelling salts, etc. It can be prepared by the condensation of methyl alcohol and cinnamic acid by means of dry hydrochloric acid in the same way as methyl benzoate. It forms a low melting crystalline mass having the following characters:—

Specific gravity	1·0663 at 40°
Refractive index	1·56816 ,, 35°
Melting-point	34° to 36°
Boiling-point	256 at 745 mm.
,, ,, ...	262° to 265° at 760 mm.

Methyl Malonate.—This ester is an artificially prepared body, having a fruity odour, somewhat similar to the above-described esters of the fatty acids. It has the formula $CH_2(CO_2CH_3)_2$, and boils at 181°. It may be prepared by treating potassium cyan-acetate with methyl alcohol and hydrochloric acid. On saponification with alcoholic potash it yields malonic acid, which melts at 132°, and serves well for the identification of the ester.

Methyl Methyl-anthranilate.—This ester is quite similar in all its characters to methyl anthranilate. It has the constitution—

$$C_6H_4(NH . CH_3)(CO . OCH_3),$$

that is, one of the hydrogen atoms in the amido group of the anthranilic acid has been substituted by a methyl group. Its odour and fluorescence are quite similar to those of methyl anthranilate, and its estimation may be effected in the manner described for that ester. Its identification is easy, as it yields methyl-anthranilic acid, melting at 179° on saponification. The ester melts at 18·5° to 19·5°, boils at 130° to 131° at 13 mm., is optically inactive, and has a specific gravity 1·1238 at 20°, and a refractive index 1·57963.

Methyl Phenyl-acetate. — Phenyl-acetic acid can be prepared by

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[1] *Berichte*, **35**, 24 (1902); *J. Amer. Chem. Soc.*, 1921, 377.

chlorinating toluene, thus converting it into benzyl chloride, which is then converted into benzyl cyanide, which, on digestion with sulphuric acid, yields phenyl-acetic acid or α-toluic acid. This is condensed with methyl alcohol, forming the methyl ester of the formula $C_6H_5 . CH_2 . COOCH_3$. It has a powerful "honey" odour, and is very useful in scent bases of this type.

Methyl Phenyl-propionate.—Phenyl-propionic acid, also known as hydrocinnamic acid, forms a methyl ester of the formula

$$C_6H_5 . CH_2 . CH_2COO . CH_3.$$

The acid is obtained by the reduction of cinnamic acid by means of sodium amalgam. The acid is then esterified by the condensing action of a mineral acid in methyl alcohol solution. The ester is an oil of very sweet odour, and is very useful for flower bouquets.

Methyl Salicylate.—This ester is practically identical with oil of wintergreen or oil of sweet birch, both of which contain about 99 per cent. of the ester. It is also present in numerous other plants, and its artificial production is carried out on a very large scale. The artificial ester is quite suitable for replacing the natural oil, and is used to a very large extent for flavouring tooth powders, pastes, and washes, being exceedingly popular in America. The ester has the constitution

$$C_6H_4(OH)(COOCH_3).$$

The best method for producing it artificially is to condense salicylic acid and methyl alcohol by means of sulphuric acid. It is a colourless oil, optically inactive, and possessing an intense wintergreen odour. It has the following characters:—

Specificgravity at 0° . .	1·1969
,, ,, ,, 16° .	1·1819
Boiling-point . . .	224°
Melting-point . . .	– 8° to – 9°
Refractive index at 20° .	1·5375
Solubility	1 in 6 to 8 volumes of 70 per cent. alcohol

Esters of Ethyl Alcohol.

Ethyl Acetate.—This ester does not play a very important rôle in synthetic perfumery, but its intensely fruity odour, together with the fact that it is found naturally in the perfume of the magnolia gives it certain possibilities, if used in very minute quantities. It is an oil of the formula $CH_3COO . C_2H_5$. It boils at 76°, and has a specific gravity 0·908. It is easily soluble in the usual organic solvents, and fairly soluble in water.

Ethyl Anisate.—Very similar to the methyl ester of anisic acid is its ethyl ester. This is a crystalline compound of the formula

$$C_6H_4(OCH_3)(COOC_2H_5)$$

with a fine odour of chervil.

Ethyl Anthranilate.—This ester, of the formula

$$C_6H_4 . (NH_2)(COOC_2H_5),$$

is a liquid boiling at 260°. It can be prepared by the action of hydrochloric acid and ethyl alcohol on isatoic acid. It has the characteristic neroli odour possessed by the methyl ester, but is both sweeter and softer in perfume, and does not discolour so readily as the methyl ester.

Ethyl Benzoate.—This ester has not been found, so far, to occur naturally in essential oils. It has, however, been prepared by synthetic processes, for example, by condensing ethyl alcohol with benzoic acid by means of dry hydrochloric acid gas. Its odour is very similar to that of methyl benzoate (q.v.), but not quite so strong. It is an oil of specific gravity 1·0510, refractive index 1·5055, and boiling-point 213° at 745 mm. It is soluble in two volumes of 70 per cent. alcohol.

Ethyl Butyrate.—The butyric ester of ethyl alcohol has the formula

$$CH_3(CH_2)_2COO \, . \, C_2H_5.$$

It is a liquid boiling at 121°, and has a very fruity odour, very similar to that of the pine apple.

Ethyl Valeriànate.—This ester, $C_4H_9COOC_2H_5$, is an oil with a pine-apple odour. Its specific gravity is 0·894, and boiling-point about 133°.

Ethyl Heptoate.—This ester, which has the formula

$$CH_3(CH_2)_5COO \, . \, C_2H_5,$$

is also known as "œnanthylic ether," and is of a fragrant odour, recalling that of the secondary constituents of brandy. It is used and sold as an artificial oil of cognac. It is an oil boiling at 187° to 188°.

Ethyl Caprylate.—This ester is an oil reminding one of the secondary products of fermentation. It boils with decomposition at 275° to 290°, and has the formula $CH_3(CH_2)_6COOC_2H_5$.

Ethyl Cinnamate.—The cinnamic ester of ethyl alcohol is a natural constituent of a few essential oils, including camphor oil and storax. It is formed synthetically by condensing cinnamic acid and ethyl alcohol by dry hydrochloric acid gas. It has a soft and sweet odour, and is particularly suitable for blending in soap perfumes. It is an oil at ordinary temperatures, melting at 12°, and boiling at 271°. Its specific gravity is 1·0546, and its refractive index 1·5590.

Ethyl Laurinate.—The laurinic ester of ethyl alcohol has also, quite recently, come into vogue in synthetic perfumery. It is an oil of peculiar fruity odour, intensely strong, having the constitution

$$CH_3(CH_2)_{10}COOC_2H_5.$$

It boils at 269°.

Ethyl Malonate.—Ethyl malonate is not a member of the paraffinoid acid esters, but is sufficiently nearly related to this series to be included here as a matter of convenience. It is of considerable value in modifying flower odours, having a more or less characteristic apple odour, but of a much sweeter type than the valerianic ester perfume. It is an oil of specific gravity 1·068, and boils at 198°.

Ethyl Myristinate.—This is the highest ester of the series that is of any practical value in perfumery. It is an intensely odorous oil, melting at 10° to 11° and boiling at 295°. Its constitution is

$$CH_3(CH_2)_{12}COOC_2H_5.$$

Ethyl Nonylate.—This ester has, during the past year or two, been recognised as having a most useful odour for modifying flower bouquets. It is a fruity oil boiling at 227° to 228°, and having the constitution

$$CH_3(CH_2)_7COOC_2H_5.$$

Ethyl Octylate.—This ester is a fruity oil boiling at 207° to 208°. It has the formula $CH_3(C \, . \, H_2)_6COOC_2H_5$.

Ethyl Phenyl-acetate—This ester has the formula

$$C_6H_5 \; CH_2 \, . \, COOC_2H_5$$

It is very similar in odour and use to methyl phenyl-acetate

Ethyl Salicylate—The ethyl ester of salicylic acid resembles the lower homologue, methyl salicylate, in its general characters and perfume value It is an oil of specific gravity 1 1372, refractive index 1 52338, and optically inactive It boils at 234° It solidifies at low temperatures, and melts at + 1 3°.

ESTERS OF AMYL ALCOHOL

Amyl Acetate—This is, with the exception of amyl formate, which is not of practical importance, the simplest possible ester of amyl alcohol, and has the formula $CH_3 \, . \, COO \; C_5H_{11}$. It is a fruity oil, with a strong odour resembling that of the pear and is known as artificial oil of pear. It is prepared on a very large scale by, for example, treating 100 parts of dry sodium acetate, 100 parts of amyl alcohol, and 130 parts of sulphuric acid for twelve hours at ordinary temperature, and then distilling off the ester It has a specific gravity 0 876 and boils at 138°. The alcohol in this ester is not normal amyl alcohol, but isoamyl alcohol

Amyl Valerianate—This ester is an oil of strong apple odour, and is used for the preparation of cider essence Its formula is $C_5H_{11} \; C_5H_9O_2$

Amyl Benzoate—This ester has the formula $C_5H_{11} \; (O_2C)(C_6H_5)$ It is one of the best fixatives known, and has a slight but distinct amber odour It is prepared by condensing amyl alcohol and benzoic acid with dry hydrochloric acid gas

Amyl Heptylate—This ester is one of the newest synthetic odours, and is also one of the very expensive ones It has the formula $CH_3(CH_2)_5COOC_5H_{11}$, and is an oil of powerful fruity odour It can be identified by saponifying it and examining the resulting fatty acid, which should melt at − 10° and boil at 223°

Amyl Salicylate—All the perfumes of the orchid type, and many of the Trèfle variety, have amyl salicylate as one of their most important bases The ester is known under the names orchidée, trefle or trefoil, and artificial orchid essence It is used to a considerable extent in artificial perfumery It is a colourless liquid of the formula

$$C_5H_{11}(O_2C)(OH)(C_6H_4)$$

boiling at 276° to 277° at 760 mm., or at 151° to 152° at 15 mm Its specific gravity is about 1 052, and its refractive index is about 1 5055. It is dextro-rotatory about + 2° It is easily identified as on saponification it yields the characteristic odour of amyl alcohol, and salicylic acid, which can easily be identified by the usual reactions and by its melting-point

ESTERS OF HIGHER FATTY ALCOHOLS

Heptyl Heptoate—This is one of the most recent introductions to synthetic perfumery and one of the most expensive It has the formula $CH_3(CH_2)_5OOC \; (CH_2)_5CH_3$ It has a fine, powerful, fruity odour

Hexyl Acetate—Hexyl acetate, $CH_3(CH_2)_5OOC \; CH_3$ is an ester found naturally in the oil of *Heracleum giganteum* It has a fruity odour, and boils at 169° to 170° Its specific gravity is 0 890 at 10°

Hexyl Butyrate.—This ester is also a powerful fruit oil, and boils at 205°.

Octyl Acetate.—This ester has the formula $CH_3(CH_2)_7 . OOC . CH_3$. It is an oil boiling at 207°, and has a distinct orange odour. Its specific gravity is 0·885.

Octyl Butyrate.—This occurs naturally in a few essential oils. It is an oil boiling at 244°. and having a strong, fruity odour. Its formula is $CH_3(CH_2)_7OO . C . (CH_2)_2,CH_3$.

Octyl Heptylate.—This is the highest ester of the series that is found to be useful as a perfume. It has the formula

$$CH_3(CH_2)_7OOC(CH_2)_5CH_3.$$

THE GERANYL ESTERS.

The esters belonging to the geraniol series of alcohols are absolutely indispensable in the manufacture of artificial perfumes. When it is remembered that these esters are present in such oils as bergamot, rose, geranium, lavender, petit-grain. neroli, and numerous other sweet-smelling essential oils, it will readily be seen how useful they are in building up similar perfumes artificially.

Geranyl Formate.—The lowest of the fatty acids, formic acid, forms an ester with geraniol, having the constitution $C_{10}H_{17} . OOC . H$. It has not, apparently, been found in nature, but it is manufactured by allowing anhydrous formic acid to react with geraniol in the presence of a little mineral acid to act as a condensing agent. It is an ester of a sweet rose-geranium type, boiling at 113° to 114° at 15 mm. It is not possible to manufacture it quite pure on a commercial scale, and the best samples to be met with contain about 92 per cent. of true ester. Such samples have a specific gravity between 0·924 and 0·926 at 15°, are optically inactive, have a refractive index 1·4640 to 1·4660, and are soluble in 10 volumes of 70 per cent. alcohol. To decide on the quality of a given sample, these characters should be determined and a saponification performed quantitatively. At least 90 per cent. of geranyl formate should be indicated. The geraniol obtained in the saponification process should be separated, washed with water, and examined. It should have the general characters given under the alcohol geraniol above.

Geranyl Acetate.—The acetic ester of geraniol having the formula $C_{10}H_{17} . OOC . CH_3$ is probably the most largely employed of the series. It is found naturally in palmarosa oil, lemon-grass oil, sassafras leaf oil, geranium oil, petit-grain oil, neroli oil, coriander oil, lavender oil, and numerous others. It is best prepared artificially by the action of acetic anhydride on geraniol in the presence of anhydrous sodium acetate, which assists the reaction materially. Geranyl acetate has an exceedingly sweet odour of great fragrance. Its delicate and distinctive perfume makes it invaluable for the preparation of the various rose odours, and it is also very useful in the perfumes of the ylang-ylang and orange flower type. In its pure state it has the following characters:—

Specific gravity	0·9388 at 0°, or 0·9174 at 15°
Boiling-point at 14·5 mm. . . .	130° to 130·5°
,, ,, ,, 760 ,, . . .	242° ,, 245°
Refractive index	1·4628 at 15°

In the manufacture of geranyl acetate on a commercial scale it would not pay to make it absolutely pure, so that samples as met with in the ordinary way are not quite pure geranyl acetate. The acetylisation process, by which esters are made, is not always a quantitative one, and in some cases it is impossible to acetylate an alcohol to its full theoretical extent. Commercial samples, however, contain 95 per cent. or more of true ester, and should have the following characters :—

Specific gravity at 15°	0·910 to 0·918
Optical activity	0°
Refractive index	1·4617 to 1·4662

it should be soluble in 7 to 10 volumes of 70 per cent. alcohol; it should contain at least 95 per cent. of true ester.

Geranyl Butyrate.—This ester of the formula $C_{10}H_{17} . OOC(CH_2)_2CH_3$ is an oil having a fine rose odour, distinct from the esters of the lower fatty acids, and is largely employed in perfuming soaps, and in compounding artificial otto of rose. It can be prepared by heating geraniol with butyryl chloride in the presence of anhydrous pyridine, and is an oil boiling at 142° to 143° at 13 mm. pressure.

Geranyl Isobutyrate.—This ester is isomeric with the last described, and is quite similar in character, but with a slightly different odour. Its formula is $C_{10}H_{17} . OOC(CH)(CH_3)_2$, and it is an oil which boils at 135° to 137° at 13 mm. pressure.

Geranyl Isovalerianate.—This ester has the constitution

$$C_{10}H_{17}O_2C(CH_2)(CH)(CH_3)_2.$$

The rose odour is still further modified by the presence of the five carbon acid radicle, and judicious blending of the various geranyl esters is capable of giving numerous characteristic bouquets to the various rose odours. This ester boils at 135° to 138° at 10 mm. pressure.

LINALYL ESTERS.

Linalyl Formate.—The formic acid ester of linalol, $C_{10}H_{17}OOCH_3$, has a distinctive odour somewhat resembling that of the acetate. It is an oil boiling at 189° to 192°, and is prepared by treating linalol with formic acid, but the reaction is not complete and commercial samples are never pure esters.

Linalyl Acetate.—Linalyl acetate is an ester of extreme value in the reproduction of bergamot and lavender odours, since the natural ester is the characteristic odour bearer of the former, and to a large extent of the latter. It also occurs in ylang-ylang oil, petit-grain oil, neroli oil, jasmin oil, gardenia oil, and many others. As the alcohol linalol is very susceptible to alteration under the influence of heat or chemicals, it is not practicable to prepare anything like pure linalyl acetate by the usual process of acetylation. Tiemann has prepared it in a pure condition by the interaction of linalol sodium and acetic anhydride. Linalyl acetate is a colourless oil, with a very characteristic odour of bergamot, and is optically active in the same sense as the linalol from which it has been prepared. It has the formula $C_{10}H_{17}OOC . CH_3$, and when pure boils at 96·5° to 97° at a pressure of 10 mm., or 115° to 116° at 25 mm. pressure. At atmospheric pressure it boils at about 220° with decomposition. Its specific gravity is 0·913 and optical rotation about + 6° or − 6°. The preparation yielding these figures contained 97·6 per cent.

of true linalyl acetate. Commercial specimens of the best make have the following characters:—

Specific gravity	0·902 to 0·912
Refractive index at 20°	1·4500 ,, 1·4550
Ester value	88 to 95 per cent.

This ester is indispensable in the reproduction of numerous flower oils in addition, of course, to artificial bergamot oil.

Linalyl Propionate.—This ester is also produced by condensing the free alcohol and the free acid by means of sulphuric acid. It has a somewhat fruity odour recalling that of bergamot, and is especially suitable for perfumes of the lily of the valley type. It is a colourless oil, boiling at 115° at 10 mm. pressure.

Linalyl Butyrate.—The butyric ester of linalol has the formula, $C_{10}H_{17}OOC . CH_2 . CH_2CH_3$. It resembles geranyl butyrate in odour, but is somewhat heavier. It is most useful for imparting fruity odours to flower perfumes. It is prepared by condensing the alcohol and the acid by means of sulphuric acid.

BENZYL ESTERS.

Benzyl Acetate.—This ester is a constituent of the oils of jasmin, ylang-ylang, and similar flower oils. It has not a very intense odour, but is essential to the successful production of such perfumes as artificial jasmin. It has the formula $C_6H_5 . CH_2 . O . OCCH_3$. It is a colourless oil, boiling at 206° at ordinary pressure, and has a specific gravity 1·0570 at 16° and a refractive index 1·5034. The propionic ester has the formula $C_6H_5CH_2OOCCH_2CH_3$, and closely resembles the acetate in odour.

Benzyl Benzoate.—This ester is a constituent of balsam of Peru, and also occurs in tuberose and ylang-ylang oils. It is prepared on a very large scale, as it has the extra virtue of being one of the best fixers of odours, and a remarkably good solvent for artificial musk, so that it serves a triple purpose of imparting its own delicate odour to the blend, of acting as a vehicle for the otherwise poorly soluble musk, and acting as a good fixer. A method of preparing it in an almost pure condition is to dissolve sodium in benzyl alcohol and then add benzoic aldehyde, and then heat for a day in a water-bath. The mixture is then acidified with acetic acid and the benzyl benzoate precipitated with water. It forms a colourless oil, which, when free from chlorine, does not darken, having a slight, but sweet, odour. It is, when absolutely pure, a solid, melting at 21°, and boiling at 323° to 324°, and having a refractive index 1·5681 at 21°, and a specific gravity 1·1224. The best commercial samples are liquid at the ordinary temperature, and have the following characters:—

Specific gravity	1·1200 to 1·1220
Boiling-point at 760°.	about 310° to 320°
Refractive index	1·567 to 1·5685

If cooled to a very low temperature crystallisation will take place, and the ester then melts at 20° to 21°.[1]

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[1] According to Ellis, the melting-point is 19·5°. The specimen was partially melted and the liquid poured off three times, and the product was twice recrystallised from ether. (*Private communication from the laboratories of Messrs. A. Boake, Roberts, & Co., Ltd.*).

Benzyl Cinnamate.—The cinnamic acid ester of benzyl alcohol is a natural constituent of storax, tolu, and Peru balsams. It is a crystalline substance with a characteristic sweet balsamic odour. It may be prepared by heating sodium cinnamate, alcohol, and benzyl chloride together under a reflux condenser. It is a useful ester where a sweet balsamic odour is required to be introduced into a perfume, especially of the heavy type. It forms white, glistening prisms, which melt at 39°, and decompose when heated to 350°. The best commercial specimens have the following characters:—

Melting-point	31° to 33·5°
Boiling-point at 5 mm.	195° ,, 200°

or under atmospheric pressure at 335° to 340° with decomposition; ester value, 96 to 98 per cent.; it is soluble in 1 volume of 95 per cent. alcohol.

BORNYL ESTERS.

Bornyl Formate.—This ester occurs naturally. It can be prepared synthetically by the action of anhydrous formic acid on borneol in the presence of a small amount of a mineral acid. It has a fragrant odour, and is useful in blending with borneol itself. Its optical rotation depends on that of the borneol from which it has been prepared. Dextro-rotatory bornyl formate has, in the purest state in which it has been prepared, the following characters:—

Boiling-point	225° to 230°
,, ,, at 15 mm. pressure	98° ,, 99°
Specific gravity	1·0170
Optical rotation	+ 48° 45′
Refractive index	1·47078

The purest laevo-bornyl formate examined had a specific gravity 1·016, optical rotation − 48° 56′, refractive index 1·47121, and boiling-point 97° at 15 mm. pressure. The ester has the constitution

$$C_{10}H_{17}.OOCH.$$

Bornyl Acetate.—The acetic acid ester is the most important of the series. It is a constituent of pine-needle and rosemary oils, and has a most fragrant and refreshing odour. It is prepared artificially by the action of acetic anhydride on borneol, in the presence of sodium acetate, or by the condensation of borneol with glacial acetic acid in the presence of a small amount of a mineral acid. It is absolutely necessary in the reproduction of any pine odour. It is a crystalline body, crystallising from petroleum ether in rhombic hemihedric crystals melting at 29°. The optical activity depends on that of the borneol from which it has been prepared. It has the following characters:—

Specific gravity	0·991
Optical rotation	+ or − about 40°
Refractive index	1·4650 to 1·4665
Boiling-point at 10 mm. pressure	about 98°
Melting-point	29°

It is soluble in 3 volumes of 70 per cent. alcohol. The commercial product is usually a mixture of dextro-rotatory and laevo-rotatory bornyl acetate. It should contain not less than 98 per cent. of ester, and should have a specific gravity from 0·988 to 0·992; and it should melt at about 29°. Bornyl acetate has the constitution $C_{10}H_{17}OOC.CH_3$. It can be kept for a long time in a state of superfusion when it has once been liquefied.

Bornyl Butyrate.—The next higher ester of borneol is the butyrate. It is a similar camphoraceous ester, having the formula

$$C_{10}H_{17}OOC.CH_2CH_2CH_3$$

and the following characters:—

Boiling-point at 10 mm. pressure	120° to 121°
Optical rotation	+ 22°
Specific gravity	0·966
Refractive index	1·4638

It usually contains 98 to 99 per cent. of true ester.

Bornyl Isovalerianate.—This is the highest ester of borneol met with in commerce. It has the composition $C_{10}H_{17}OOC.CH_2.CH:(CH_3)_2$. It occurs naturally in several essential oils, and is prepared artificially by esterifying borneol with anhydrous isovalerianic acid. It is a colourless oil, boiling at 255° to 260°, and has a specific gravity of 0·956. It is an ester, like terpinyl acetate, that requires two hours' saponification, and it also requires a large excess of alkali. Good commercial specimens have the following characters:—

Specific gravity	0·953 to 0·956
Optical rotation	about − 35°
Refractive index	1·4620 to 1·4635
Boiling-point at 10 mm. pressure	128° ,, 130°

It has a strong camphoraceous odour.

Bornyl Propionate.—The propionic acid ester of borneol closely resembles the acetic ester, but as is, of course, usual in homologous series, its odour is slightly different. It has the formula

$$C_{10}H_{17}OOC.CH_2CH_3,$$

and has the following characters:—

Specific gravity	0·979
Optical rotation	+ or − about 25°
Boiling-point at 10 mm. pressure	109° to 110°
Refractive index	1·46435

It usually contains 95 to 97 per cent. of true ester.

Citronellyl Esters.

Citronellyl Formate.—Citronellyl formate, $C_{10}H_{19}O.OCH$, is an artificial ester resulting from the action of concentrated formic acid on citronellol. It is an easily decomposed ester which is, on a commercial scale, rarely produced of more than 90 to 93 per cent. strength. Such commercial specimens have the following characters:—

Specific gravity	0·910 to 0·912
Optical rotation	− 1° to − 1° 30'
Refractive index	1·4507 to 1·4515
Boiling-point	about 100° at 10 mm.
True ester	90 to 93 per cent.

Citronellyl Acetate.—The odour of the acetic ester of citronellol recalls to some extent that of bergamot. It is a natural constituent of geranium oil, and is useful in small amounts for blending with rose and geranium odours. It is prepared by the action of acetic anhydride on citronellol. When pure it has the following characters :—

Specific gravity	0·8928
Optical rotation	about + 2° 30′ to − 2° 30′
Refractive index	1·4456
Boiling-point at 15 mm. pressure	119° to 121°

The best commercial samples vary in their characters within very narrow limits, which should be as follows :—

Specific gravity	0·894 to 0·902
Optical rotation	− 2° ,, + 2°
Refractive index	1·4465 ,, 1·4490

The odour of the ester varies slightly, according as it is made from the dextro-rotatory or the laevo-rotatory variety of the alcohol. That of the former is rather fuller and deeper in its rose odour than that of the latter. Both esters blend excellently with the corresponding citronellols, and are very useful in preparing synthetic otto of rose. The formula of this ester is $C_{10}H_{19}OOC.CH_3$.

CINNAMYL ESTERS.

Cinnamyl Propionate.—The propionic acid ester has a distinct grape-like odour, and is very useful for fruit and flower blends. It has the constitution $C_6H_5.CH:CH.CH_2OOC.CH_2.CH_3$.

Cinnamyl Butyrate.—This ester has the formula

$$C_6H_5.CH:CH.CH_2OOC(CH_2)_2CH_3.$$

It has a characteristic fruity odour, and is most useful for imparting a fruity bouquet to a flower perfume, but must be used in small quantities.

Cinnamyl Cinnamate.—This ester is known as styracin, and is found in storax and other balsamic products, and possibly also in oil of hyacinths. It has the constitution

$$C_6H_5.CH:CH.COOCH_2CH:CH.C_6H_5.$$

It has an odour resembling that of benzyl cinnamate. It forms crystals melting at 44°. It yields a characteristic dibromide, melting at 151°, which serves to characterise this ester.

HOMOLINALOL ESTER.

Homolinalyl Acetate.—This body has the constitution $C_{11}H_{19}OOCCH_3$, and is prepared by the action of homolinalol-sodium on acetyl chloride, or by the action of acetic anhydride on homolinalol. It is an oil with a marked bergamot odour, similar to that of linalyl acetate, but not identical with it. It boils at 111° to 117° at 15 mm.

TERPINYL ESTERS.

Terpinyl Formate.—The formic acid ester of terpineol, $C_{10}H_{17}OOCH$, occurs naturally in Ceylon cardamom oil. It is prepared artificially by the action of formic acid on terpineol, but on a commercial scale is prepared most economically by the action, for a week, of anhydrous formic acid on turpentine oil. It has a fragrant odour, resembling, but superior to, that of geranyl formate. It has the following characters:—

Specific gravity	0·998
Boiling-point	135° to 138° at 40 mm.
Specific rotation	+ or − 69°

Terpinyl Acetate.—The acetic acid ester of terpineol is also a natural ester. It has a refreshing odour, and is often described as being a bergamot and lavender substitute. The writer, however, considers this description unjustifiable, and that it is really due to the fact that it is so often used and recommended as an adulterant for these two essential oils. Terpinyl acetate is a colourless oil, of the formula

$$C_{10}H_{17}OOC . CH_3,$$

and can be prepared by various methods. If terpineol be heated with acetic anhydride and sodium acetate it is largely converted into terpinyl acetate, but the yield never exceeds about 84 per cent. It can be obtained by heating pinene with excess of acetic acid for sixty-four hours. It is either dextro- or laevo-rotatory or inactive. A sample prepared by heating limonene with acetic acid gave the following values:—

Specific gravity	0·9828
Optical rotation	+ 52° 30'
Boiling-point at 40 mm. pressure	140°

The best commercial samples are optically inactive, and have the following characters:—

Specific gravity	0·955 to 0·965
Optical rotation	practically nil
Refractive index	1·4648 to 1·4660
Ester content	86 to 92 per cent.

It is soluble in about 5 volumes of 70 per cent. alcohol. This ester has the character of being saponified much more slowly than most other esters, so that in any determination in which it is involved it is necessary to saponify the sample for two hours before it is safe to consider the reaction complete. This fact also assists in determining whether terpinyl acetate is present as an adulterant in natural essential oils, for if the saponification value as determined by thirty minutes' saponification is materially lower than that as determined by a two hours' saponification, it may be fairly safely inferred that terpinyl acetate or some similar ester is present.

Terpinyl Propionate.—This ester, which has the formula

$$C_{10}H_{17}OOC . CH_2 . CH_3,$$

is regarded as an excellent lavender substitute—that is, for use in conjunction with other bodies. By many perfumers it is regarded as the best lavender odour existing amongst synthetic perfumes. It is a colourless oil of sweet and fragrant odour, and is very lasting in its effects.

Terpinyl Cinnamate.—Cinnamic acid forms an ester with terpineol, which has an indescribable odour, but which is exceedingly sweet. It is a useful oil to blend with lilac and similar odours. It is a heavy oil of the constitution $C_{10}H_{17}OOC . CH : CH . C_6H_5$.

PHENYL-ETHYL ESTERS.

Phenyl-ethyl Acetate.—Phenyl-ethyl alcohol yields a series of highly aromatic esters. That of acetic acid has the formula

$$C_6H_5 . C_2H_4 . OOC . CH_3.$$

Its odour is usually described as such as to give fine "leaf" effects if used properly. It is a liquid boiling at 232°, of specific gravity 1·038.

Phenyl-ethyl Propionate.—The propionic ester of phenyl-ethyl alcohol has the formula $C_6H_5 . C_2H_4 . OOC . CH_2CH_3$. It has a pronounced rose odour, differing slightly from that of the acetic ester. It is very useful in blending rose odours.

VARIOUS ESTERS.

Phenyl-propyl Cinnamate.—This ester occurs in storax, and has a perfume resembling that balsamic substance. It has the formula

$$C_6H_5CH_2 . CH_2CH_2OOC . CH : CH . C_6H_5.$$

It is a powerful fixative as well as being useful on account of its rich, heavy odour.

Pinenyl Acetate.—By passing nitrous fumes into well-cooled pinene and steam-distilling the reaction product, an alcohol, pinenol, is obtained. It has the formula $C_{10}H_{15}OH$. It can be acetylated, and the resulting acetate has the formula $C_{10}H_{15}—OOCCH_3$. It has an odour resembling that of lavender oil. It boils at 150° at a pressure of 40 mm.

Pinoglycyl Acetate.—This ester can be prepared by the direct acetylation of pinoglycol, $C_{10}H_{16}O(OH)_2$, an alcohol resulting from the oxidation of pinol with permanganate of potassium. It can also be prepared from pinol dibromide and acetate of silver. It is an ester with an excellent fruity odour, of the formula $C_{10}H_{16}O(C_2H_3O_2)_2$, melting at 97° to 98°, and boiling at 155° at 20 mm. pressure, or at 127° at 13 mm.

Pinolglycyl Propionate.—This ester, of the formula $C_{10}H_{16}O(C_3H_5O_2)_2$, is a quite similar ester, prepared in a similar manner. It also has a fine fruity odour.

Styrolyl Acetate.—Styrolene alcohol, or phenyl-ethyl glycol, is an alcohol prepared from styrolene dibromide by the action of caustic potash. It can be esterified, and forms an acetic ester of the formula $C_6H_5 . CH(OH)CH_2 . OOC . CH_3$. It is an ester with a fine flower odour, which has been described as "fragrant and dreamy". It is generally stated by those who have used it that it is indispensable in the preparation of fine flower bouquets with a jasmin odour.

Styrolyl Propionate.—This body, having the formula

$$C_6H_5CH(OH)CH_2OOC . CH_2CH_3,$$

is very similar to the acetate, and also has a fine flower odour which is very lasting and powerful.

Styrolyl Valerianate.—The valerianic ester of styrolol has the formula $C_6H_5CH(OH)CH_2OOC . CH_2 . CH(CH_3)_2$. It has a most powerful odour resembling jasmin and narcissus, and is very useful for the preparation of these odours. It is very powerful in odour, and care is required in its use, or the effects will be spoiled by a too powerful odour.

MENTHYL ESTERS.

Menthyl Acetate.—This ester, of the formula $CH_3 . CO . OC_{10}H_{19}$, is present in oil of peppermint, its odour being an important characteristic of that oil. It can be prepared by heating menthol with acetic anhydride and sodium acetate. Its characters are as follows:—

Boiling-point	227° to 228°
Specific gravity at $\frac{20^\circ}{0^\circ}$	0·925
„ „ „ 15°	0·9298
Optical rotation	− 73°
Refractive index	1·4468

Menthyl Isovalerianate.—This ester, having the formula

$$C_4H_9COO . C_{10}H_{19},$$

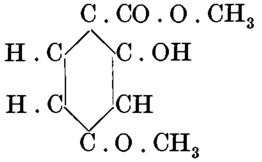
exists naturally in American oil of peppermint. It can be prepared artificially by boiling menthol with isovalerianic acid and sodium acetate. It is a very stable ester and requires a considerable excess of alkali, and at least two hours boiling, for complete saponification. It has the following characters:—

Specific gravity	0·907 to 0·908
Optical rotation	− 56° 30′
Refractive index	1·4485 to 1·4486

METHYL METHOXYRESORCYLATE AND METHYL METHOXYSALICYLATE.

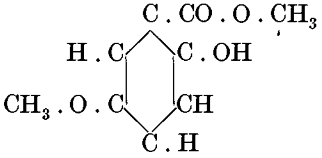
Two glucosides have been separated from the roots of *Primula officinalis* by Goris, Mascré, and Vischniac,[1] which have been termed primeverin and primulaverin, and which are both hydrolysed, yielding the two constituents of the essential oil.

Primaverin has the formula $C_{20}H_{28}O_{13}$ and melts at 206°, and on hydrolysis yields sugars and the methyl ester of β-methoxyresorcylic acid, of the formula



This is the solid constituent of the essential oil, melting at 49°. It has been described by Mutschler[2] as primula camphor.

Primulaverin, $C_{20}H_{28}O_{13}$, melts at 163°, and on hydrolysis yields the liquid portion of the essential oil, which is the methyl ester of *m*-methoxysalicylic acid, of the formula



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[1] Roure-Bertrand Fils, *Bulletin*, October, 1912, 3.

[2] *Annalen*, 185 (1877), 222.

5. ALDEHYDES.

A number of the aldehydes, both of the aliphatic and aromatic series, are of the highest importance in synthetic perfumery. The relationship existing between alcohols, aldehydes, and acids is shown by the following example:—

$CH_3 . CH_2OH$	$CH_3 . CO . H$	$CH_3CO . OH$
Ethyl alcohol	Ethyl aldehyde	Acetic acid

Generally speaking, aldehydes are prepared by the following method, *inter alia*: (1) Oxidation of primary alcohols, (2) by the dry distillation of a mixture of the calcium or barium salts of two monobasic fatty acids. For the approximate determination of aldehydes, an absorption process of shaking with a solution of either neutral or acid sulphite of sodium is most generally used. Five or 10 c.c. of the oil to be examined are shaken in a flask holding about 150 c.c. with about 100 c.c. of 30 per cent. solution of sodium bisulphite, the flask being kept in a water-bath for one to three hours as may be necessary. The agitation is repeated frequently, and when absorption is complete, the oil is driven up into the graduated neck of the flask by adding more of the bisulphite solution, and the unabsorbed oil can be measured, the remainder representing the aldehyde (or ketone). The aldehyde citral in small quantities is better determined by means of hydroxylamine. The determination of aldehydes will be dealt with in a subsequent chapter. The following are the principal synthetic or isolated aldehydes which will require description: (1) The aldehydes of the fatty series. (2) The aldehydes of the geraniol series. (3) The aldehydes of the aromatic series. The use of the higher aldehydes of the fatty series has during the past year or two become a matter of some importance to the synthetic perfumer. These aldehydes possess intensely powerful odours, and must be used in very minute quantities or they will spoil any perfume in which they are used.

The following[1] are the general methods by which the higher fatty aldehydes may be produced.

1. The corresponding alcohol may be oxidised:—

$$R . CH_2OH + O_2 = R . CHO . + H_2O.$$

2. The barium or calcium salt of the corresponding acid may be distilled with barium formate:—

$$(R . COO)_2Ba + (H . COO)_2Ba = 2BaCO_3 + 2R . CHO.$$

Schimmel & Co.[2] have prepared a number of fatty aldehydes by a modification of this reaction. They distilled mixtures of barium formate with the barium salt of the corresponding acid, in a vacuum, as it was well known that this increases the yield when working with the higher aldehydes, which volatilise with difficulty.

3. Darzens[3] claims a method in which a ketone is condensed with chloracetic-ether in the presence of an alkaline condensing agent. For example, acetone reacts with chloracetic-ether as follows:—

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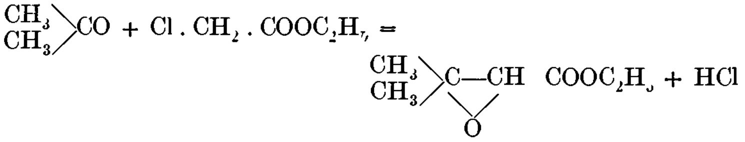
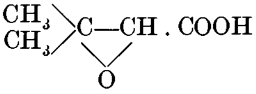
[1] Radcliffe, *P. and E.O.R.*, **1917**, 65.

[2] *D.R.P.*, 126, 736 of 1902.

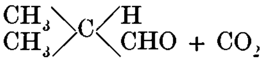
[3] *Ibid.*, 174, 239, and 174, 279.



The resulting product is then hydrolysed, giving—



and, finally, this compound on heating evolves carbon dioxide and undergoes a slight molecular change, yielding a butyric aldehyde of the formula —



$$\frac{CH_3}{CH_3}>C<\frac{H}{CHO} + CO_2$$

4. Aldehydes are also formed by the action of nascent hydrogen (sodium amalgam) upon the chlorides of acid radicles or their oxides (the acid anhydrides) —

(1) $CH_3COCl + 2H = CH_3 \, CHO + HCl$
(2) $(CH_3 . CO)_2O + 4H = 2CH_3 \, CHO + H_2O$

5. Aldehydes are formed by the reduction of the ester of the corresponding acid to the alcohol, and then oxidising the alcohol with heated copper as catalyst It is well known that when primary alcohols in the gaseous state are passed over finely-divided copper dust, obtained by reduction of copper oxide, at 250° to 400°, they yield hydrogen, and aldehydes or ketones respectively.

Aldehydes are usually most easily separated from the essential oils in which they occur, by means of acid sodium sulphite. The oil—or the suitable fraction thereof—is well shaken for a time varying according to the nature of the aldehyde, with an equal volume of a saturated solution of sodium bisulphite, with a little ether added, in order to hinder the non-aldehydic portion of the oil from becoming occluded in the crystals of the bisulphite compound of the aldehyde. These crystals are separated and washed well with ether They are then decomposed by warming with a solution of sodium carbonate, and the regenerated aldehyde is extracted by means of ether.

Neuberg and Tiemann[1] propose the following method, depending on the fact that most aldehydes form a compound with thiosemi-carbazide. The oil containing aldehyde is heated in alcoholic solution on a water-bath, with thiosemi-carbazide. Various salts of the heavy metals will form insoluble precipitates with the thiosemi-carbazone formed, and such precipitate is dissolved in alcohol, and a current of hydrogen sulphide passed through until the metal is precipitated, leaving the thiosemi-carbazone dissolved in the alcohol.

The following are the most effective compounds to prepare for the identification of an aldehyde.

Semi-carbazones.—Most aldehydes react with semi-carbazide, forming

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[1] *Berichte* (1902), xxxv., 2049.

condensation products known as semi carbazones, which are usually of a well-defined crystalline character with a sharp melting-point the reaction taking place is as follows —

$$R.CHO + NH_2\ NH\ CO.NH_2 = R.CH:N\ NH\ CO\ NH_2 + H_2O.$$

Aldehyde *Semi carbazide* *Semi-carbazone*

They are usually best obtained by dissolving the aldehyde in alcohol, and adding excess of an equimolecular mixture of semi carbazide hydrochloride, and acetate of sodium. The mixture is allowed to stand for some time and the semi-carbazone then precipitated by the addition of water. Some semi-carbazones are more easily prepared by substituting free acetic acid (glacial) for the acetate of sodium Semi-carbazones are best recrystallised from hot methyl alcohol

Oximes —Most aldehydes yield a condensation product with hydroxylamine, according to the equation —

$$R\ CHO + NH_2.OH = R\ CH\ NOH + H_2O.$$

Aldehyde *Hydroxylamine.* *Oxime*

To obtain the oximes, equimolecular quantities of the aldehyde and hydroxylamine are heated in alcoholic solution on the water-bath for thirty to sixty minutes The hydroxylamine is best added in the form of hydroxylamine hydrochloride, and the necessary amount of alcoholic solution of potash added to liberate the hydroxylamine. Most, but not all, the oximes are crystalline.

Phenylhydrazones —Nearly all aldehydes form condensation products with phenylhydrazine, known as phenylhydrazones, according to the following equation —

$$R\ CHO + NH_2\ NH\ C_6H_5 = R.CH\ N\ NH\ C_6H_5 + H_2O.$$

Aldehyde. *Phenylhydrazine* *Phenylhydrazone*

They are best prepared by heating the aldehyde in alcoholic solution, on the water-bath, under a reflux condenser, with slightly more than the equimolecular quantity of phenylhydrazine hydrochloride, with acetate of sodium added Thirty to sixty minutes is usually sufficient for the reaction.

Pyruvic Acid Compounds —Lubrzynska and Smedley[1] have recently shown that a number of aldehydes such as heliotropin, anisic aldehyde, benzaldehyde, and cinnamic aldehyde, condense with pyruvic acid in slightly alkaline solution, with the formation of β-unsaturated-α-ketonic acids For example, if heliotropin and pyruvic acid in alkaline solution be left standing for about eight days at ordinary temperature, dihydroxymethylene-benzal-pyruvic acid is formed This body forms yellow needles, melting at 163° Similarly anisic aldehyde yields methoxybenzal-pyruvic acid, melting at 130°, and cinnamic aldehyde yields cinnamal-pyruvic acid, melting at 73°

Doebner[2] showed that certain aldehydes, citral, for example, form condensation products with pyruvic acid and β-naphthylamine, known as naphthocinchoninic acids The reaction takes place as follows —

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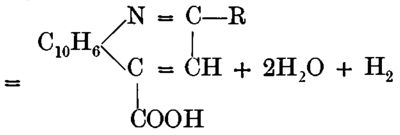
[1] *Chem. Zentral* (**1914**), 561.

[2] *Berichte*, **27** (1894), 354 and 2026

$$R.CHO + CH_3CO.COOH + C_{10}H_7NH_2$$

Aldehyde. Pyruvic acid β Naphthylamine



$$= C_{10}H_6\begin{cases} N = C—R \\ C = CH \end{cases} + 2H_2O + H_2$$

$$\phantom{C_{10}H_6}COOH$$

Naphthocinchoninic acid.

Schlogl[1] has shown that para-aminophenylglycine, para-aminophenyloxamic acid, and para-aminoacetanilide form compounds with aldehydes, which have sharp melting-points and are suitable for the characterisation of aldehydes With *p*-aminophenylglycine condensation takes place when the glycine, mixed with alcohol and the aldehyde in question, is warmed For the purpose of condensing with *p*-aminophenyloxamic acid and with *p*-aminoacetaldehyde the alcoholic suspension of the amino-body is acidulated slightly with hydrochloric acid and the solution is warmed after the aldehyde has been added This method yields the hydrochloride of the condensation products

Condensation Product		M p	Designation	
of	with			
Cinnamic aldehyde	*p* Aminophenylglycine	120°	Cinnamic aldehyde anilglycine	
Furfurol	,,	135°	Furfurol anilglycine .	
Benzaldehyde	*p* Aminophenyloxamic acid	180°	Benzaldehyde aniloxamic acid	Hydrochloride
Vanillin	,, ,,	170°	Vanillin aniloxamic acid .	
Cinnamic aldehyde	,, ,,	125°	Cinnamic aldehyde aniloxamic acid	
Furfurol	,, ,,	130°	Furfurol aniloxamic acid .	
Benzaldehyde	*p*-Aminoacetanilide	165°	Benzaldehyde acetaminoanile	
Vanillin	,,	208°	Vanillin acetaminonile . .	
Cinnamic aldehyde .	,,	195°	Cinnamic aldehyde acetaminoanile	

THE ALIPHATIC ALDEHYDES.

The following are the principal members of the fatty series of aldehydes which either occur in essential oils, or are used in synthetic perfumery —

Formic Aldehyde.—This aldehyde, H.CHO, is the lowest member of the aliphatic series It has been found, but rarely, in the distillation waters of a few essential oils It can be identified by evaporation on a water-bath with ammonia when crystals of hexamethylene-tetramine are formed

Acetic Aldehyde.—Acetic aldehyde, $CH_3.COH$, occurs in a number of essential oils or their distillation waters It is a liquid boiling at 21°.

Butyric Aldehyde.—This body, C_3H_7COH, has been found in the oils of *Eucalyptus globulus* and *Cajuput* It boils at 75° and forms a para-nitro-phenylhydrazone, melting at 91° to 92°

Isovalerianic Aldehyde.—This aldehyde, which has the constitution $CH_3.CH(CH_3).CH_2$ CHO, exists in American peppermint oil. I

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[1] *Jour. prakt. Chem.*, ii. **88** (1913), 251.

boils at 92·5°, and forms a thiosemi-carbazone, melting at 52° to 53°. Its specific gravity is 0·804.

Valerianic Aldehyde.—The normal valerianic aldehyde,

$$CH_3(CH_2)_3 . CHO,$$

is a liquid boiling at 102°, of specific gravity 0·816.

Hexylic Aldehyde—Hexylic or caproic aldehyde, $C_5H_{11}CHO$, has been identified in oil of *Eucalyptus globulus*. It is a liquid boiling at 128° at 740 mm., and having a specific gravity 0·837.

Heptylic Aldehyde.—This aldehyde, also known as oenanthylic aldehyde, is formed by distilling castor oil under reduced pressure. It is an oil of powerful fruity odour, boiling at 155°, or at 45° at 10 mm. pressure, and having a specific gravity 0·820, and refractive index 1·4150. It forms an oxime melting at 50°.

Octyl Aldehyde.—The eight-carbon aldehyde has the formula

$$CH_3(CH_2)_6CHO.$$

It is a natural constituent of neroli and rose oils. It is described as having a deep honey-like odour, and is useful in rounding off perfumes with a heavy odour. It is a liquid boiling at 82° at 13 mm., and has a specific gravity about 0·826, and refractive index 1·41955. If absolutely pure its specific gravity is only 0·821. It melts at − 13° to − 16°. It yields an oxime melting at 60°, a semi-carbazone melting at 101°, and a naphthocinchoninic acid compound melting at 234°.

Nonyl Aldehyde.—The nine-carbon aldehyde has the formula

$$CH_3(CH_2)_7CHO.$$

This aldehyde belongs to the rose and orange types of odour. It is present naturally in both these essential oils. It can be used successfully, in very small quantity, in all perfumes of the rose, geranium, orange, and neroli types. It is an oil having a specific gravity 0·8277, refractive index 1·4245, and boils at 92° at a pressure of 13 mm. Its melting-point is + 5° to + 7°. It yields an oxime melting at 69°, and a semi-carbazone melting at 100°, which serve to identify it.

Decyl Aldehyde.—This body, which has the formula $CH_3(CH_2)_8CHO$, is also a constituent of rose, orange, and other essential oils. It is most useful in minute quantities in reproducing the odours of orris, neroli, cassie flowers, rose, and orange. It is probably the most generally useful of the whole of this series of aldehydes. It is an oil boiling at 207° to 209° at 755 mm. pressure, and at 80° to 81° at 6 mm. The specific gravity is 0·828 and refractive index 1·42977. Its melting-point is +2° to + 5°. It yields a naphthocinchoninic acid compound, melting at 237°, an oxime melting at 69°, and a semi-carbazone melting at 102°. On oxidation it yields capric acid melting at 30° to 31°.

Undecylic Aldehyde.—This has recently been prepared, and is now being used in the blending of flower bouquets. It has the formula

$$CH_3(CH_2)_9CHO.$$

It melts at − 4°.

Duodecylic Aldehyde.—The twelve-carbon aldehyde, also known as lauric aldehyde, has the constitution $CH_3(CH_2)_{10}CHO$. It was originally introduced for blending with violet perfumes, but it is not very suitable for this purpose. It is, however, of considerable value in mixed flower perfumes and fancy bouquets. It is a solid body and rapidly oxidises to lauric acid, melting at 23° to 24° and boiling at 128° at 13 mm. It should therefore be kept in solution in alcohol. It yields a semi-carbazone melting at 102°.

Tredecyl Aldehyde.—This aldehyde has the constitution

$$CH_3(CH_2)_{11}CHO.$$

American perfumers go so far as to state that it has created quite a furore amongst progressive perfumers. It has no distinct flower perfume, and can be used to modify the odour of almost any combination. It is stated that it is so characteristic that nothing can replace it. It is very expensive, but must only be used in minute quantities.

Tetradecyl Aldehyde.—This is the highest of this series of aldehydes, and has the formula $CH_3(CH_2)_{12}CHO$. It resembles the thirteen-carbon aldehyde somewhat, and is very useful for blending in flower combinations.

Hexylenic Aldehyde.—This aldehyde, of the constitution

$$CH_3 . CH_2 . CH_2 . CH = CH . CHO,$$

is an unsaturated compound, and exists in a number of plants, for example in the leaves of the vine and strawberry. It forms a hydrazone melting at 167°.

Undecylenic Aldehyde.—This aldehyde is closely related to those just described, but belongs to the unsaturated series. It has the formula $CH_2 : CH(CH_2)_8CHO$. It is very similar to the aldehydes just described, and is used in exactly the same way, namely, for modifying the odour of flower combinations. It melts at + 5° to + 7° and boils at 118° at 13 mm.

Oleic Aldehyde.—Oleic aldehyde, $C_{17}H_{33} . CHO$, is found in oil of orris root. It has the following characters :—

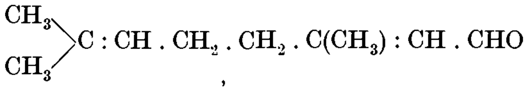
Boiling-point at 4 mm.	168° to 169°
Specific gravity	0·8513
Refractive index	1·4557

It forms a semi-carbazone melting at 87° to 89°.

The aldehydes of the geraniol series are of very great commercial importance. The only two which are of common occurrence are citral and citronellal.

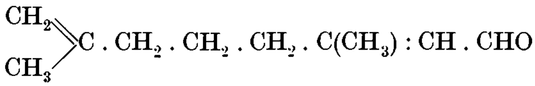
CITRAL AND NERAL.

Citral, or geranaldehyde, and neral or neraldehyde, are, as indicated under geraniol, the two stereoisomeric forms of the aldehydes derived from geraniol and nerol. Citral is best described as α-citral, and neral corresponds with β-citral. The constitution of the two aldehydes is either that indicated under geraniol, namely,



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C : CH . CH_2 . CH_2 . C(CH_3) : CH . CHO,$$

or



$$\begin{matrix} CH_2 \\ CH_3 \end{matrix}\!\!>C . CH_2 . CH_2 . CH_2 . C(CH_3) : CH . CHO$$

The former is the more probable constitution. Citral as found in commerce, is probably almost invariably a mixture of the two isomers, which are very similar in their general characters. It occurs to a considerable extent in various essential oils, being the principal constituent of lemon grass oil, and of the oil of *Backhousia citriodora*, and occurring to the extent of about 4 to 6 per cent in lemon oil, which owes its characteristic flavour to this aldehyde.

It can be obtained artificially by the oxidation of the alcohols geraniol, nerol, and linalol, by means of chromic acid. To prepare it from these sources, the following process may be used. Ten grams of potassium bichromate are dissolved in a mixture of 12.5 grams of sulphuric acid and 100 c.c. of water. To this mixture 15 grams of geraniol are gradually added, care being taken that the mixture is kept cold at first and then allowed to get warm, the whole being well shaken for about half an hour. It is then rendered slightly alkaline and a current of steam passed through it. To separate the citral from other products and from unchanged geraniol, the distillate is shaken with a saturated solution of sodium bisulphite and shaken from time to time, for about twenty four hours in the cold or for an hour or so at water bath temperature. In the cold, crystals of the compound of citral with bisulphite separate, which are dried, washed with ether, mixed with sodium carbonate and steam distilled, when citral passes over. By careful manipulation about 35 per cent of the theoretical amount is obtained.

Citral can also be obtained in a pure state by distilling a mixture of the calcium salt of geranic acid with calcium formate according to the usual method for the production of aldehydes.

Citral can also be obtained from essential oils such as lemon grass oil, by means of the bisulphite process, but care should be taken that the temperature be kept low, as otherwise a considerable loss occurs, due to the conversion of part of the citral into sulphonic acid compounds. Citral combines with 4 atoms of bromine and under the influence of dehydrating agents such as potassium hydrogen sulphate, yields cymene, $C_{10}H_{14}$. Under the influence of alkalis citral condenses with acetone, with the splitting off of water to form pseudo ionone, $C_{13}H_{20}O$, which is converted into isomeric ionones by means of acids. These bodies are the characteristic artificial violet perfume, which will be mentioned later. Reduction with sodium and alcohol produces the alcohol, geraniol. Various derivatives of citral have been prepared such as the oxime, anilide and phenylhydrazone, which are oily liquids, and the semicarbazone, which appears to exist in several isomeric forms of different melting-points. Most characteristic, however is the citryl-β-naphthocinchoninic acid, discovered by Doebner. This can be prepared by warming together in alcoholic solution 20 parts of citral, 20 parts of β-naphthylamine, and 12 parts of pyruvic acid. This acid, $C_{23}H_{23}NO_2$, melts sharply at 197° and is the most useful compound for characterising citral. Indeed Doebner has applied its preparation to the quantitative estimation of citral in oils containing it. The determination of this body in essential oils is by no means an easy matter, and will be mentioned later. A study of citral and its derivatives has caused the most recent investigators to assign one or other of the formulæ given on p. 53 to the stereoisomeric varieties of citral.

According to Tiemann the following are the characters of α-citral and β-citral, but as these were determined before the exact relationships of geraniol and nerol and the stereoisomeric aldehydes were as well understood as they now are, they must be accepted with some reserve.

α-Citral.

Boiling-point at 20 mm.	118° to 119°
Specific gravity at 20°	0·8898
Refractive index	1·4891

β Citral.

Boiling-point at 20 mm.	117° to 118°
Specific gravity at 20°	0·8888
Refractive index	1·49001

The purest specimens which have been prepared of natural citral, either from lemon-grass oil, lemon oil, or the oil of *Tetranthera citrata*, have the following characters:—

Specific gravity	0·892 to 0·8955 at 15°
Optical rotation	± 0°
Refractive index	1·4880 to 1·4900
Boiling-point at 12 mm.	110° ,, 112°
,, ,, 760 ,,	228° ,, 229°

Several years ago Tiemann[1] carried out a great deal of work on the chemistry of citral, in connection with which the following points are especially noteworthy. He has shown that in addition to the normal bisulphite of sodium compound of citral, three hydrosulphonic acid derivatives are formed, according to the conditions under which the experiment is performed (acidity, alkalinity, temperature, etc.). He considered that the explanation of the existence of two well-defined isomeric semi-carbazones (melting at 164° and 171°) was the existence of two stereoisomeric forms of citral in lemon-grass oil. To support this, he mixed the normal bisulphite compound with water and added sodium carbonate. The liquid was then shaken with ether, and about half the citral set free and dissolved in the ether (fraction *a*); the remainder was set free by the addition of caustic alkali and extracted with ether (fraction *b*). Whilst both fractions have exactly the same physical properties, it is found that fraction *a* gives only one semi-carbazone, melting at 164°, whilst fraction *b* gives both, melting at 164° and 171° respectively. The same was found to be the case with the cyanacetic compound fraction *a* yielding only one citralidene cyanacetic acid, melting at 122°, whilst fraction *b* gave this, and also one melting at 80°, which is now known to be impure, the pure compound melting at 94° to 95°. This view has been confirmed by the discovery of the alcohol nerol, as mentioned above (and see also under ionone).

Further important work on the pure chemistry of citral by Semmler and by Skita has been published during the past few years. Semmler has shown[2] that aldehydes which possess one or more labile hydrogen atoms adjoining the CHO group, possess the property of forming enolic acetates, that is, acetates in which a double bond has migrated into the conjugated position. He draws the following general conclusions in regard to this property of this type of aldehyde:—

1. All the aldehydes hitherto studied, which contain next to the functional aldehydic group one or more *labile* hydrogen atoms are cap-

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[1] *Berichte*, **42** (1909), 1161, 2014; **44** (1911), 991.

[2] *Ibid.*, xxxi. 3278, 3324; xxxii. 107.

able of reacting with the organic anhydrides and acids in their enolic forms giving unsaturated esters.

2. These unsaturated esters, by oxidation, permit of the elimination of the CHO group and the preparation of aldehydes or acids with fewer carbon atoms.

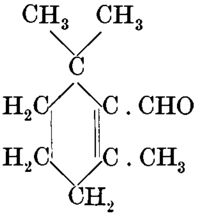
3. This reaction shows that the estimation of alcohols in essential oils containing aldehydes may lead to numbers which are too high.

4. The enolic esters, on saponification, regenerate the aldehydes. With sodium and alcohol, the saturated alcohol corresponding to the aldehyde is obtained.

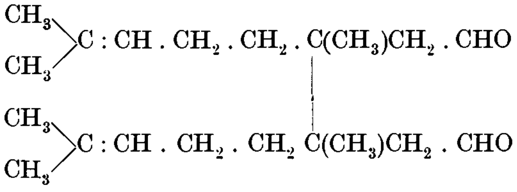
This migration has been described under geraniol (p. 17).

Enklaar[1] has shown that when citral is reduced by metals in a stream of hydrogen, it yields not only reduced aliphatic compounds, but that the ring is also closed, and a series of cyclic compounds is also formed.

Cyclo-citral thus formed appears to have the following constitution :—



According to Skita, the reaction proceeds in a different manner if the reduction be effected with palladium chloride and hydrogen. In this case the citral in alcoholic solution is mixed with an aqueous solution of palladium chloride and the whole thickened with gum-arabic. Hydrogen gas is then forced into this solution under pressure. The products of the reduction include citronellal and citronellol and a dimolecular aldehyde, $C_{20}H_{34}O_2$, which probably has the following constitution :—



$$\begin{array}{l} (CH_3)_2 > C : CH . CH_2 . CH_2 . C(CH_3)CH_2 . CHO \\ \qquad\qquad\qquad\qquad\qquad\qquad | \\ (CH_3)_2 > C : CH . CH_2 . CH_2\ C(CH_3)CH_2 . CHO \end{array}$$

Schossberger has recently isolated the isomeric form of citral which is known as isocitral, corresponding to the isogeraniol resulting from enolised citral acetate.

Isocitral is left as a residue when reduced enolised citral is freed from isogeraniol by means of phthalic anhydride, and has the following characters :—

Specific gravity at 20°	0·8976
Refractive index	1·4810
Boiling-point at 15 mm.	103° to 108°

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[1] *Chem. Weekblad*, 4 (1907), 322.

It yields a β-naphthocinchoninic acid compound melting at 206°.

Citral is used on a very large scale for the manufacture of ionone, the base of the artificial violet perfumes (*q.v.*)

The identification of citral is a matter of considerable importance, and may be effected by the preparation of several well-defined crystalline derivatives.

The semi-carbazones, $C_{10}H_{16} : N . NH . CO . NH_2$, are well defined. That of α-citral melts at 164° and that of β-citral at 171°, a mixture of the two in equal amounts melting at 135°. If it is desired to obtain mainly the semi-carbazone of α-citral, 5 parts of citral should be dissolved in 30 parts of glacial acetic acid. Four parts of semi-carbazide hydrochloride are dissolved in a little water and added to the citral solution. After standing for a short time, a considerable quantity of crystals separate in fine needles. These are recrystallised several times from methyl alcohol, when 60 to 70 per cent. of the theoretical yield can be obtained of the α-citral semi-carbazone, melting at 164°. The mother liquors yield β-citral semi-carbazone, melting at 171°. If the reaction be allowed to take place in a neutral, instead of an acid, solution, about 10 per cent. of β-citral semi-carbazone can be obtained, leaving a mixture of the two isomers, melting at 135° as the main yield. The isomeric semi-carbazones may be separated in the following manner: The dry mixture of semi-carbazones is finely powdered, and repeatedly exhausted with boiling ether. The liquid is filtered and deposits crystals melting at 135°. The ethereal mother liquor on concentration yields only the same product, but the insoluble residue has a higher melting-point and can be washed with ether until this rises to 160°. This product can now be recrystallised from alcohol, when the pure β-citral semi-carbazone melting at 171° is obtained, the alcoholic mother liquors yielding the α-citral compound, which on a second recrystallisation is obtained pure, melting at 164°.

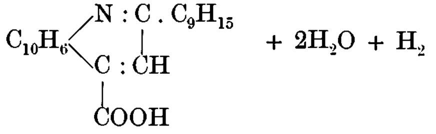
In order to resolve the mixture melting at 135°, it should be dissolved in cold acetic ether to saturation, and allowed to stand so that the solvent evaporates very slowly. Two distinctly different forms of crystals separate which can be picked out and recrystallised separately, when the two semi-carbazones are obtained in a state of purity.

Very characteristic of citral is the compound which it forms with β-naphthocinchoninic acid. It is obtained in the following manner: Twenty grams of citral and 20 grams of pyruvic acid are dissolved in absolute alcohol, and 20 grams of β-naphthylamine are added. The whole is heated for three hours on the water-bath under a reflux condenser.

On cooling α-citryl-β-naphthocinchoninic acid separates in fine needles, melting at 199° to 200°, which are filtered off and washed with ether, and recrystallised from alcohol. If too little citral is present α-methyl-β-naphthocinchoninic acid is formed as well, but this is less soluble than the citral compound, and is separated from it by dissolving the latter in hot alcohol and recrystallising it. The reaction taking place is as follows:—

$C_9H_{15}.CHO + CH_3.CO.COOH + C_{10}H_7NH_2 =$

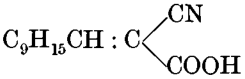
Citral. Pyruvic acid. β-naphthylamine.



$$C_{10}H_6\left\langle\begin{matrix}N:C.C_9H_{15}\\ \quad\;|\\ C:CH\\ \;\;|\\ \;COOH\end{matrix}\right. + 2H_2O + H_2$$

α-citryl-β-naphthocinchoninic acid.

Citral also forms a crystalline derivative with cyanacetic acid, citrylidene-cyanacetic acid of the formula—



$$C_9H_{15}CH:C\left\langle\begin{matrix}CN\\ COOH\end{matrix}\right.$$

It is obtained by mixing 1 molecule of cyanacetic acid, 1 molecule of citral, and 2 molecules of caustic soda. The reaction liquid is extracted with ether, in order to remove non-aldehydes, and the clear liquid acidified with acetic acid. The separated acid is dissolved in benzene and precipitated by petroleum ether when it forms yellow crystals, melting at 122° in the case of α-citral, and at 94° to 95° in the case of β-citral.

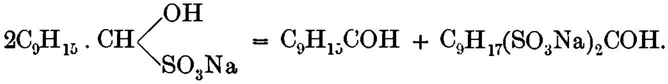
In a similar manner citrylidene-malonic acid can be prepared, melting at 191°.

The oxime and phenylhydrazone are liquid, and not suitable for identification purposes.

On oxidation by weak oxidising agents, citral yields geranic acid, $C_{10}H_{16}O_2$; on reduction it yields geraniol.

Citral forms condensation compounds with sulphites and acid sulphites which are exceedingly useful in the estimation of the aldehyde. Tiemann has isolated three separate hydrosulphonic acid compounds. The normal bisulphite compound is best prepared by shaking citral with a hot solution of sodium bisulphite containing free sulphurous acid.

When the normal sodium bisulphite compound is dissolved in water and submitted to steam distillation, half of the citral passes over, the remainder being converted into the sodium salt of the so-called " stable " citraldihydrodisulfonic acid :—



$$2C_9H_{15}.CH\left\langle\begin{matrix}OH\\ SO_3Na\end{matrix}\right. = C_9H_{15}COH + C_9H_{17}(SO_3Na)_2COH.$$

This compound is readily soluble in water without regeneration of the citral from the solution either by sodium carbonate or hydrate.

When citral is agitated with an aqueous solution of neutral sodium sulphite, the sodium salt of the " labile " citraldihydrodisulfonic acid results according to the following equation :—

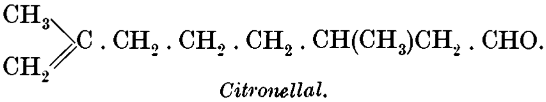
$$C_9H_{15}COH + 2Na_2SO_3 + 2H_2O = C_9H_{17}(SO_3Na)_2COH + 2NaOH.$$

This differs from the isomeric " stable " compound in being quantitatively decomposed by the action of sodium hydrate into citral and neutral sodium sulphite.

A thiosemi-carbazone, melting at 107° to 108°, and a semi-oxamazone, melting at 190° to 191°, have been prepared.

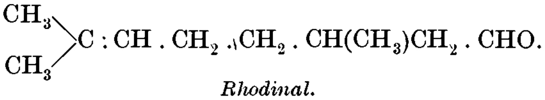
CITRONELLAL AND RHODINAL.

These aldehydes, of the formula $C_{10}H_{18}O$, are those corresponding to the alcohols citronellol and rhodinol (assuming, as is apparently true, that they are distinct compounds as indicated under citronellol. Their constitutions would therefore be as follows :—



$$\left.\begin{matrix}CH_3\\ CH_2\end{matrix}\right\rangle C . CH_2 . CH_2 . CH_2 . CH(CH_3)CH_2 . CHO.$$

Citronellal.



$$\left.\begin{matrix}CH_3\\ CH_3\end{matrix}\right\rangle C : CH . CH_2 . CH_2 . CH(CH_3)CH_2 . CHO.$$

Rhodinal.

Citronellal which was originally termed citronellone, is one of the characteristic constituents of citronella oil, in which it occurs to a considerable extent. It can be prepared by shaking the essential oil with a hot solution of sodium bisulphite, and decomposing the resulting bisulphite compound by means of sodium carbonate and distilling the citronellal in a current of steam. Citronellal is optically active, and it is probable that the specimens isolated from natural sources are mixtures of the two optically active isomers, so that the actual theoretical rotation is not known with certainty.

It can be prepared artificially by the reduction of citronellol, $C_{10}H_{20}O$, and the isomeric rhodinal can, according to Bouveault, be prepared by the reduction of rhodinal from oil of rose.

According to Tiemann and Schmidt, citronellal has the following characters :—

Boiling-point	205° to 208°
,, ,, at 25 mm.	103° ,, 105°
Specific gravity at 17·5°	0·8538
Refractive index	1·4481
Molecular refraction	48·29

Commercial specimens of a high degree of purity have the following characters :—

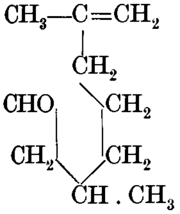
Boiling-point	205° to 208°
Specific gravity	0·855 ,, 0·358
Optical rotation	+ 10° ,, + 11°
Refractive index	1·4450 ,, 1·4485

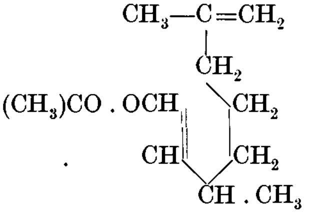
Citronellal prepared from Java citronella oil is laevo-rotatory to the extent of about − 3°.

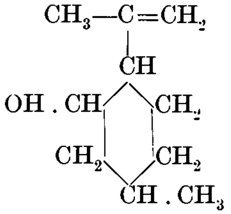
For the identification of citronellal, the semi-carbazone is the easiest crystalline compound to prepare. It results if an alcoholic solution of citronellal be well-shaken with a solution of semi-carbazide hydrochloride and acetate of sodium. It is purified by recrystallisation from a mixture of chloroform and petroleum ether, and then melts at 84°. It also forms a well-defined naphthocinchoninic acid, which is prepared in the same manner as the corresponding citral compound. It melts at 225°.

It also forms citronellylidene-cyanacetic acid, melting at 137° to 138°. It forms additive compounds with sodium bisulphite, which are similar in characters to the corresponding citral compounds.

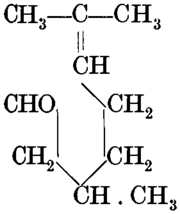
On oxidation it yields citronellic acid, $C_{10}H_{18}O_2$. On acetylation, citronellal is converted into the alcohol isopulegol, which is acetylated, forming isopulegyl acetate, so that this aldehyde is included in the results of determinations of geraniol in oils in which both constituents are present. For example, the total acetylisable constituents of citronella oil, which are usually returned as "geraniol," really include the citronellal present as well. According to Tiemann,[1] citronellal, under the influence of acetic anhydride forms an enolic ester which is gradually converted, by heating with the anhydride, into isopulegol acetate—the relationships being shown as follows:—

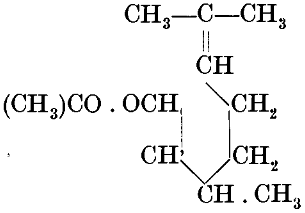

Citronellal.

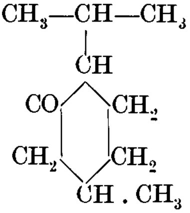

Enolic acetate.


Isopulegol.

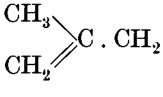
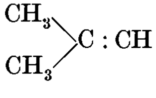
Rhodinal, under similar circumstances, appears to give rise to menthone, the relationships being shown as follows:—


Rhodinal.


Enolic acetate.


Menthone.

The work of Harries and Himmelmann[2] provides considerable confirmation of the individuality of the aldehydes citronellal and rhodinal. By the action of ozone on the aldehyde, results differ materially according to the source of the "citronellal," and those chemists are of opinion that the two complexes—


and


are present, which is in accordance with the assumption stated previously. They consider that the first complex becomes less stable as the acid-carrying group in the molecule increases.

This view would explain the observation made by Tiemann and Schmidt, that citronellal when heated with acetic anhydride, only yields about 50 per cent. isopulegol; or the fact noted by Harries and

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[1] *Berichte*, **42**, 2014.

[2] *Ibid.*, **41** (1908), 2187.

Schauwecker, that when citronellal acetal is oxidised by permanganate, there is formed the acetal of the semi-aldehyde of β-methyladipic acid and a glycol The indistinct melting-points observed in citronellal derivatives (for example in the semi-carbazone) can also thereby be explained It would appear that commercial citronellal contains the two isomeric forms in varying proportions

H J Prins[1] has isolated two isomerides of citronellal by repeated fractionation The first boils at 203° to 204°, has a specific gravity of 0 888 at 14°, and forms a semi-carbazone, melting-point 85° to 86° The second boils at 198° to 199°, has a specific gravity of 0 8745 at 14°, and yields a semi-carbazone, melting-point 83° to 84°. It is suggested that the formula of the first is—

$$CH_2\ CMe\ CH_2 . CH_2\ CH_2CHMe . CH_2 . CHO,$$

whilst that of the second is—

$$CMe_2\ CH\ CH_2\ CH_2\ CHMe . CH_2 . CHO$$

These results would suggest that ordinary "citronellal" is a mixture of citronellal and rhodinal

The aldehydes of the cyclic series include a number of compounds which are of common occurrence in essential oils, and a certain number which are prepared synthetically for perfumery purposes.

The simplest of these, in reference to chemical constitution, is —

BENZALDEHYDE

Benzaldehyde, C_6H_5COH, is the main constituent of oil of bitter almonds and other oils of the same family It can be formed in various ways, including the oxidation of benzyl alcohol, or, as is usually done, by acting on benzal chloride, $C_6H_5CHCl_2$, with sulphuric acid or with milk of lime, or by heating benzyl chloride, $C_6H_5CH_2Cl$, with water and lead nitrate. Artificial benzaldehyde is manufactured and sold largely as "artificial oil of almonds" It is almost identical with the natural oil, but possesses a rather harsher odour, probably due to the presence of traces of impurities, which generally consist of chlorinated compounds A very pure variety, however, is now produced, which is free from these impurities The natural benzaldehyde results from the decomposition of a glucoside, amygdalin, under the influence of the ferment emulsin in the presence of water (*vide* oil of bitter almonds)

The starting-point in the synthesis of benzaldehyde,[2] which requires a good deal of skill for its successful manufacture, is the hydrocarbon toluene, and this must first be separated from the benzene and other hydrocarbons accompanying it in its crude form by suitable fractional distillation The initial reaction of the toluene is with chlorine, and this reaction takes place far better in sunlight than away from it The toluene is heated to boiling in as strong a light as possible, and a current of perfectly dry chlorine is passed through it until 100 parts has increased in weight to 140 parts The weather and light will determine the time which is taken to complete this reaction, during the winter the whole day may be necessary, whereas on a fine summer day the reaction may be finished in two to three hours The chlorinated compound so formed

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[1] *Chem Weekblad*, **14** (1917), 692 95

[2] Radcliffe, *P and E.O R* (1917), 298

is benzalchloride, $C_6H_5 . CH . Cl_2$, which has now to be converted into benzaldehyde.

The crude benzalchloride obtained by the above-described chlorination of toluene is mixed with three times its weight of water and its own weight of finely precipitated calcium carbonate, and the mixture is heated for four hours in a bath of oil or similar material to a temperature of 130°. After the expiration of this time steam is passed through the contents of the reaction vessel, which is maintained at the temperature of 130° until no more oil distils over. The resulting crude benzaldehyde contains a fair amount of benzoic acid which must be removed. The bulk of the benzoic acid, however, is left in the reaction vessel, and may be recovered by filtering the hot liquid and adding hydrochloric acid, by which means the benzoic acid separates out and may be filtered off, washed, and dried. If recrystallised from hot water it can be obtained in a state of purity. The crude benzaldehyde which has been steam distilled, together with the watery distillation liquid, is now treated with a concentrated solution of acid sulphite of sodium and the whole well shaken until almost the whole of the oily liquid has gone into solution. If crystals of the double compound of benzaldehyde and sodium sulphite separate, more water must be added and the liquid well shaken until the crystals are dissolved again. The aqueous solution is now filtered from any small quantity of oil which remains undissolved, and the filtrate treated with anhydrous sodium carbonate until it acquires a decided alkaline reaction. The alkaline liquid is now subjected to distillation with steam, when the benzaldehyde distils over.

There is, of course, always the risk of the purified benzaldehyde containing traces of chlorine—in fact, samples manufactured with merely ordinary care may be found to contain up to 2·5 per cent. of this impurity. It is very objectionable when the benzaldehyde is to be used, as, for example, a soap perfume in pale-coloured soaps, since the presence of chlorine compounds invariably causes the product to change colour, which renders the soap more or less unsaleable. One of the causes of the presence of chlorine in the finished product is that chlorine reacts with toluene, especially if the temperature is a little too low when the current of chlorine starts, in such a way that one atom enters the nucleus, forming chlorotoluene, $C_6H_4ClCH_3$. Chlorine reacts with toluene in such a manner, at higher temperatures, as to replace the atoms of hydrogen in the methyl side chain, so as to form benzal chloride, $C_6H_5CHCl_2$. But the reaction of chlorine on chlorotoluene is quite similar, and the result is the presence of a certain amount of chlorobenzal-dichloride, $C_6H_4Cl . CHCl_2$. In the subsequent reaction with water and calcium carbonate, it is only the chlorine in the side chain which is eliminated, so that we shall, under the above conditions, have a certain amount of chlorobenzaldehyde formed, $C_6H_4Cl . COH$. It is obvious, therefore, that the greatest care must be exercised in carrying out the synthesis of benzaldehyde if a product free from chlorine is to be obtained. In the actual course of the reaction in practice, the mixture contains several chlorinated compounds, including benzal chloride, which is the principal constituent of the mixture, and which is eventually converted into benzaldehyde, benzyl chloride, chlorotoluene, and benzotrichloride. If the mixture is boiled with water, with the addition of calcium carbonate, the resulting reaction-mass consists essentially of benzaldehyde, benzyl alcohol, and traces of the chlorinated products which do not enter into the hydrolytic reaction, and also a considerable quantity of benzoic acid which remains behind in the still as calcium benzoate, when the volatile bodies are steam distilled. By rendering the distillation residue acid with dilute sulphuric acid, or preferably dilute hydrochloric acid, the free benzoic acid is obtained. A large proportion of the so-called "benzoic acid ex toluol" is obtained in this manner as a by-product in the manufacture of benzaldehyde.

The process of Lauth and Grimaux is also very largely employed; a mixture of benzyl chloride 5 kilos, nitrate of lead or copper 7 kilos, and water 10 litres, is boiled for seven or eight hours in an apparatus provided with a reflux cooler; the reaction being as follows:—

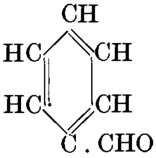
$$C_6H_5CH_2Cl + O = C_6H_5CHO + HCl.$$

When the reaction is complete the oil is distilled, or more usually decanted off, and the benzaldehyde thoroughly agitated with fifteen times its weight of bisulphite of soda. This results in the formation of the solid sodium bisulphite compound. This is washed with alcohol and then decomposed by a solution of sodium carbonate, and finally the benzaldehyde is distilled in a current of steam.

A process giving a chlorine free product is as follows:—[1]

A mixture of 300 kilos of toluene and 700 kilos of 65 per cent. sulphuric acid is thoroughly agitated, and 90 kilos of finely powdered manganese dioxide added little by little. The temperature is maintained about 40°. The process is a very slow one, and finally a mixture of unchanged toluene and benzaldehyde is obtained, and from this the sulphite compound is prepared, purified, and the pure benzaldehyde isolated as usual.

Benzaldehyde has the following constitution:—



Its characters are as follows:—

Boiling-point at 760 mm.	179° to 180°
,, ,, ,, 5 mm.	45°
Specific gravity	1·052
Optical rotation	± 0°
Refractive index	1·5450

It forms a semi-carbazone melting at 214°, and a phenylhydrazone melting at 156°.

On oxidation it readily yields benzoic acid, melting at 121°. Exposure to the air is sufficient to effect this oxidation.

For the examination of benzaldehyde for chlorine, see p. 352.

SALICYLIC ALDEHYDE.

Salicylic aldehyde, $C_7H_6O_2$, is the simplest representative of the ortho-hydroxy aldehydes, which are, generally speaking, strongly odorous

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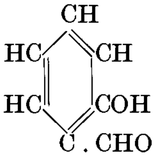
[1] *D.R.P.*, 101221 of 1897.

compounds. It occurs naturally in the essential oil of several varieties of *Spiraea*, and can be manufactured artificially with considerable ease if the following details be followed:—

One hundred grams of caustic soda are dissolved in 100 c.c. of water and placed in a round-bottomed flask. To this are added 30 grams of phenol. The mixture should be warmed to 60° to 65° and then attached to a reflux condenser. Seventy-five grams of chloroform are then added gradually in the following manner: One-third is first to be added through the condenser, and as the temperature rises the mixture must be cooled to 65° by immersion in cold water. In ten minutes, a second third of the chloroform is added with the same precautions, and after another twenty minutes the remainder is added. After allowing the whole to remain for two hours at 65°, with constant shaking, the chloroform in excess is distilled off in a current of steam, and the alkaline liquid then acidified with dilute sulphuric acid, and steam passed through until no more oily drops pass over. The distillate is extracted with ether, and the ether evaporated. The residue now consists of salicylic aldehyde with unchanged phenol. It is treated with strong solution of sodium bisulphite, and the resulting crystalline compound is washed with alcohol to remove phenol, and finally once with ether. The crystals are decomposed by dilute sulphuric acid, and the liberated salicylic aldehyde extracted with ether, and, on evaporation of the ether, purified by distillation.

Salicylic aldehyde is an almost colourless oil with a fragrant odour of meadowsweet. Its constitution is as follows:—



It has the following characters:—

Specific gravity	1·170
Boiling-point	196° to 197°
Solidifying-point	– 20°

It yields an oxime, melting at 57°, and a phenylhydrazone, melting at 96°.

On oxidation it yields salicylic acid, melting at 155° to 156°.

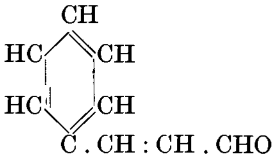
CINNAMIC ALDEHYDE.

Cinnamic aldehyde, C_9H_8O, is the principal odorous constituent of cinnamon and cassia oils, and is manufactured to a considerable extent artificially. It can be extracted from the oils in which it occurs by means of sodium bisulphite, the sodium bisulphite compound being decomposed with dilute sulphuric acid, and distilled in a current of steam. The preparation of artificial cinnamic aldehyde, which is used in perfumery as a substitute for the natural oils, is usually carried out by a condensation of benzaldehyde and acetaldehyde, according to the following reaction:—

$$C_6H_5 . CHO + CH_3CHO = C_6H_5 . CH : CH . CHO + H_2O.$$

A mixture of 10 parts of benzaldehyde, 15 parts of acetaldehyde, 900 parts of water, and 10 parts of 10 per cent. solution of caustic soda are allowed to stand for ten days at 30° with constant stirring. The cinnamic aldehyde formed is extracted with ether and purified by fractional distillation.

Cinnamic aldehyde is a sweet, odorous liquid, resembling cinnamon oil, but without its delicacy of odour. It has the following constitution:—



Its characters are as follows:—

Boiling-point	252° to 254°
„ „ at 20 mm.	128° „ 130°
Specific gravity	1·0540 „ 1·0570
Optical rotation	± 0°
Refractive index	1·6195
Melting-point	− 7·5°

Its phenylhydrazone melts at 168°, and its semi-carbazone at 208°.

PHENYLACETIC ALDEHYDE.

Phenylacetic aldehyde, C_8H_8O, is one of the most important of modern synthetic perfumes. It has not been found naturally in essential oils. It possesses a powerful odour of hyacinths, and is extremely useful for the reproduction of all odours of this and the narcissus type.

Phenylacetic aldehyde can be prepared by various methods, of which the following are the principal:—

Methyl cinnamate[1] (16 parts) is dissolved in methyl alcohol (20 parts) and treated with bromine (20 parts). The mixture solidifies in the cold. It is shaken with a solution of caustic soda (12 parts) in water (24 parts), the temperature being kept down to 40°. After two hours the mixture is neutralised with dilute sulphuric acid, and an oily layer separates. This is mixed with water (to 250 parts) and sodium carbonate (5·5 parts) added, and the aldehyde distilled in a current of steam, and extracted with ether, and the ether evaporated. The yield is about 75 per cent. of the theoretical.

By allowing phenylmagnesium bromide to react with ethoxyacetal, Späth[2] has shown that the following reaction takes place:—

$$C_6H_5 . MgBr . + (OC_2H_5) . CH_2 . CH(OC_2H_5)_2$$
$$= C_2H_5O . MgBr . + C_6H_5 . CH(OC_2H_5) . CH_2(OC_2H_5).$$

The ether thus formed reacts with a second molecule of magnesium phenylbromide, thus:—

$$C_6H_5CH(OC_2H_5) . CH_2(OC_2H_5) + MgC_6H_5Br$$
$$= C_2H_5OMgBr + C_6H_6 + C_6H_5 . CH : CH(OC_2H_5).$$

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[1] *Bull. Soc Ind. Mulhouse*, **83** (1913), 805.

[2] *Monatshefte*, **36**, (1915), 1.

On saponification this last compound yields vinyl alcohol and phenylacetaldehyde and alcohol, thus:—

$$C_6H_5 . CH : CH(OC_2H_5) + H_2O = C_6H_5 . CH_2 . CHO + C_2H_5OH.$$

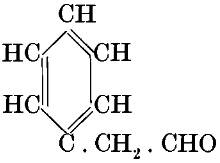
Phenylacetaldehyde can also be prepared by treating sodium cinnamate with bromine, and then adding oxalic acid. The sodium salt of phenylbromolactic acid results. On steam distillation this gives off CO_2, and yields phenylacetaldehyde (the reaction is probably more complicated than the equation indicates):—

$$C_6H_5 . CHBr . CHOH . COONa = C_6H_5 . CH_2 . CHO + KBr + CO_2.$$

It also results by reducing phenylethyl alcohol in vapour with copper dust at 250°, when hydrogen is evolved:—

$$C_6H_5 . CH_2CH_2OH = C_6H_5 . CH_2 . CHO . + H_2.$$

Phenylacetaldehyde is very apt to polymerise, especially in the presence of acid or alkali, so that its preparation in the pure state is a matter of some difficulty. It has the following constitution:—



Its characters are as follows:—

Boiling-point	205° to 207°
" " at 11 mm.	78°
Refractive index	1·5300
Specific gravity	1·085

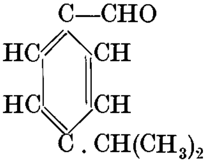
Cumic Aldehyde.

Cumic aldehyde, or isopropyl-benzaldehyde, is present in cummin oil and in the oils of boldo leaf, cassie flower oil, and, probably, in certain eucalyptus oils. It is an oil of powerful odour, having the formula $C_{10}H_{12}O$. Its characters are as follows:—

Boiling-point	235° to 236°
" " at 14 mm.	116°
Specific gravity	0·982

It yields a semi-carbazone melting at 210° to 211°, oxime melting at 58° to 59°, and phenylhydrazone melting at 126° to 127°.

Its constitution is as follows:—



It can be prepared by extraction from the oils in which it occurs by means of sodium bisulphite in the usual manner.

On oxidation it yields cuminic acid, melting at 114° to 115°.

METHOXY-CINNAMIC ALDEHYDES.

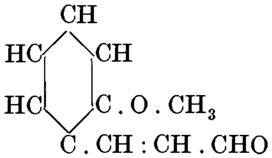
Ortho-methoxy-cinnamic aldehyde is present in small amount in cassia oil. It has the composition $C_{10}H_{10}O_2$, and its physical characters are as follows:—

Melting-point	45°
Boiling-point	295°
Melting-point of phenylhydrazone	116°

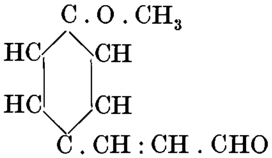
Para-methoxy-cinnamic aldehyde has been isolated from tarrago oil. It has the following characters:—

Boiling-point at 14 mm.	170°
Specific gravity	1·137
Melting-point of oxime	138°
,, ,, ,, semi-carbazone	220° (?)
,, ,, ,, phenylhydrazone	138°

The constitution of these aldehydes is as follows:—



o-methoxy-cinnamic aldehyde.



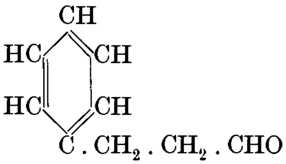
p-methoxy-cinnamic aldehyde.

The *ortho*-compound yields, on oxidation by permanganate of potassium, methyl-salicylic acid melting at 99°, whilst the *para*-compound yields anisic acid melting at 184°.

An aldehyde was isolated from the oil of the root of a variety of *Chlorocodon*, by Goulding and Pelly,[1] which Friedlander[2] has shown to be *p*-methoxy-cinnamic aldehyde. This aldehyde has been obtained artificially by Tiemann and Parrisius[3] by acting with chloroform on an alkaline-solution of methylresorcinol.

HYDROCINNAMIC ALDEHYDE.

Hydrocinnamic aldehyde, $C_9H_{10}O$, exists in cinnamon bark oil. It has the constitution—



It forms a semi-carbazone melting at 130° to 131°.

PARA-METHYL-HYDROCINNAMIC ALDEHYDE.

This aldehyde is a homologue of hydrocinnamic aldehyde, having the following constitution:—

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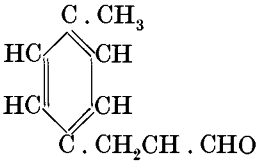
[1] *Proc. Chem. Soc.* **24** (1908), 62.

[2] *Monatshefte*, **30** (1909), 879.

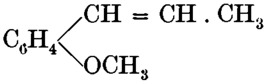
[3] *Berichte*, **B** (1880), 2366.



It is prepared synthetically and has an intensely powerful odour of the lily or lilac type.

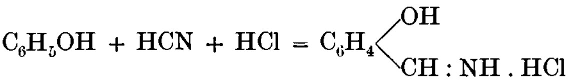
Anisic Aldehyde.

Anisic aldehyde, $C_8H_8O_2$, is a methyl ether of para-oxy-benzaldehyde, which is found to a small extent in the oils of fennel and aniseed. It is manufactured on an extensive scale artificially, and is the basis of all the perfumes of the hawthorn or "May blossom" type. It is known commercially as "aubepine". A certain amount of anisic aldehyde is obtained as a by-product in the manufacture of coumarin, but the greater part of it is obtained by very careful oxidation of anethol, the characteristic constituent of aniseed oil, which has the constitution—



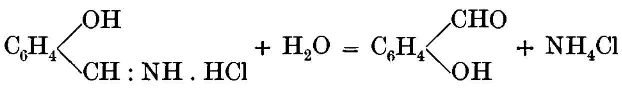
$$C_6H_4\begin{array}{l}\diagup CH = CH \, . \, CH_3 \\ \diagdown OCH_3\end{array}$$

The aldehyde is obtained by gently warming the oil for about an hour with three times its volume of nitric acid (specific gravity 1·1), and separating the heavy oil so formed, and washing it with potash solution. The crude oil is agitated with a warm concentrated solution of sodium bisulphite, with which the aldehyde combines, and the resulting crystalline magma is washed with alcohol and pressed in blotting-paper, and dissolved in warm water. Excess of sodium carbonate is added, when the aldehyde is liberated and floats on the surface of the liquid. It can be further purified by distillation. It can also be prepared from phenol, which is treated in ethereal solution, with a mixture of hydrochloric and hydrocyanic acid gases, using zinc chloride as the condensing reagent. An imide hydrochloride is formed according to the following equation:—



$$C_6H_5OH + HCN + HCl = C_6H_4\begin{array}{l}\diagup OH \\ \diagdown CH : NH \, . \, HCl\end{array}$$

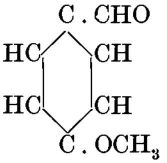
which on reaction with water forms *p*-oxy-benzaldehyde—



$$C_6H_4\begin{array}{l}\diagup OH \\ \diagdown CH : NH \, . \, HCl\end{array} + H_2O = C_6H_4\begin{array}{l}\diagup CHO \\ \diagdown OH\end{array} + NH_4Cl$$

This on methylation in the usual manner yields anisic aldehyde.

Anisic aldehyde has the following constitution:—



Its physical characters are as follows:—

Boiling-point	245° to 246°
,, ,, at 4 mm.	91°
Specific gravity	1·1275
Optical rotation	± 0°
Refractive index	1·5730

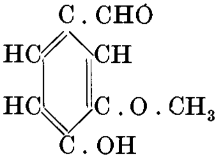
It readily oxidises to anisic acid, melting at 184°, so that it should be kept in amber glass, well-stoppered bottles, in order to prevent oxidation. It forms a semi-carbazone melting at 203° to 204°, and two oximes, one melting at 63° and the other at 132°.

There is a solid "aubepine" met with in commerce, which appears usually to be the sodium bisulphite compound of anisic aldehyde.

VANILLIN.

Vanillin, $C_8H_8O_3$, is one of the most important synthetic perfumes. It is the active odorous ingredient of the vanilla pod, in which it occurs to the extent of about 2 per cent., appearing on the surface of the bean as a fine white crystalline efflorescence. It occurs naturally also in Sumatra benzoin (about 1 per cent.), Siam benzoin (·15 per cent.), and the balsams of Tolu and Peru (traces). Numerous other bodies have been recorded as containing it, such as asafœtida, beetroot and asparagus, the seeds of *Lupinus albus*, the seeds of *Rosa canina*, etc.

It was first artificially prepared by Tiemann from the glucoside coniferin, which occurs in the cambium of various coniferous woods. The constitution of vanillin is that of methyl protocatechuic aldehyde—



Vanillin.

and coniferin, $C_{16}H_{22}O_8 + 2H_2O$, which is a glucoside melting at 185°, was the substance which Tiemann first used for preparing vanillin from, and for whose process Haarmann and Reimer took out a patent. Coniferin was decomposed, either by emulsin or by boiling with dilute acids, into glucose and coniferyl alcohol, $C_6H_3(OH)(OCH_3)C_3H_4OH$, and this body on oxidation yields vanillin: or the oxidation may take place first and the hydrolysis afterwards. The process then consisted of the following reactions. When coniferin is oxidised with an aqueous solution of chromic acid it is converted into gluco-vanillin.

$$C_6H_3(O.CH_3)(O.C_6H_{11}O_5)(CHO),$$

the glucoside of vanillin, a crystalline body melting at 170°. For this purpose a solution of 10 parts of coniferin in 200 parts of water is treated at the ordinary temperature with a solution of 8 parts of chromic acid dissolved in a small quantity of water, and the mixture allowed to stand for several days. Barium carbonate is then added to precipitate the chromium. The solution is evaporated to a small bulk, treated with alcohol and filtered. The filtrate on evaporation yields crystals of gluco-vanillin, melting at 170°. On treating this body with the ferment emulsin, or by boiling it with dilute mineral acids, it is decomposed into glucose and vanillin. The latter may be extracted with ether. This process, however, has only an historical interest to-day.

The most important method, however, by which vanillin is now prepared is by the oxidation of eugenol, the chief constituent of oil of cloves. This process proved the subject-matter of a patent taken out in England in 1876 by Tiemann, and an almost simultaneous one in France by De Laire. The eugenol was instructed to be separated by diluting the oil with three times its volume of ether and agitating the ethereal solution with a dilute solution of potash or soda. The aqueous liquid is separated and acidified, and the eugenol separated by extraction with ether. The eugenol is first acetylated by means of acetic anhydride, and the resulting acet-eugenol is dissolved in acetic acid and oxidised with permanganate of potassium. The liquid is then filtered, and rendered alkaline, and the whole is then evaporated, and the residue treated with moderately dilute acid, and extracted with ether. The ethereal solution is extracted with a solution of sodium bisulphite, which combines with the vanillin. The double sulphite compound is decomposed with dilute sulphuric acid, and the vanillin is extracted with ether, from which solvent it is obtained in fine white crystals.

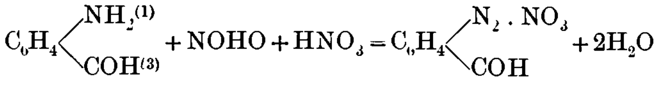
The best yield, however, is obtained by first converting the eugenol into iso-eugenol, $OH . OCH_3 . C_6H_3 . CH \quad CH . CH_3$, by treating it with solution of potassium hydrate. The acetylation product is oxidised, by which acetyl-vanillin is chiefly formed, which yields vanillin by splitting off the acetyl group.

By direct oxidation by means of ozone, isoeugenol is converted into vanillin.

$$\underset{\text{isoeugenol}}{OH . OCH_3 . C_6H_3 . CH \quad CH . CH_3} + 2O_3 =$$

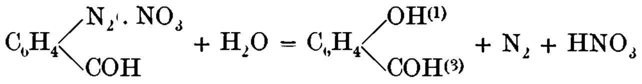
$$CH_3COH + \underset{\text{vanillin.}}{C_8H_8O_3}$$

Vanillin is also obtained by starting from meta-amido-benzaldehyde, which is converted into its diazo compound, which yields meta-oxybenzaldehyde, on treatment with water. These reactions may be represented as follows —



$$C_6H_4\left\langle\begin{matrix}NH_2{}^{(1)}\\COH^{(3)}\end{matrix}\right. + NOHO + HNO_3 = C_6H_4\left\langle\begin{matrix}N_2 . NO_3\\COH\end{matrix}\right. + 2H_2O$$

Meta-amido-benzaldehyde Diazo nitrate.



$$C_6H_4\left\langle\begin{matrix}N_2 . NO_3\\COH\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}OH^{(1)}\\COH^{(3)}\end{matrix}\right. + N_2 + HNO_3$$

Meta-oxybenzaldehyde.

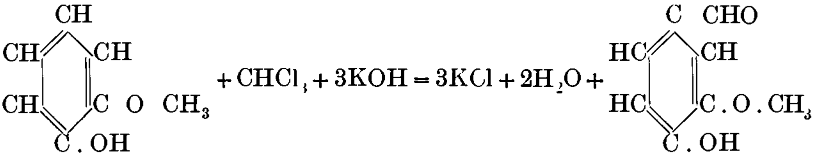
The *meta*-oxybenzaldehyde is then nitrated and methylated, by which means *para*-nitro*meta*-methoxy-benzaldehyde

$$C_6H_3 . NO_2{}^{(4)} . OCH_3{}^{(3)} . COH^{(1)}$$

is formed. By reduction this is altered to the corresponding amidoaldehyde, which is again diazotised and the amido-group replaced by hydroxyl in the usual way, when *para*-oxy*meta*-methoxy-benzaldehyde results, which is, of course, identical with vanillin, or protocatechuic aldehyde methyl ether, $C_6H_3 \cdot COH^1 \cdot OCH_3^3 \cdot OH^4$ Another complicated method, which is the subject of a patent, is to nitrate *meta*-methoxy-cinnamic acid methyl ester, by which means the corresponding *meta*-methoxy-*para*-nitro-cinnamic methyl ester is formed This body, $C_6H_3 \cdot OCH_3^{(3)} \cdot NO_2^{(4)}\ (C_2H_2CO_2CH_3)^{(1)}$ is hydrolysed and the free acid is converted into its ammonium salt, which is dissolved in water and reduced to the corresponding *meta*-methoxy-*para*-amido-cinnamic acid. This is diazotised in the usual way, and the amido-group is replaced by hydroxyl, by which means an acid termed ferulic acid is formed. This is *meta*-methoxy-*para* oxycinnamic acid, $C_6H_3(OCH_3)OH \cdot (C_2H_2COOH)$. This acid is oxidised (best as an acetyl compound) with potassium permanganate, and thus converted into vanillin. The two methods last described, *viz* those starting from *meta*-oxybenzaldehyde and methoxy-cinnamic acid are only of theoretical interest

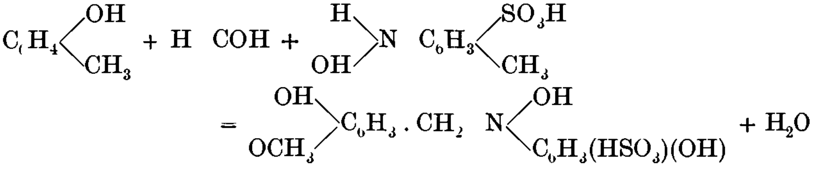
Vanillin is also produced in several ways from guaiacol. A recent patent (D R P 189,307—German patent) for this is as follows Guaiacol is treated with hydrocyanic acid in the presence of hydrochloric acid and zinc chloride The reaction mass, after forty-eight hours, is treated with hot water and filtered, the unaltered guaiacol is removed by extracting the vanillin from ethereal solution by means of sodium bisulphite and recovering it in the usual manner. Care must be taken to remove all traces of guaiacol, as the slightest taint with this phenol entirely spoils the odour and flavour of the vanillin

Tiemann and Reimer have prepared vanillin by the action of chloroform on guaiacol in an alkaline medium. The mixture is boiled under a reflux condenser for six hours A mixture of vanillin and *meta*-methoxysalicylic aldehyde results The mixed aldehydes are separated from the reaction mass by means of bisulphite in the usual manner, and the liberated aldehydes are separated in a current of steam. The vanillin is formed according to the following reaction—



(Guaiacol) (Vanillin)

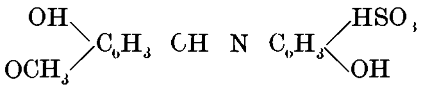
Another method of obtaining vanillin from guaiacol is as follows Formic aldehyde is allowed to react with guaiacol in the presence of phenylhydroxylamine sulphonate —



$$C_6H_4\begin{matrix}OH\\CH_3\end{matrix} + H \cdot COH + \begin{matrix}H\\OH\end{matrix}N \cdot C_6H_3\begin{matrix}SO_3H\\CH_3\end{matrix}$$

$$= \begin{matrix}OH\\OCH_3\end{matrix}C_6H_3 \cdot CH_2 \cdot N\begin{matrix}OH\\C_6H_3(HSO_3)(OH)\end{matrix} + H_2O$$

This body gives up another molecule of water, yielding



$$\begin{matrix}OH\\OCH_3\end{matrix}C_6H_3 \cdot CH \cdot N \cdot C_6H_3\begin{matrix}HSO_3\\OH\end{matrix}$$

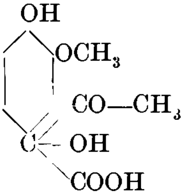
which, on hydrolysis by means of sodium acetate, yields vanillin and a methyl-amido-sulphonic acid.

Guyot and Gey have prepared vanillin by a synthesis depending on the property possessed by compounds containing two carbonyl groups in juxtaposition, of condensing with guaiacol giving products from which it is easy to pass to vanillin.

Acetylglyoxylic acid

$$CH_3—CO—CO—COOH$$

for example, yields with guaiacol the compound

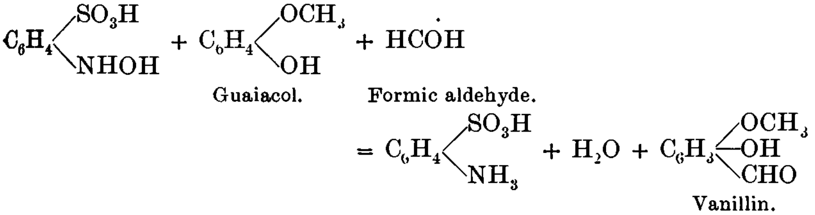


which is converted by oxidation into vanilloyl carboxylic acid

$$(CH_3O)(OH)C_6H_3—CO—COOH.$$

This latter, when heated at 150° to 160° C. with dimethyl-*p*-toluidine is decomposed with the production of vanillin.

Gattefossé and Morel (*La Parfumerie Moderne*, 1919, **114**) describe a method for the production of vanillin by reducing nitrobenzene-sulphonic acid with iron filings and hydrochloric acid in the presence of guaiacol and formic aldehyde. The first-named body is reduced to phenyl-hydroxylamine-sulphonic acid, which reacts with the guaiacol as follows:—



$$C_6H_4\left\langle\begin{matrix}SO_3H\\NHOH\end{matrix}\right. + C_6H_4\left\langle\begin{matrix}OCH_3\\OH\end{matrix}\right. + HCOH = C_6H_4\left\langle\begin{matrix}SO_3H\\NH_3\end{matrix}\right. + H_2O + C_6H_3\left\langle\begin{matrix}OCH_3\\OH\\CHO\end{matrix}\right.$$

Guaiacol. Formic aldehyde. Vanillin.

Vanillin yields a number of well-defined crystalline derivatives, of which the following are the principal: Bromovanillin,

$$C_6H_2Br(CHO)(OCH_3)(OH),$$

melts at 160° to 161° and results when an aqueous solution of vanillin is treated with bromine. Iodo-vanillin melts at 174°. Vanillin methyl ether melts at 42° to 43°, and the ethyl ether at 64° to 65°. The oxime melts at 121° to 122°.

Vanillin forms fine white needles melting at 81° to 82°, or when absolutely pure at 82° to 84°, and possessing an intense vanilla odour. Some of the cheaper commercial samples are heavily adulterated with the quite odourless compound, acetanilide. The effect of this body is to lower the melting-point even if present in large quantity, but it is very easily detected, as by boiling with solution of potash, aniline is formed, which is easily detected by any of the usual reactions. A quantitative separation may be effected as follows: The substance is dissolved in ether and the liquid repeatedly shaken with concentrated solution of sodium bisulphite. The vanillin is thus extracted, and the ether, after being washed twice with water, is allowed to evaporate, when the acetanilide remains. This will then be found to have a melting-point close to 113°. A little isovanillin, $C_6H_3(CHO)^1(OH)^3(OCH_3)^4$, is occasionally present, but this is due to the fact that it is generally formed in small quantity with vanillin, in many reactions.

Acet-iso-eugenol, one of the intermediate bodies in the manufacture of vanillin, is sometimes found in commercial samples; it lowers the melting-point of the sample, yields acetic acid in hydrolysis, and gives a fine red colour with strong sulphuric acid, whereas pure vanillin only gives a lemon-yellow colour. Benzoic acid is also found as an adulterant. This is easily detected by the high acid value of the substance (vanillin is neutral), and by dissolving the sample in ether, extracting the vanillin by means of sodium bisulphite solution, and neutralising the residue from the ethereal solution with potash, dissolving it in water, and testing it with a neutral solution of ferric chloride, when red ferric benzoate is precipitated.

In examining vanilla beans the determination of the vanillin is a matter of importance. Busse recommends the following process for the determination: 20 grams of the pods, crushed with sand, are exhausted with ether in a Soxhlet tube, and the ethereal extract is shaken out with 20 per cent. sodium bisulphite solution. From the latter, vanillin is removed by treatment with dilute H_2SO_4, the SO_2 generated removed by a current of CO_2, and the vanillin extracted by shaking out with ether, evaporating the solvent and weighing the residue. In East African vanilla the author found 2·16 per cent. of vanillin, in that from Ceylon 1·48 per cent., and in Tahiti vanilla from 1·55 to 2·02 per cent. Tiemann and Haarman found in the best Bourbon vanilla 1·94 to 2·90 per cent., in the best Java vanilla 2·75 per cent., and in Mexican vanilla from 1·7 to 1·9 per cent. Tahiti vanilla sometimes contains less than 1 per cent. of vanilla.

In suspected cases the crystals on the beans should be carefully separated and examined for benzoic acid as above described.

Hanus[1] recommends that β-naphthyl hydrazine hydrochloride should be added to the solution of vanillin in such proportion that from two to three parts are present for each part of vanillin. After standing for five hours the precipitate is transferred to a tared filter, washed with hot water until the washings no longer precipitate silver nitrate, dried at 90° and weighed. The weight of the hydrazine formed, divided by 1·92 gives that of the vanillin present. This method is available in all cases where an aqueous solution of the vanillin can be prepared.

Hanus has more recently recommended the following method for the determination of vanillin in vanilla beans and in preparations thereof.[2] Three grams of the crushed pods are extracted for three hours in a Soxhlet tube with ether, the solvent distilled off cautiously, and the residue dissolved in a little ether, the solution filtered and the filtrate evaporated cautiously. The residue is treated with 50 c.c. of water at 60° on a water-bath; 0·25 gram of *meta*-nitrobenzhydrazide is then added to the aqueous solution in a stoppered flask, which is kept for two to three hours

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[1] *Analyst*, xxv. 318.

[2] *Pharm. Zeit.*, **50**, 1022, 157.

at 60°, and then set aside with occasional shaking for twenty-four hours. The vanillin is precipitated quantitatively as vanillin-*meta*-nitrobenzhydrazone, $NO_2 . C_6H_4 . NH_4 . N : CH . C_6H_3(OCH_3) . OH$. The precipitate is washed with three successive quantities of petroleum ether to remove fat, then washed with water, and then again with petroleum ether, and then dried at 100° for two hours. The weight, multiplied by 0 4829 gives the amount of vanillin present. Preparations of vanillin are treated similarly, alcohol being removed by evaporation. The presence of other aldehydes, such as heliotropin, of course, will vitiate the results

Essence of Vanilla.—The substance sold under this name is, properly, a spirituous extract of the vanilla bean. Many samples, however, are little more than alcoholic solutions of artificial vanillin, coloured with caramel. Some samples, which cannot be described as adulterated, contain a little coumarin or other odorous substance, added to vary the characteristic vanillin odour and flavour somewhat.

A genuine extract can be recognised by the fact that it contains some dark red or red-brown resin, soluble in 50 per cent. alcohol, but precipitated on further dilution.

Coumarin, or extract of Tonka beans, which contain coumarin, may be detected as follows : A small quantity of the essence is evaporated to dryness, the residue fused with caustic potash, saturated with hydrochloric acid and treated with a drop of ferric chloride solution. If coumarin be present, a violet colour due to the formation of salicylic acid, will be produced.

Winton and Silverman[1] recommend the following methods for examining essence of vanilla :—

De-alcoholise 25 grams of the extract in an evaporating dish upon a water-bath, at a temperature of about 80° C., adding water from time to time to retain the original volume. After removal of the alcohol, add normal lead acetate solution, drop by drop, until no more precipitate forms. Stir to facilitate flocculation of the precipitate, filter through a moistened filter, and wash three times with a few c.c. of hot water. Cool the filtrate and extract with ether by shaking out in a separator. Use 15 c.c. to 20 c.c. of ether at each separation, repeating the process three or four times, or until a few drops of the ether, evaporated upon a watch glass, leaves no residue. Place the combined ether extracts containing all of the vanillin and coumarin in a clean separator, and shake out four or five times with 2 per cent. ammonia, using 10 c.c. for the first, and 5 c.c. for each subsequent shaking.

Set aside the combined ammoniacal solutions for the determination of vanillin.

Wash the ether solution into a weighed dish, and allow it to evaporate at the room temperature. Dry in a desiccator and weigh. Usually the dried residue is pure coumarin. Treat the residue with 5 c.c. to 10 c.c. of cold petroleum ether, boiling between 30° C. and 40° C., and decant off the clear liquid into a beaker. Repeat the extraction with petroleum ether until a drop evaporated on a watch glass, leaves no residue. Dry the dish for a few moments in a water oven, cool and weigh. Subtract the weight of the dish and the residue (if any) from the weight previously obtained after evaporation with ether, thus obtaining the weight of pure coumarin. Allow the petroleum ether to evaporate at the room temperature, and dry, if necessary, in a desiccator. The residue should be

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[1] *Jour. Amer. Chem. Soc.*, **24**, 1128.

crystalline and have a melting-point of 67° C This, with the characteristic odour of coumarin, is sufficient for its identification.

Slightly acidulate the reserved ammoniacal solution of vanillin with 10 per cent. hydrochloric acid Cool and shake out in a separatory funnel with four portions of ether of about 15 c.c. to 20 c c each Evaporate the ether at room temperature in a weighed platinum dish, dry over sulphuric acid, and weigh. Treat the residue with boiling petroleum ether (boiling-point 80°) decanting into a dry beaker. Repeat the treatment until all vanillin is removed Dry the dish and residue (if any) for a few moments at 100° C. and weigh, deduct the weight from the weight of the ether residue. The difference is the weight of the vanillin. Evaporate the petroleum ether at ordinary temperatures, and dry in a desiccator The residue should be crystalline, and melt at 80° C to 81° C

Tests for Caramel.—Valuable indications of the nature of an extract are obtained in the process of determination of vanillin and coumarin. Pure extracts of vanilla beans give, with lead acetate, a bulky, more or less glutinous, brown-grey precipitate, and a yellow or straw-coloured filtrate, whereas purely artificial extracts coloured with caramel give a slight dark brown precipitate and a dark brown filtrate If both vanilla bean extract and caramel are present the precipitate is more or less bulky and dark coloured, and the filtrate is more or less brown The solution remaining after extraction of the vanillin and coumarin with ether, if dark coloured, should be tested for caramel.

The most satisfactory test for caramel is to shake with Fuller's earth, as recommended by Crampton and Simons. If the colour is due to caramel and a grade of Fuller's earth is used, which experience has proved suitable, the solution, after filtering, is yellow or colourless. This test does not positively identify the colour, as some other brown substances may give similar reactions, but no such substance is liable to be present in vanilla extract.

Winton and Bailey determine vanillin, coumarin, and acetanilide (which is sometimes found as an adulterant of artificial vanillin, and therefore indicates its presence) in the following manner, which is a modification of the method devised by Hess and Prescott —[1]

Twenty-five grams of the essence are weighed into a 200 c.c. beaker, marked to indicate volumes of 25 c c and 50 c c The essence is diluted with water to 50 c.c. and evaporated on a water-bath to 25 c.c. at a temperature not exceeding 70° It is now again diluted to 50 c.c. and evaporated to 25 c.c. Solution of acetate of lead is then added until no further precipitation takes place. The liquid is then, after being well stirred, filtered through a moistened filter paper, and washed three times with hot water, so that the total filtrate does not exceed 50 c.c The filtrate, when cold, is shaken with 20 c c. of ether in a separator. The ether is separated, and the liquid extracted with three further portions of 15 c c of ether. The combined ether extracts are then shaken with 10 c.c, of 2 per cent. ammonia solution and with three subsequent portions of 5 c.c The ethereal solution is reserved (B) and the combined ammoniacal solutions are rendered slightly acid with 10 per cent hydrochloric acid. The liquid is then extracted four times with ether, and the ether evaporated and the residue dried at room temperature, and finally in a desiccator and weighed (A). If acetanilide is absent, this may be taken as

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[1] *Jour Amer Chem Soc* (1899), 256

pure vanillin, which should melt at 79° to 81°. If acetanilide has been detected (*vide infra*), the residue should be dissolved in 15 c.c. of 10 per cent. ammonia, and the liquid shaken twice with ether. The ether, on evaporation, will leave a residue of acetanilide, which is dried at room temperature and then in a desiccator and the weight deducted from the "vanillin" (A) previously weighed. The total amount of acetanilide is the amount thus obtained, together with that present in the ethereal solution (B) reserved above. The latter is transferred to a tared dish and the ether allowed to evaporate at room temperature. The residue is dried in a desiccator and weighed. It is then extracted several times by stirring well with petroleum ether, which is decanted each time. If the residue is thus completely dissolved, it may be taken to be entirely coumarin. Any undissolved residue is probably acetanilide (melting-point 112° to 113°) and its weight deducted from the total residue gives the coumarin.

The acetanilide here found is added to the amount extracted with the vanillin to give the total amount present.

The presence of acetanilide in these residues may be confirmed by boiling the residue for two to three minutes with HCl, and when cool, adding a few drops of 0·5 per cent of chlorinated lime solution, in such a manner that the liquids do not mix A fine blue colour results if acetanilide be present.

Commercial essence of vanilla is usually made with about 5 per cent. of vanillas, the menstruum varying in strength from 40 to 50 per cent alcohol in the best varieties. Sugar is sometimes added, but not always. The average vanillin content is 0·1 to 0·2. Much higher values than these indicate the presence of synthetic vanillin

Dox and Plaisance[1] have described the following method for the determination of vanillin in extracts of vanilla. In depends on the use of thiobarbituric acid in the presence of 12 per cent hydrochloric acid as a precipitating agent. The precipitate consists of a condensation product 3-methoxy-4-hydroxy-benzal-malonyl-thiourea. The method of procedure is as follows. 25 c.c. of the extract is freed from alcohol, transferred to a 50 c.c. standard flask, and filled up with lead acetate solution. After standing for several hours at about 37° C., the contents of the flask are filtered through a dry filter. The filtrate should be a straw colour, indicating absence of caramel. Forty c.c. of the filtrate is transferred to another 50 c.c. flask, and sufficient concentrated hydrochloric acid is added to make the volume 50 c.c. After standing a few minutes the lead chloride is removed by filtration and 40 c.c. of the filtrate is taken for the determination. On adding thiobarbituric acid in 12 per cent hydrochloric acid solution, an orange-coloured precipitate results, which, after standing overnight, is filtered on a Gooch filter, washed with 12 per cent. hydrochloric acid, and dried at 98°. A correction is made for the solubility of the condensation product which amounts to 2·6 milligrammes. The conversion factor for the vanillin equivalent to the weight of condensation product obtained is 0·5462, or $\frac{6}{11}$, after correcting for the solubility and the aliquot part taken. Thus, the weight of precipitate obtained from 64 per cent. of 25 c.c. of extract was 0·450, and corrected for solubility 0·476, equivalent to 0·026 gramme of vanillin, or 0·16 per cent. of the original extract

The method is not applicable to artificial extracts where caramel is

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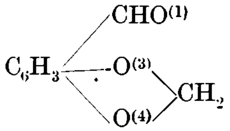
[1] *Amer Jour. Chem.* **(1916)**, 481

added, since caramel contains furfural derivatives which react with thiobarbituric acid. A delicate test for caramel is the reaction with phloroglucinol. After clarification and removing excess of lead as chloride, on the addition of a solution of phloroglucinol a brown precipitate is formed. If caramel is absent a delicate rose-pink colour or a slight pink precipitate may be obtained.

HELIOTROPIN.

This body, also known as piperonal, is a white crystalline compound possessing a powerful odour of heliotrope. It is the methylene ether of protocatechuic aldehyde, of the constitution—



The source from which it was originally made is the base piperine, $C_{17}H_{19}NO_3$. Ground pepper, preferably white Singapore pepper (which contains up to 9 per cent. of the alkaloid), is mixed with slaked lime and water, and the whole evaporated to dryness on a water-bath. The dry mass is then extracted with ether, which deposits the piperine on evaporation; or the pepper may be exhausted with alcohol, and the alcohol recovered. The semi-solid residue is mixed with potash solution, and the insoluble powder left is washed with water and recrystallieed from alcohol, when the piperine is obtained nearly pure. When boiled with solution of caustic potash in alcohol, the base is converted into potassium piperate, which on oxidation with potassium permanganate yields heliotropin. The heliotropin of commerce, however, is manufactured by the oxidation of safrol. This body (*q.v.*) and its isomer isosafrol yield large quantities of heliotropin on oxidation with potassium permanganate or chromic acid.

To prepare heliotropin from isosafrol (which results from the isomerisation of safrol with alkalis), 5 parts of isosafrol are treated with a solution of 25 parts of potassium bichromate, 38 parts of concentrated sulphuric acid, and 80 parts of water. The reaction product is steam distilled and the distillate is extracted with ether, and the heliotropin obtained is purified by means of alkaline bisulphite in the usual manner.

Heliotropin melts at 37°, but its perfume is injured by exposure to a temperature several degrees below this, and it should always be stored in cool dark places. In very hot weather the stock may with advantage be kept dissolved in alcohol, ready for use. Its perfume is a powerful heliotrope odour, and is improved by blending it with a little coumarin or vanillin, or with bergamot, lemon, or neroli oil. Attention should be drawn to the fact that the fancy perfumes whose names resemble heliotrope are usually mixtures of heliotropin—the cheaper ones being chiefly acetanilide, the more expensive ones containing vanillin or coumarin.

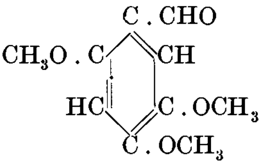
Heliotropine forms a number of well-defined crystalline compounds, which are suitable for its identification. Bromopiperonal

$$C_6H_2Br\,.\,(CHO)(O_2CH_2)$$

is prepared by treating heliotropine dissolved in carbon bisulphide, with a slight excess of bromine. It forms crystalline needles melting at 129°. The oxime of heliotropine exists in two isomeric forms, one melting at 110° to 112°, and the other at 146°. The semi-carbazone melts at 146°. It also yields a mononitro-derivative which melts at 94·5°, and on oxidation yields piperonylic acid melting at 228°, which on reduction yields piperonyl alcohol melting at 51°.

ASARYLIC ALDEHYDE.

Asarylic aldehyde, $C_{10}H_{12}O_4$, is present in calamus oil, and also results from the oxidation of asarone. It has the constitution—



Asarylic aldehyde is a crystalline body melting at 114°, and yields asaric acid on oxidation, which melts at 144°.

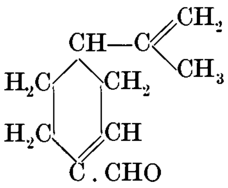
Fabinyi and Széki[1] give the following details of the compounds yielded by this aldehyde, which are serviceable for identification purposes. When the aldehyde is heated on the water-bath with 25 per cent. hydrochloric acid, it yields a triphenylmethane derivative, nonamethoxytriphenylmethane, a body consisting of snow-white crystals, melting at 184·5°. The action of concentrated nitric acid upon the solution in glacial acetic acid of this triphenylmethane derivative gives rise to 1, 2, 5-trimethoxy-4-nitrobenzene (melting at 130°). With bromine, nonamethoxytriphenylmethane combines, with separation of a molecule of trimethoxy bromobenzene, into a tribromo additive compound of hexamethoxy diphenylmethane, a deep violet-blue body. The 1, 2, 5-trimethoxy-4-bromobenzene (melting at 54·5°) may be obtained more readily from asaronic acid.

PERILLIC ALDEHYDE.

Perillic aldehyde, $C_{10}H_{14}O$, is present in the essential oil of *Perilla nankinensis*. It has been examined by Semmler and Zaar,[2] who isolated it from the oil by means of its sodium sulphite compound. Perillic aldehyde has the following characters:—

Boiling-point at 10 mm.	104° to 105°
Specific gravity at 18°	0·9617
Refractive index	1·50746
Specific rotation	− 146°

Its constitution is as follows:—



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[1] *Berichte*, **43** (1910), 2676.

[2] *Ibid.*, **44**, 52 and 815.

By reduction with zinc-dust and acetic acid it yields the acetic ester of perillic alcohol, from which the alcohol itself is separated by saponification.

The oxime of perillic aldehyde melts at 102°, and when heated with acetic anhydride in presence of sodium acetate, is converted into the nitrile of perillic acid, a liquid having the following characters:—

Boiling-point at 11 mm.	117°
Specific gravity at 20°	0·944
Refractive index	1·4977
Specific rotation	− 115°

On saponification the nitrile yields perillic acid, $C_{10}H_{14}O_2$, a solid body having the following characters:—

Melting-point	130° to 131°
Boiling-point at 10 mm. pressure	164° ,, 165°
Specific rotation	− 20°

Furukawa and Tomizawa[1] state that perillic aldehyde has the following characters:—

Specific gravity at 15°	0·9675
Boiling-point	237°
Specific rotation	− 145·8°

and that it yields two oximes. Of these the α-anti-aldoxime melts at 102° and is 2000 times as sweet as sugar. The β-syn-aldoxime melts at 129° and is not sweet. The phenylhydrazone melts at 107·5° and the semicarbazone at 190° to 199°. The nitrile, according to these chemists boils at 123° at 15 mm., and has a specific gravity 0·949 at 15°. They give 132° to 133° as the melting-point of perillic acid, which yields an amide $C_9H_{13} . CO . NH_2$ melting at 164° to 165°. Perillic alcohol has a specific gravity 0·969 and boils at 118° to 121° at 11 mm.

Dibromoperillic acid melts at 166° to 167°.

These results show that the structure of perillic aldehyde is similar to that of limonene, and that, consequently, the reducible double bond is next to the aldehydic group.

When perillic acid is dissolved in five times its weight of amyl alcohol and is reduced by sodium at the boiling temperature, dihydroperillic acid, $C_{10}H_{16}O_2$, is obtained. This acid melts at 107° to 109° C. By the reduction of its methyl ester by means of sodium, dihydroperillic alcohol is formed, which is a liquid with a rose odour and having the following characters:—

Boiling-point at 10 mm.	114° to 115°
Specific gravity at 19°	0·9284
Optical rotation	± 0°
Refractive index	1·4819

MYRTENAL.

Myrtenal, $C_{10}H_{14}O$, is an aldehyde found in the oil of *Perilla nankinensis*, associated with perillic aldehyde. It is also formed by the reduction of myrtenol, an alcohol of the formula $C_{10}H_{16}O$, occurring in oil of myrtle leaves. Myrtenal has the following characters:—

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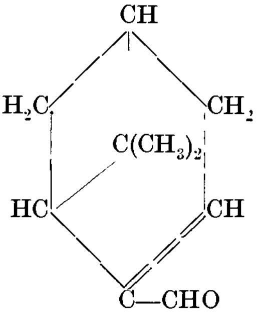
[1] *Jour. Chem. Ind. Tokyo*, 23 (1920), 342.

Boiling-point at 10 mm.	87° to 90°
Specific gravity at 20°	0·9876
Refractive index	1·5042
Melting-point of semi-carbazone	230°
„ „ „ oxime	71° to 72°

Its constitution is—



AROMADENDRAL.

This aldehyde has been isolated from various *Eucalyptus* oils by Baker and Smith. It has a pleasant odour resembling that of cumic aldehyde, with which Schimmel & Co. have considered it to be identical. This, however, is improbable, and Baker and Smith[1] consider it to have the formula $C_9H_{12}O$, which would make it to be a lower homologue of the terpenic aldehydes. Its physical characters, however, are somewhat doubtful, as specimens isolated from the oils of *Eucalyptus hemiphloia* and *Eucalyptus salubris* show. These are as follows:—

	From E. Hemiphloia.	From E. Salubris.
Boiling-point	210°	218° to 219°
Specific gravity	0·9478	0·9576
„ rotation	− 49° 12'	− 90° 25'
Refractive index	—	1·5141

It forms an oxime melting at 85°, and a phenylhydrazone melting at 104° to 105°, or possibly a few degrees higher. It also forms a naphthocinchoninic acid melting at 247°, and on oxidation yields aromadendric acid melting at 137° to 138°, when dried at 110°. These figures are to be accepted with reserve, as it is not certain that aromadendral has yet been separated free from cumic aldehyde.

CRYPTAL.

Baker and Smith[2] have isolated an aldehyde from the oils of *Eucalyptus hemiphloia* and *Eucalyptus bractata*, of the formula $C_{10}H_{16}O$, which they have named cryptal. Two specimens prepared from the former oil had the following characters:—

Specific gravity at 20°	0·9431	0·9426
Optical rotation	− 76·02°	− 76·2°
Refractive index at 20°	1·4830	1·4830
Boiling-point at 10 mm.	98° to 100°	99° to 100°
Melting-point of semi-carbazone	176° „ 177°	176° „ 177°

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[1] *Jour. Proc. Roy. Soc., N.S.W.* (1900), xxxiv.

[2] *A Research on the Eucalypts*, 2nd edition, 383.

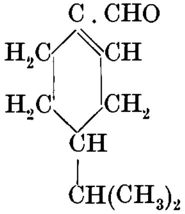
When prepared from the latter oil, two specimens had the following characters :—

Specific gravity at 20°	0·9443	0·9446
Optical rotation	− 49·7°	− 50·2°
Refractive index at 20°	1·4849	1·4842
Melting-point of semi-carbazone	180°	180°

All these specimens may be mixtures of the two optically active varieties of the aldehyde.

PHELLANDRAL.

Phellandral, $C_{10}H_{16}O$, is a hydroaromatic aldehyde of the constitution—



It occurs in oil of water-fennel, from which it can be extracted by means of its bisulphite of sodium compound. It also results from the oxidation of β-phellandrene.

Phellandral has the following characters :—

Boiling-point at 5 mm.	89°
Specific gravity	0·9445
Optical rotation	− 36° 30′
Refractive index	1·4911

It is a liquid with an odour of cummin oil. It forms a semi-carbazone melting at 204° to 205°, and an oxime melting at 87° to 88°. Its phenylhydrazone, which melts at 122° to 123°, is not very serviceable for identification purposes, as it very rapidly resinifies.

On oxidation with moist silver oxide or even by exposure to the air it yields an acid, tetrahydrocuminic acid (of which it is the corresponding aldehyde) melting at 144° to 145°. This body is very useful for the identification of the aldehyde, and is easily prepared in the following manner. A few grams are exposed in a watch glass to the air for three or four days, when a crystalline mass results, which is purified by combination with sodium hydroxide in aqueous solution, extracting the solution with ether, and precipitating the free acid by means of sulphuric acid. If the aldehyde be oxidised by means of potassium permanganate, it yields a dibasic acid of the formula $C_9H_{16}O_4$, melting at 70° to 72°.

NOR-TRICYCLOEKSANTALAL.

This aldehyde, which has the formula $C_{11}H_{16}O$, appears to be the only aldehyde with eleven atoms of carbon yet found in essential oils. It was isolated from santal oil by Schimmel & Co.,[1] who gave the follow-

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[1] *Report*, October (1910), 122.

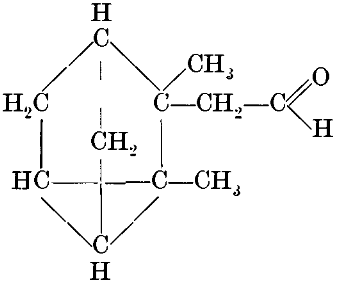
ing details in regard to it: It was separated by means of its bisulphite compound, and was found to have the following characters:—

Boiling-point at 6 mm.	86° to 87°
" " " 761 "	222° " 224°
Specific gravity at 20°	0·9938
Optical rotation	− 38° 48′
Refractive index	1·4839
Molecular refraction	47·2

It forms a semi-carbazone melting at 223° to 224° and an oxime, which is liquid, and boils at 135° to 137° at 7 mm. It is probable that this aldehyde is identical with that obtained by Semmler[1] as a decomposition product of tricycloeksantalal. To substantiate this belief, Schimmel & Co. transformed the aldehyde into teresantalic acid. Twelve c.c. of the aldehyde were heated for ninety minutes with 24 c.c. of acetic anhydride and 2·5 grams ot sodium acetate to boiling under a reflux condenser. The reaction mixture was washed with water, and fractionated, the resulting product being found to be a mixture of mono- and diacetates. By oxidation by means of permanganate of potassium, in acetone solution, teresantalic acid, melting at 148° to 152°, was obtained. The identity of this acid with the teresantalic acid occurring naturally in santal oil was established, and the following figures indicate the differences—doubtless due to want of purification between natural nor-tricycloeksantalal, and that obtained from santalol:—

	From E.I. Sandalwood Oil (Schimmel & Co.).	From Santalol (Semmler).
Boiling-point	86° to 87° (6 mm.)	92° to 94° (11 mm.)
Specific gravity	0·9938	0·9964
Optical rotation	− 38° 48′	− 30·8°
Refractive index	1·48393	1·48301
Molecular refraction	47·20	47·00
Semi-carbazone	melting-point 223° to 224°	224°
Nor-tri*cyclo*eksantalic acid	" " 91° " 93°	93°
Teresantalic acid	" " 148° " 152°	156°

This aldehyde has the following constitution:—



SANTALAL.

This aldehyde, $C_{15}H_{22}O$, was isolated from santal oil by Guerbet[2] who considered it to have the formula $C_{15}H_{24}O$. It has the following characters:—

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[1] *Berichte*, **43** (1910), 1890.

[2] *Comptes rendus* (**1900**), cxxx. 417.

Boiling-point at 10 mm	152° to 155°
Specific gravity at 20°	0·995
Optical rotation	+ 13° to + 14°
Refractive index	1·51066
Melting point of semi-carbazone	about 230°
" " " oxime	104° to 105°

It yields santalic acid, $C_{15}H_{22}O_2$, on oxidation

FARNESAL

Farnesol, $C_{15}H_{26}O$, yields, on oxidation, the aldehyde farnesal, $C_{15}H_{24}O$ It forms a semi-carbazone melting at 133° to 135°. Its characters are as follows —

Boiling point at 14 mm	173°
Specific gravity at 18°	0·893
Refractive index	1·4995

Its constitution is probably as follows —

$$(CH_3)_2C\ \ CH\,.\,CH_2\,.\,CH_2\,.\,C(CH_3)\ \ CH\,.\,CH_2\,.\,CH_2\ \ C(CH_3)CH\,.\,CHO.$$

6. KETONES.

Ketones are bodies of the type R . CO . R′, where R and R′ may be identical or different radicles. Ketones are prepared either by the oxidation of secondary alcohols or by the distillation of the calcium salts of the corresponding acids. Like the aldehydes, the ketones, in general, give condensation products with hydroxylamine and with phenylhydrazine. They also, as a general rule, form semi-carbazones The following is a useful method for determining whether a ketone is present in a given mixture By acetylating the oil, with a consequent saponification the amount of alcohols present is indicated. The specimen is then treated with sodium and alcohol, which will reduce most ketones to their corresponding alcohols. The reduced oil is now acetylated and saponified. If it now shows a greater alcohol value this is probably due to the presence of ketones Ketones may frequently be determined by absorption by acid or neutral sodium sulphite, but the generally most useful method is that based on the reduction of the ketones to alcohols To carry out this process 15 c.c of the mixture is dissolved in 60 c c. of absolute alcohol in a flask attached to a reflux condenser. From 5 to 6 grams of sodium in small pieces are then added, and the mixture kept at the boiling-point. When the metal is dissolved the mixture is cooled, and the oil is washed with water until quite neutral, after having been washed first with acetic acid The amount of alcohols present is then estimated by the usual acetylation process, and compared with that found in the unreduced sample. The difference is accounted for by the amount of ketone present

Only a few of the ketones of the fatty series are found as natural constituents of essential oils, the majority of them belonging to the aromatic or hydroaromatic series. The following members of the open-chain series are found in essential oils —

ACETONE.

Acetone, $CH_3\,.\,CO\,.\,CH_3$, is found in the distillation waters of a few essential oils such as that of the Atlas cedar. It is a mobile and very volatile liquid, miscible with water and with oils, and having the following characters :—

Specific gravity	0·7985
Boiling-point	56° to 57°

It forms an oxime melting at 59° to 60°, and a *para*-bromphenylhydrazone melting at 94°.

Methyl-amyl Ketone.

This ketone, of the constitution $CH_3 . CO . CH_2 . CH_2 . CH_2 . CH_2 . CH_3$, is found in oils of clove and cinnamon. It can be isolated by means of its sodium bisulphite compound. Its characters are as follows :—

Specific gravity	0·826
Boiling-point	151° to 152°
Melting-point of semi-carbazone	122° ,, 123°

Ethyl-amyl Ketone.

Ethyl-amyl ketone, $CH_3 . CH_2 . CO . CH_2 . CH_2 . CH_2 . CH_2 . CH_3$, has been isolated from French lavender oil. Its characters are as follows :—

Specific gravity	0·825
Boiling-point	170°
Refractive index	1·4154
Melting-point of semi-carbazone	117·5°

It does not form a crystalline compound with sodium bisulphite.

Methyl-heptyl Ketone.

This ketone has been isolated from oil of rose, and in traces, from oil of cloves. It has the following constitution :—

$$CH_3 . CO . CH_2 . CH_2 CH_2 . CH_2 . CH_2 . CH_2 . CH_3.$$

Its characters are as follows :—

Specific gravity	0·835
Boiling-point	196°
,, ,, at 15 mm.	80° to 82°
Melting-point	− 17°

It forms a crystalline semi-carbazone melting at 118° to 119°. Its oxime is liquid. On oxidation with hypobromite of sodium it yields caprylic acid.

Methyl-nonyl Ketone.

Methyl-nonyl ketone,

$$CH_3 . CO . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH_3,$$

is the principal constituent of French oil of rue. It is a solid compound of low melting-point, having a characteristic odour of rue. Its characters are as follows :—

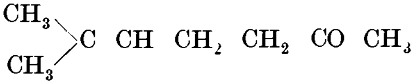
Specific gravity	0·8295
Boiling-point	233°
Melting-point	+ 13°

It yields an oxime melting at 46° to 47°, and a semi-carbazone melting at 123° to 124°.

METHYL-HEPTENONE

Methyl-heptenone, $C_8H_{14}O$, occurs in various essential oils, especially lemon-grass oil, in which it is associated with, and difficult to separate from, the aldehyde citral

It is a liquid of strong odour, recalling that of amyl acetate, and has the constitution —



$$\left.\begin{matrix}CH_3\\ CH_3\end{matrix}\right>C\ CH\ CH_2\ CH_2\ CO\ CH_3$$

Methyl-heptenone has the following characters —

	From Lemon grass Oil	From Decomposition of Citral
Boiling point . . .	173°	173° to 174°
Specific gravity . . .	0 855	0 8656
Refractive index at 15°	1 4380	—
Optical rotation . . .	± 0°	± 0°

It forms a semi-carbazone melting at 136° to 138°, which can be obtained as follows Ten c c of methyl-heptenone are dissolved in 20 c c of glacial acetic acid, and a mixture of 10 grams of semi-carbazide hydrochloride and 15 grams of sodium acetate dissolved in 20 c c of water is added After half an hour the semi-carbazone is precipitated by the addition of water, and recrystallised from dilute alcohol

Methyl-heptenone also forms a bromine derivative which is well suited for the identification of the ketone This body, which has the formula $C_8H_{12}Br_3O\ OH$, melts at 98° to 99°, and is obtained as follows Three grams of methyl-heptenone are mixed with a solution containing 3 grams of caustic soda, 12 grams of bromine, and 100 c c of water After a time an oily substance is deposited, which is extracted with ether The solvent is evaporated, and the residue, redissolved in ether, is treated with animal charcoal and filtered On slow evaporation the product is obtained in well-defined crystals

Methyl-heptenone combines with sodium bisulphite On reduction by means of sodium and alcohol, it forms the corresponding alcohol, methyl-heptenol, $C_8H_{15}OH$, which has the following characters —

Boiling point	174° to 176°
Specific gravity . .	0 8545
Refractive index . . .	1 4505

This alcohol has been identified in oil of linaloe.

Ciamician and Silber[1] have found that light has a marked effect on methyl-heptenone The ketone was kept in a glass flask, exposed to the light for five months, the flask being exhausted of air, which was replaced by oxygen When the seal was broken, the contents of the flask were found to be at reduced pressure, and the oxygen was mainly converted into carbon dioxide

The methyl-heptenone was decomposed, with the formation of acetone, a ketonic glycol, $C_8H_{16}O_3$, and a hydroxydiketone, $C_8H_{14}O_2$

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[1] *Berichte*, **46** (1913), 3077

DIACETYL.

Diacetyl, $CH_3 . CO . CO . CH_3$, is a diketone found in the distillation waters of santal, caraway, orris, savin, pine, and other essential oils. It has the following characters —

Boiling-point	87° to 88°
Specific gravity at 22°	0 9734
Melting-point of osazone	243°
„ „ „ phenylhydrazone	133° to 134°

PUMILONE.

Pumilone, $C_8H_{14}O$, has been isolated from the oil of *Pinus pumilio* It is a ketone having the characteristic odour of the oil, and whose characters are as follows :—

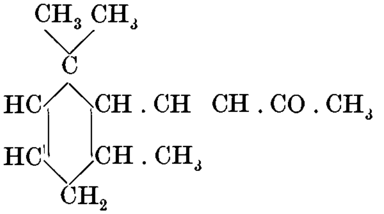
Specific gravity	0·9314
Boiling-point	216° to 217°
Optical rotation	− 15°
Refractive index	1·4646

IONONE.

The ketone, ionone, is one of the most important of all the synthetic perfumes, and one most valued by perfumers as being indispensable for the preparation of violet odours.

In 1893, after many years of patient research, Tiemann and Kruger[1] succeeded in preparing this artificial violet perfume which they termed ionone. The chemical relationships of this body are so interesting and important that Tiemann's work is here dealt with fairly fully.

The characteristic fragrance of the violet is also possessed to a considerable extent by dried orris root (iris root), and believing, although apparently erroneously, that both substances owed their perfume to the same body, Tiemann and Kruger used oil of orris for their experiments, instead of oil of violets, of which it was impossible to obtain a sufficient quantity. The root was extracted with ether, the ether recovered, and the residue steam distilled. The non-volatile portion consists chiefly of resin, irigenin, iridic acid, and myristic acid, whilst the volatile portion consists of myristic acid and its methyl ester, oleic acid, oleic anhydride, oleic esters, and the characteristic fragrant body which they termed irone. Irone (*q.v.*) has the formula $C_{13}H_{20}O$, and is an oil scarcely soluble in water The smell of this oil is quite unlike violets when in concentrated form, but if diluted, resembles them to some extent. Irone is clearly a methyl ketone of the constitution—



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[1] *Berichte*, **26** (1893), 2675.

In order to attempt to synthesise irone, experiments were made which finally led to the condensation of citral with acetone, in the presence of alkalis. Irone was not obtained, but an isomer, which Tiemann called pseudo-ionone, as follows —

$$C_{10}H_{16}O + (CH_3)_2CO = C_{13}H_{20}O + H_2O$$

Pseudo-ionone is an oil, having the following characters —

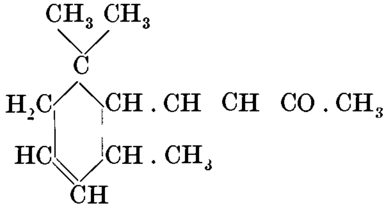
Specific gravity at 20°	0·8980
Refractive index	1·53346
Boiling-point at 12 mm	143° to 145°

If pseudo-ionone be heated with dilute sulphuric acid and a little glycerine, it is converted into another isomeric ketone, and now well-known ionone, $C_{13}H_{20}O$.

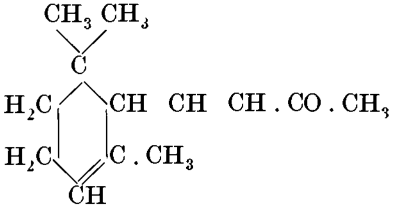
This body is now recognised to be a mixture of two isomeric ketones, known as α-ionone and β-ionone The commercial article, which is a mixture of the two ketones has approximately the following characters —

Boiling-point	126° to 128° at 10 mm.
Specific gravity	0·935 to 0·940
Refractive index	1·5035 ,, 1·5070
Optical rotation	± 0°

It has a characteristic violet odour, and at the same time recalls the vine blossom. Tiemann originally assigned to this body the formula—

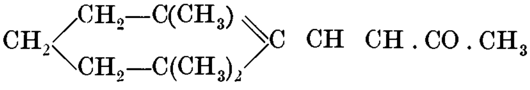


But further researches on the chemistry of citral caused him later to support the formula—



which is now accepted as representing α-ionone.

Barbier and Bouveault,[1] however, assigned to it the unlikely formula—



$$CH_2\left<\begin{matrix}CH_2\text{—}C(CH_3)\\CH_2\text{—}C(CH_3)_2\end{matrix}\right>C\ CH\ CH.CO.CH_3$$

Tiemann later [2] succeeded in resolving ionone into the two isomeric

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[1] *Comptes rendus* (**1897**), 1308

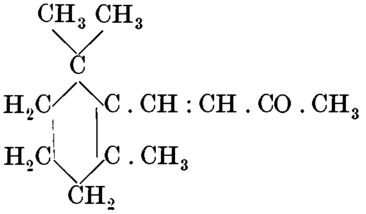
[2] *Berichte*, **31** (1898), 808, 867.

compounds, which he terms α-ionone and β-ionone. Tiemann and Krüger obtained ionone by heating pseudo-ionone with dilute sulphuric acid. De Laire, using strong acid, obtained a quite similar body, but one which yielded different derivatives. This body is the original *iso*-ionone, or, as it is now called, β-ionone. α-Ionone is prepared from the commercial product by converting it into the crystalline oxime, which is recrystallised from petroleum, and regenerating the ketone by means of dilute sulphuric acid, when α-ionone results. It has the constitution given above, and its characters are as follows :—

Specific gravity	0·934
Refractive index	1·4990
Boiling-point	127° to 128° at 12 mm.
Melting-point of oxime	89° to 90°
,, ,, ,, semi-carbazone . . .	107°
,, ,, ,, bromphenylhydrazone . .	142° to 143°

β-ionone is obtained from the commercial mixture by means of the semi-carbazone, which crystallises more readily than the corresponding derivative of the α-ketone, and can thus be separated.

The constitution of β-ionone is—



Its characters are as follows :—

Specific gravity	0·949
Boiling-point	134° to 135° at 12 mm.
Refractive index	1·5198
Melting-point of semi-carbazone . . .	148° to 149°
,, ,, ,, bromphenylhydrazone . .	116° ,, 118°

Some of the most important modern work, which has led to good practical results, on the ionone question, is that of Dr. Philippe Chuit. Recognising the distinct differences between α-ionone and β-ionone from a perfumer's point of view, Chuit has devoted considerable time to devising practicable methods for their separation. The chief constituent of the ionone of commerce is α-ionone. By the use of concentrated sulphuric acid in the cold, the principal isomerisation product of pseudo-ionone appears to be β-ionone, and under the name violettone this product was put on the market. Numerous patents have been taken out for the preparation of the separate ionones, which need not be here discussed. Although ionone does not readily combine with alkaline bisulphite, yet it does so by prolonged boiling with the solution of bisulphite, a discovery made by Tiemann and utilised by him to remove impurities from crude ionone. Further, it was shown that the hydrosulphonic compound of α-ionone crystallised more readily than that of β-ionone, whilst the corresponding compound of β-ionone was the more easily decomposed by a current of steam. These facts constituted a step towards the effectual separation of the isomeric ionones.

It has been proved that whilst concentrated sulphuric acid at a low temperature caused isomerisation of pseudo-ionone, so that the resulting product consists chiefly of β-ionone, the use of phosphoric, hydrochloric, and hydrobromic acids at low temperatures yields chiefly α-ionone.

In conjunction with Bachofen, Chuit has devised a method for separating the isomeric ionones depending on the following facts The method is based on the insolubility of the sodium salt of the hydrosulphonic compound of α-ionone in the presence of sodium chloride, whilst the corresponding β-compound remains in solution It sodium chloride be added to a hot solution of the hydrosulphonic compounds, separation of the α-salt takes place slowly as the solution cools and the salt crystallises in fine white scales, which can be recrystallised from hot water The β-compound remains in solution

As an example of the efficacy of this separation the following is given - 5 grams of α-ionone and 5 grams of β-ionone were boiled with bisulphite solution for four and a halt hours To the solution, measuring 165 c c , 40 grams of sodium chloride were added On cooling and standing, 11 grams of moist crystals were obtained, which on decomposing in the usual manner, by caustic soda solution, yielded on steam distillation 5 grams of α-ionone The β-ionone was recovered from the mother liquor with a trifling loss

The composition of the ordinary hydrosulphonic sodium compound of α-ionone is, according to Chuit,

$$(C_{13}H_{21}O\ SO_3Na\ )_2 + 3H_2O,$$

whilst that of β-ionone is $C_{13}H_{21}O\ SO_3Na + 2H_2O$

From the point of view of practical perfumery, Chuit points out that the possession of the two pure isomers enables perfumers to produce numerous shades of violet perfume, with characteristic and distinct odours α-ionone has a sweeter and more penetrating odour, rather resembling orris than violets, whilst β-ionone is said to more closely resemble the true fresh violet flower

Patents covering the separation of the ionones are numerous

The following is a copy of the provisional and complete specifications provided by the original patentee. The patent has now expired Further examination of the bodies in question has shown that a few unimportant details require correction —

Provisional Specification —I, Johann Carl Wilhelm Ferdinand Tiemann, member of the firm of Haarmann and Reimer, of Holzminden, residing at Berlin, Germany, do hereby declare the nature of this invention to be as follows —

I have found that a mixture of citral and acetone, if it is subjected, in the presence of water, for a sufficiently long time to the action of hydrates of alkaline earths or of hydrates of alkali metals, or of other alkaline agents, is condensed to a ketone of the formula $C_{13}H_{20}O$ This substance, which I term " Pseudo ionone," may be produced for instance in shaking together for several days equal parts of citral and acetone with a solution of hydrate of barium, and in dissolving the products of this reaction in ether

The residue of the ether solution is fractionally distilled under a reduced pressure and the fraction is collected, which boils under a pressure of 12 mm at a temperature of from 138° to 155° C., and from it the unattacked citral and unchanged acetone and volatile products of condensation are separated in a current of steam, which readily carries off these bodies

The product of condensation remaining in the distilling apparatus is purified by the fractional distillation *in vacuo*. Under a pressure of 12 mm a liquid distils off at a temperature of from 143° to 145° C. This product of condensation which I term " Pseudo-ionone," is a ketone readily decomposable by the action of alkalis. Its formula is $C_{13}H_{20}O$, its index of refraction is $nD = 1·527$, and its specific weight 0·904.

The pseudo-ionone has a peculiar but not very pronounced odour; it does not combine with bisulphite of sodium as most of the ketones of the higher series, but, in other respects, it possesses the ordinary characteristic properties of the ketones, forming, in particular, products of condensation with phenylhydrazine, hydroxylamine and other substituted ammonias

Although the odour of the pseudo-ionone does not appear to render it of great importance for its direct use in perfumery, it is capable of serving as raw material for the production of perfumes, the pseudo-ionone being converted by the action of dilute acids into an isomeric ketone, which I term "Ionone," and which has most valuable properties for perfumery purposes. This conversion may be effected, for example, by heating for several hours in an oil bath 20 parts of "pseudo-ionone" with 100 parts of water, 2·5 parts of sulphuric acid, and 100 parts of glycerine to the boiling-point of the mixture The product resulting from this reaction is dissolved in ether, the latter is evaporated, and the residue subjected to the fractional distillation *in vacuo*. The fraction distilling under a pressure of 12 mm. at a temperature of from 125° to 135° C. is collected. This product may be still further purified by converting it by means of phenylhydrazine or other substituted ammonias into a ketone condensation product decomposable under the action of dilute acids.

The ketone derivatives of the pseudo-ionone are converted under similar conditions into ketone-derivatives of the ionone. The pure ionone corresponds to the formula $C_{13}H_{20}O$, it boils under a pressure of 12 mm. at a temperature of about 128° C., its specific weight is 0·935, and its index of refraction $nD = 1·507$.

The ionone has a fresh flower-perfume recalling that of violets and vines, and is peculiarly suitable for being used in perfumery, confectionery, and distillery.

The ionone, when subjected at a higher temperature to the action of hydroiodic acid, splits off water and gives a hydrocarbon corresponding to the formula $C_{13}H_{18}$, boiling under a pressure of 12 mm at a temperature of from 106° to 112° C. This hydrocarbon is converted by strong oxidising agents into an acid of the formula $C_{12}H_{12}O_6$, melting at a temperature of 214° C

Complete Specification.—I, Johann Carl Wilhelm Ferdinand Tiemann, member of the firm of Haarmann & Reimer, of Holzminden, residing at Berlin, Germany, do hereby declare the nature of this invention, and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

I have found that a mixture of citral and acetone, if it is subjected in the presence of water for a sufficiently long time to the action of hydrates of alkaline earths or of hydrates of alkali metals, or of other alkaline agents, is condensed to a ketone of the formula $C_{13}H_{20}O$ This substance, which I term "Pseudo-ionone," may be produced, for instance, in shaking together for several days equal parts of citral and acetone with a solution of hydrate of barium, and in dissolving the products of this reaction in ether.

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The ketone derivatives of the pseudo-ionone are converted under similar conditions into ketone derivatives of the ionone. The pure ionone corresponds to the formula $C_{13}H_{20}O$, it boils under a pressure of 12 mm. at a temperature of about 128° C., its specific weight is 0·935, and its index of refraction $nD = 1{\cdot}507$.

The ionone has a fresh flower-perfume recalling that of violets and vines, and is peculiarly suitable for being used in perfumery, confectionery, and distillery.

The ionone, when subjected at a temperature surpassing 100° C. to the action of hydroiodic acid, splits off water and gives a hydrocarbon corresponding to the formula $C_{13}H_{18}$, boiling under a pressure of 12 mm. at a temperature from 106° to 112° C. This hydrocarbon is converted by strong oxidising agents into an acid of the formula $C_{12}H_{12}O_6$ melting at a temperature of 214° C.

Having now particularly described and ascertained the nature of this invention, and in what manner the same is to be performed, I declare that what I claim is:—

1. A new chemical product termed pseudo-ionone obtained by the reaction of citral upon acetone in the presence of alkaline agents and subsequent treatment of the products, substantially as described.
2. A new article of manufacture termed ionone suitable for perfumery and the like and having the characteristics hereinbefore set forth, obtained from pseudo-ionone referred to in the preceding claim, substantially as described.
3. The process for the production of the pseudo-ionone referred to in the first claim, consisting in the subjection of a mixture of citral and acetone to the action of an alkaline agent, and in purifying the product of this reaction, extracted by means of ether, by fractional distillation, substantially as described.
4. The process for the production of the ionone referred to in the second claim, consisting in treating the pseudo-ionone referred to in the first claim or its ketone condensation products with phenylhydrazine or other ammonia derivatives, finally with acids, substantially as described.

The commercial product, as put on to the market, was originally a 10 per cent. solution of ionone in alcohol. This was due not only to the expensive nature of the product, but also to the fact that its odour is very intense, and when pure, not like that of violets. Ten grams of this solution are sufficient to produce 1 kilo of triple extract of violets when diluted with pure spirit. But to-day 100 per cent. violet perfumes, such as the violettone, above mentioned, are regular commercial articles. The perfume is improved both for extracts and soaps by the addition of a little orris oil, but in the author's opinion the odour of ionone is not nearly so delicate as that of the natural violet, although far more powerful.

With regard to the practical use of ionone, which sometimes presents a difficulty to perfumers, Schimmel & Co. have published the following remarks:—

"This beautiful article maintains its position in the front rank of preparations for perfumery, and will probably remain without a rival among artificial perfumes for some time to come. Although the violet scent has long been a favourite perfume, its popularity has doubled through the invention of ionone, and it is not too much to say that the introduction of that body alone has made it possible to produce a perfect extract. Some of the leading European perfumers produce violet extracts which may be recommended as examples of excellence, and which have deservedly become commercial articles of the first importance. The inventors of ionone have earned the gratitude of the entire perfumery industry, and may be congratulated in turn upon the remarkable success of their invention.

"As we have already pointed out on a previous occasion, the preparation of a violet extract in which ionone is made to occupy its due position is not such an easy task as is often assumed; on the contrary, it requires a long and thorough application.

"To obtain a perfect result with ionone is an art in the true meaning of the word, and on that account no inexperienced hand should attempt it. We again and again lay stress upon this fact, because in our business we are constantly brought face to face with people who think that they can make a suitable violet extract by simply mixing alcohol with ionone solution. This view is quite wrong. The employment of ionone presupposes above everything else that the user is acquainted with the peculiarities of the article and knows how to deal with them. Again and again the uninitiated come to us with the complaint that ionone has no odour at all, or that it smells disagreeably, although, as a matter of fact, these objections are usually withdrawn upon closer acquaintance with the article. The assumptions in question are only due to a blunting of the olfactory nerves, or, more correctly, to a nasal delusion, which also occurs sometimes in the case of other flower odours and to which people are known to be particularly liable when smelling freshly gathered violets.

"The principal thing in connection with the employment of ionone is to discover its proper degree of dilution. In its natural state the body is so highly concentrated as scarcely to remind one of violets. This is the reason why it was placed in trade in the form of a 10 per cent. solution, and not in its pure state This form has proved an exceedingly useful one. In using it for extracts, powders, sachets, etc., the solution must be further diluted and fixed with some orris oil, civet, and musk"

By using acetone homologues, homologous or reduced ionones are produced which have intense odours of a similar character.

The above remarks apply to the commercial product known as ionone There are, however, numerous other patents in existence for the preparation of artificial violet oil. The complete specification of one of these reads as follows —

I, Alfred Julius Boult, of 111 Hatton Garden, in the County of Middlesex, Chartered Patent Agent, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement —

This invention relates to a process for manufacturing hitherto unknown oils having a violet scent

Patents No. 8,736 of 1 May, 1893, and No. 17,539 of 18 September, 1893, describe the manufacture of ionone, which is an essential oil, boiling at 128° under 12 mm. pressure, and of specific gravity of 0·935. This oil is optically inactive.

The final product of the process according to the present invention is an oil boiling at 142° to 150° C. under 12 mm. pressure and of specific gravity of from 0 94 to 0·95 It differs from ionone by having when concentrated a very strong scent similar to that of sandalwood by producing a left handed rotation of a polarised ray and by having when diluted a scent more closely approaching that of natural violets than does that of ionone.

Analysis shows that this oil consists of several ketones of the groups $C_{13}H_{20}O$ of higher boiling-points and greater density than those of ionone. These ketones are optically active, and both their existence and their artificial production have been hitherto unknown.

The process employed in carrying out this invention is as follows A mixture of 1 to 1¼ parts acetone (45 kg.), 1 part of lemon grass oil (38 kg), 1½ to 2 parts of alcohol (75 kg.), 1 to 2 parts of a concentrated lime free solution of chloride of lime (75 kg.), to which is added a little cobaltous nitrate (30 gr.) dissolved in water, is boiled during six to eighteen hours at a temperature of 70° to 80° C. in a reflux cooling apparatus.

The alcohol and the excess of acetone are first distilled off and then an essential oil is obtained, which, after the first distilled portion (about 4 kg.) of specific gravity 0·88 has been removed, represents the stuff for producing artificial oil of violets. It is an essential oil with a boiling-point of 155° to 175° at 12 mm. pressure (about 25 kg.).

This oil is heated at 110° C. with a solution of bisulphate of sodium of 11° Beaume (42 kg. for 360 litres of water) in a vessel with a mixing device until the samples distilled every day show that the first running, which has an unpleasant smell, has reached the density of 0·936 This happens after about eight days (the first running being about 8 kg).

The crude product (about 17 kg.) in the vessel is then purified by fractional distillation, all the bad-smelling parts being removed, so that finally there remains an oil of a density of 0·948 to 0·952 (15° C.) boiling at 142° to 150° under 12 mm. pressure.

The lightest portion of this oil has a specific gravity of 0·945 and boils at 142° C. under 12 mm. pressure, the largest portion of it, which has the pleasantest and strongest smell, boils at 149° C. and has a specific gravity of 0·953. Analysis has shown that both substances belong to the group of ketones $C_{13}H_{20}O$.

By using other ketones instead of acetone homologous substances may be obtained.

The product obtained by the above-described process contains no ionone, for it contains no ingredient boiling at 128° C. under the pressure of 12 mm. and having a specific gravity 0·935. The violet-like smell of the product obtained according to the present invention is the result of the presence of substances which are different from ionone, as their specific gravity and their boiling-point are higher than those of ionone. The new product has the advantage that it can be manufactured in a very simple and economical manner, and as its smell is much more like that of real violets than is the smell of ionone, and as it is more constant and less volatile than ionone, it is much more suitable for artificial violet scent than the "ionone" which has hitherto been the only artificially made substance known for this purpose, and which is much more difficult to manufacture.

Having now particularly described and ascertained the nature of the said invention as communicated to me by my foreign correspondents and in what manner the same is to be performed, I wish it to be understood that I do not claim anything described and claimed in the Specifications of Letters Patent Nos. 8,736 and 17,539, A.D. 1893, granted to Johann Carl Wilhelm Ferdinand Tiemann, but I declare that what I claim is —

1. As an article of manufacture an essential oil having the smell of violets, boiling at 142° to 150° C. under a pressure of 12 mm. and of a specific gravity of 0·948 to 0·952 (15° C.)

2. A process for the manufacture of hitherto unknown oils having the smell of violets, which oils have a higher boiling point and higher specific gravity than ionone.

3. A process for the manufacture of hitherto unknown oils boiling at 155° to 175° C. under the pressure of 12 mm., which can be converted into violet-smelling oils of higher specific gravity and higher boiling-point than those of ionone by being boiled with different substances, such, for instance, as bisulphate of sodium.

4. The manufacture of homologous substances by using other ketones instead of acetone

5. A process for the manufacture of artificial essence of violets consisting in causing lemon-grass oil, alcohol, acetone, and concentrated solutions of salts of hypochlorous acid to react on one another at the boiling temperature.

6 Process for manufacture of artificial essence of violets consisting in causing lemon-grass oil, alcohol, acetone, and concentrated solutions of salts of hypochlorous acid to react on one another at a boiling temperature, cobaltous nitrate being added if desired.

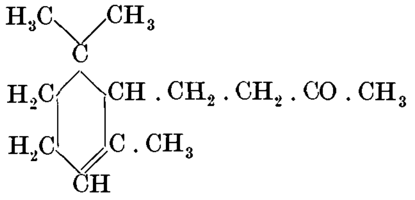
The patentees state that their invention relates to the preparation of cyclic ketones of the same group as ionone, but with higher boiling-points and higher specific gravity. They claim to have proved that, corresponding to the pseudo-ionone of the patent No. 8,736 of 1893, which distils at 143° to 145° (12 mm.), and which finally gives the ketone ionone of boiling-point 126° to 128° (12 mm.), and specific gravity 0·935 (20 C.), there exists also an iso-pseudo-ionone which distils at 149° to 151° (12 mm.), and which gives iso-ionone of boiling-point 133° to 135° (12 mm.), and specific gravity 0·943 (20 C.), and further that there exists still another iso-pseudo-ionone which distils at 157° to 160° (12 mm.), and which gives a cyclic ketone of boiling-point 142° to 146° and specific gravity 0·960 (20 C.).

They also claim that large quantities of iso-pseudo-ionone are formed in the process of Tiemann's patent, and which can be separated by distillation, coming over at a higher temperature than the ordinary pseudo-ionone.

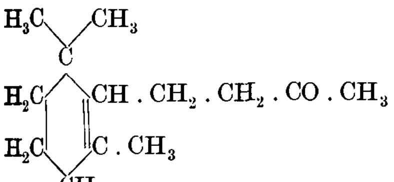
According to Hanriot ionone can be detected in very minute amount by the following reaction: If traces of it be dissolved in concentrated hydrochloric acid, the liquid becomes of an intense golden colour, and if the solution be warmed with chloral hydrate, a dirty violet colour results. The violet colouring matter is extracted by ether, and if the ether be evaporated a water-soluble violet-coloured residue is left. This test will detect 1 part of ionone in 2000.

Skita[1] has studied the reduction of ionone by means of palladium chloride. The reduction-product, dihydroionone, boils at 121° and 122° (14 mm.); it possessed a faint odour of cedarwood. By the same method, β-ionone yields a dihydroionone boiling at 126° to 129° (12 mm.). When the reduction is continued until hydrogen ceases to be absorbed, both α- and β-ionone yield tetrahydroionone, boiling at 126° to 127° at 13 mm.

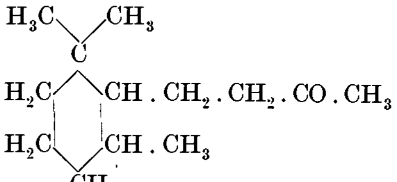
The fact that the reduction of α- and β-ionone affords two different dihydroionones indicates that the double linkage in the side chain is the first to be saturated. This agrees with the fact that continued reduction leads to the same tetrahydroionone.



Dihydroionone from α-ionone.



Dihydroionone from β-ionone.



Tetrahydroionone.

Kishner[2] has prepared the hydrocarbons corresponding to the isomeric ionones, in which the oxygen atom is replaced by two hydrogen atoms. These two hydocarbons, $C_{13}H_{22}$, are α-ionane and β-ionane. Their characters are as follows :—

	α-ionane.	β-ionane.
Boiling-point	220° to 221°	224° to 225°
Specific gravity at $\frac{20°}{0°}$	0·853	0·815
Refractive index	1·4784	1·4725

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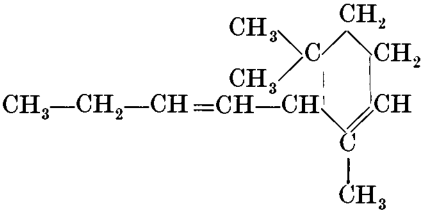
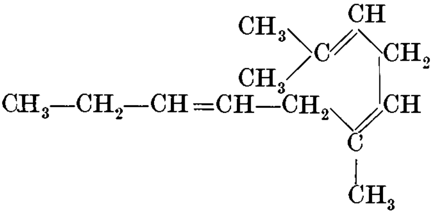
[1] *Berichte*, **45** (1912), 3312.

[2] *Jour. Phys. Chim. Russe.*, **43**, 1398.

Their constitutions are as follows :—

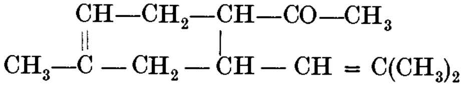


α-ionane.



β ionane.

Knoerenagel[1] has studied the products of condensation of citral with ethyl-acetoacetate, and has obtained the following bodies: β-pseudoionone $C_{13}H_{20}O$,

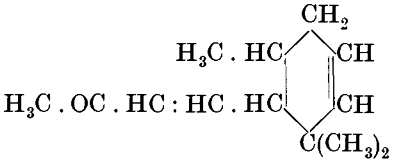


$$\begin{array}{l} \mathrm{CH{-}CH_2{-}CH{-}CO{-}CH_3} \\ \quad \| \qquad\qquad | \\ \mathrm{CH_3{-}C{-}CH_2{-}CH{-}CH = C(CH_3)_2} \end{array}$$

and α-isoionone, and β-isoionone, two other closely related isomers.

IRONE.

Irone is the odorous ketone present in oil of orris. It is isomeric with ionone, having the formula $C_{13}H_{20}O$ and the constitution—



It has also been prepared synthetically by Merling and Welde,[2] by condensing Δ^4-cyclocitral with acetone.

Irone is a colourless oil, having an odour resembling that of violets. It has the following characters :—

Boiling-point at 16 mm.	144°
Specific gravity	0·940
Refractive index	1·5011
Optical rotation	about + 40°

It forms an oxime, $C_{13}H_{20}$: NOH, melting at 121·5°. If a 10 per cent. solution of irone in glacial acetic acid be allowed to stand with p-bromphenylhydrazone, crystals of irone p-bromphenylhydrazone separate,

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[1] *J. prakt. Chem.* [2], **97**, 288.

[2] *Ann. Chem.* **(1909)**, 119.

which melt, after repeated recrystallisation from methyl alcohol, at 174° to 175°. Irone also forms a thiosemi-carbazone melting at 181°.

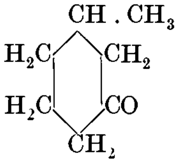
A ketone isomeric with irone has been isolated from oil of cassie flowers. It is possible that this is β-ionone, but its identity has not yet been established

METHYL-HEXANONE

Methyl-1-hexanone-3, $C_7H_{12}O$, is found naturally in pennyroyal oil, and is obtained by the decomposition of pulegone. It is an aromatic liquid having the following characters —

Boiling-point	167° to 168°
Specific gravity at $\frac{18^\circ}{4^\circ}$	0·911
Optical rotation	+ 11° 21′

Its semi-carbazone melts at 182° to 183°, and its oxime at 43° to 44°. Its constitution is—

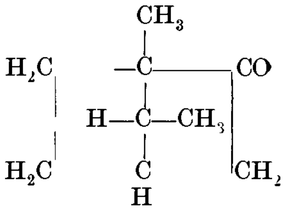


SANTENONE.

Santenone, $C_9H_{14}O$, is a lower homologue of the regular "terpenic" ketones of the formula $C_{10}H_{16}O$ It occurs naturally in sandalwood oil, and may be obtained by the oxidation of isosantenol, the alcohol resulting from the hydration of santene Santenone has the following characters —

Melting point	58° to 61°[1]
Specific rotation (in alcohol)	− 4° 40′
Boiling-point	193° to 195°

It forms a semi-carbazone melting at 222° to 224° The constitution of santenone is as follows —



SABINA KETONE

Sabina ketone, $C_{10}H_{14}O$, is not a natural constituent of essential oils, but is of considerable interest on account of its utility in the synthesis of other ketones.

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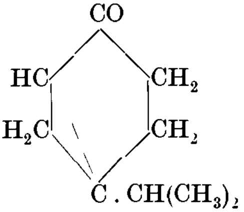
[1] The melting-point 48° to 52° given in Vol. I. was apparently determined on an impure specimen.

It results from the oxidation of sabinenic acid with peroxide of lead, sabinenic acid itself being an oxidation product of the terpene sabinene.

It is a liquid having the following characters :—

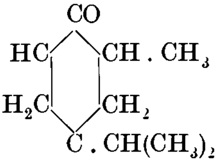
Boiling-point	218° to 219°
Specific gravity	0·953
Refractive index	1 4700
Optical rotation	– 24° 41′

It forms a semi-carbazone melting at 141° to 142°. Its constitution is probably as follows :—



Wallach[1] prepares sabina ketone in the following manner : Twenty-five grams of sabinene are treated with 60 grams of potassium permanganate, 13 grams of caustic soda, 400 c.c. of water, and 400 grams of ice. The mixture is well shaken and the unchanged hydrocarbon is distilled off in a current of steam. Manganese dioxide is then filtered off, and the sodium sabinenate separated by concentrating the filtrate, when the salt crystallises out. This is then oxidised by potassium permanganate in sulphuric acid solution.

Kotz and Lemien[2] have recently converted sabina ketone into its homologue methyl-sabina ketone, $C_{10}H_{16}O$, by first converting it into hydroxymethylene sabina ketone by Claisen's method, and then reducing this ketone, when the homologue results. It is a heavy oil, boiling at 221° and having the following formula :—



VERBENONE.

This ketone, $C_{10}H_{14}O$, is found naturally in oil of vervain, the true verbena oil. It has, when isolated from this oil, the following characters :—

Boiling-point	103° to 104° at 16 mm.
Specific gravity	0·974 at 17°
Refractive index	1·4995
Optical rotation	+ 66°

The natural ketone is, however, probably contaminated with traces of terpenes.

Verbenone results from the auto-oxidation of turpentine oil, *d*-

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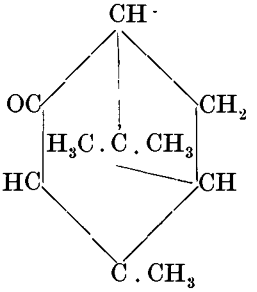
[1] *Annalen*, **359** (1908), 265.

[2] *J. prakt. Chem.*, 1914 [ii.], **90**, 314.

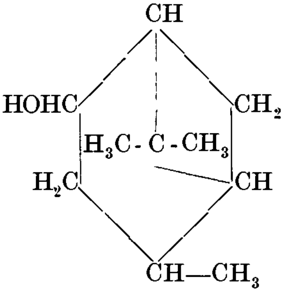
verbenone resulting from the oxidation of American, and *l*-verbenone from that of French, oil of turpentine. When purified by decomposition of its semi-carbazone, the characters of *d*-verbenone are as follows:—

Boiling-point	227° to 228°
,, ,, at 16 mm.	100°
Specific gravity	0·981
Optical rotation	+ 61° 20'
Melting-point	+ 6·5°
Refractive index	1·4993

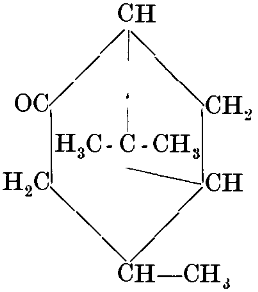
Verbenone has the following constitution :—



The constitution of verbenone has been established [1] by its reduction to the corresponding saturated secondary alcohol, dihydroverbenol, and into the corresponding saturated ketone, or dihydroverbenone.



Dihydroverbenol.



Dihydroverbenone.

Dextro-dihydroverbenol melts at 58° C. and boils at 218° C.; it yields an acetic ester, the odour of which recalls that of bornyl acetate. Dextro-dihydroverbenone is produced by the oxidation of the above alcohol by means of chromic acid, or by the reduction of verbenone by means of hydrogen in presence of colloidal palladium. It boils at 222° C. (D_{15} 0·9685; $[\alpha]_D$ + 52·1 9°; n_D^{20} 1·47535; molecular refraction 44·45) and gives a semi-carbazone melting at 220° to 221° C.; its oxime melts at 77° to 78° C. On applying Grignard's reaction to *d*-verbenone, a hydrocarbon is obtained which appears to be methylverbenene, $C_{11}H_{16}$ (boiling-point 8 mm., 49° C.; boiling-point 771 mm., 175° to 176° C.; D_{15} 0·876; D_{20} 0·872; α_D ± 0°; n_D^{20} 1·4969; molecular refraction 49·64). This inactive hydrocarbon is probably composed of a mixture of isomerides; it fixes oxygen with avidity, rapidly becoming resinified.

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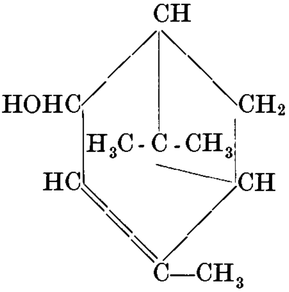
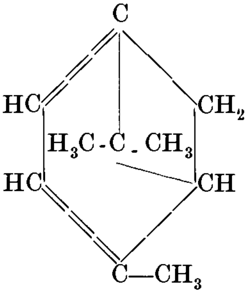
[1] Roure-Bertrand Fils, *Bulletin*, October, **1913**, 134.

When submitted to oxidation by a 2 per cent. solution of permanganate, *d*-verbenone yields pinononic acid, $C_9H_{14}O_3$, melting at 128° to 129° C., the semi-carbazone of which melts at 204° C. Lastly the constitution of verbenone, as expressed by the above formula, is further confirmed by the fact that the bicyclic system is convertible into a monocyclic system by boiling with 25 per cent. sulphuric acid, with the formation of acetone and 3-methylcyclohexene-(2)-one-(1). This cyclohexenone has been characterised by its semi-carbazone (melting-point 198° C.) and by its conversion into γ-acetobutyric acid (melting-point 36° C). The oily liquid, which did not react with sulphite, was submitted to benzoylation after dilution with pyridine. It thus gave rise to a benzoate from which was isolated *d*-verbenol. This alcohol boils at 216° to 218° C. (D_{15} 0·9742; $[\alpha]_D$ + 132·30°; $n_D{}^{20}$ 1·4890; molecular refraction 45·25). When oxidised by chromic acid it yields verbenone; with permanganate it gives pinononic acid. By the action of acetic anhydride it is converted into *l*-verbenene (boiling-point 758 mm., 159° to 160° C.; D_{15} 0·8852; α_D − 74·90°; n_D 1·49855; molecular refraction 44·61). Verbenene, when treated with powerful dehydrating agents, such as zinc chloride or phosphoric anhydride, is converted into *p*-cymene.



Verbenol.



Verbenene.

PIPERITONE.

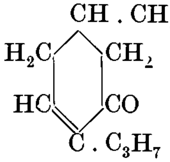
This ketone occurs in eucalyptus oils derived from a particular group of trees, the leaves of which have the venation characteristic of species yielding phellandrene-bearing oils. It follows the general rule for all constituents in eucalyptus oils, increasing in amount until the maximum is reached in one or more species. It occurs in greatest quantity in the oils of these eucalyptus trees known vernacularly as "Peppermints," such as *E. piperita*, *E. dives*, etc., and consequently is found more frequently in the oils from species growing on the eastern part of Australia.

Piperitone can be most easily obtained from the higher boiling portions of the oil of *E. dives*. It combines slowly with sodium-bisulphite, and by repeated agitation for two or three weeks eventually forms crystals in some quantity. A proportion of alcohol assists the combination. The pure ketone prepared from the purified crystals is colourless at first, but on long standing becomes slightly yellowish in tint. It has a burning peppermint-like taste and odour. The formula is $C_{10}H_{16}O$.

According to Read and Smith[1] piperitone is, under natural conditions, optically inactive. By fractional distillation under reduced pressure, it is prepared, by means of its sodium bisulphite compound, in a laevo-rotatory form. The slight laevo-rotation is probably due to the presence of traces of cryptal. By fractional distillation alone, it is usually obtained in a laevo-rotatory form; whether this is due to decomposition products or not is unknown. Piperitone has a considerable prospective economic value, as it forms thymol by treatment with formic chloride, inactive menthone by reduction when a nickel catalyst is employed, and inactive menthol by further reduction. Its characters are as follows:—

Specific gravity	0·938
Optical rotation	Laevo-rotatory − 50° or more
Refractive index	1·4837 to 1·4850
Boiling-point	229° to 230° (uncorrected)
,, ,, at 10 mm.	106° to 107°

With hydroxylamine, piperitone yields a normal oxime melting at 110° to 111°, and an oxamino-oxime melting at 169° to 170°. The semicarbazone prepared from piperitone which had been regenerated from its bisulphite compound melts at 219° to 220°. But piperitone prepared by repeated fractionation under reduced pressure yields two semi-carbazones, melting at 175° to 176° and 182° to 183° respectively. On reduction in alcoholic solution by sodium amalgam, piperitone yields a dimolecular ketone, $C_{20}H_{34}O_2$, melting at 149° to 150°. According to Smith the probable constitution of piperitone is



Givaudan & Co., however,[2] compare the properties of piperitone with those of the ketone prepared synthetically by Wallach,[3] and discovered in Japanese peppermint oil by Schimmel[4] and later in camphor oil by Schimmel, and finally in the oil of *Cymbopogon sennaarensis* by Roberts,[5]

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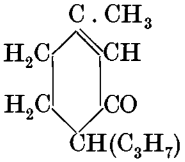
[1] *Jour. Chem. Soc.*, **1921**, 781.
[2] *P. and E.O.R.*, **1921**, 80.
[3] *Annalen*, **362** (1908), 271.
[4] Semi annual Report, French edition 1910, II., 87.
[5] *Jour. Chem. Soc.*, **107** (1915), 1465.

and consider that it is identical with this body. The constitution would then be

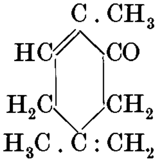


Read and Smith (*loc. cit.*) have prepared benzylidene-piperitone, of the formula $C_{10}H_{14}O : CH . C_6H_5$, by the interaction of piperitone and benzaldehyde in the presence of alcoholic sodium ethoxide. This body melts at 61°, and the discoverers claim that it is sufficiently characteristic to definitely differentiate piperitone from any of the hitherto described menthenones.

CARVONE.

Carvone, $C_{10}H_{14}O$, is the ketone characteristic of dill and caraway oils. It occurs in the dextro-rotatory form in these oils, and as laevo-carvone in kuromoji oil.

Carvone has the following constitution :—



It is a colourless oil, solidifying at low temperatures and having a characteristic odour of caraway. Its characters are as follows :—

Specific gravity	0·964
Optical rotation	± 59° 30′
Refractive index	1·5020
Boiling-point	224°

Inactive carvone can be obtained by mixing equal quantities of the optically active isomers. Carvone yields all the usual ketonic compounds such as the crystalline oxime and phenylhydrazone. The former compound is interesting on account of the fact that it is identical with nitrosolimonene (*vide* limonene). Carvone also forms a crystalline compound with sulphuretted hydrogen, $C_{10}H_{14}(OH)(SH)$. This results by passing the gas through an alcoholic solution of caraway oil saturated with ammonia gas. The resulting crystals can be purified by recrystallisation, and decomposed by alcoholic potash, when nearly pure carvone results. The following table gives the optical rotations of the purest specimens of dextro- and laevo-carvone derivatives that have been prepared :—

	Derivatives of	
	Dextro-carvone.	Laevo-carvone.
Carvone	+ 62°	− 62°
,, sulphydrate	+ 5·53°	− 5·55°
Carvoxime	+ 39·71°	− 39·34°
Benzoyl carvoxime	+ 26·47°	− 26·97°
,, hydrochlor-carvoxime	− 10·58°	+ 9·92°

The principal derivative for the identification of carvone is the oxime, which can be obtained by dissolving 5 grams of carvone in 25 c.c. of alcohol and adding a warm solution of 5 grams of hydroxylamine hydrochloride in 5 c.c. of water, and then rendering the solution alkaline by the addition of 5 grams of caustic potash in 40 c.c. of water. The carvoxime is precipitated by pouring the liquid into water, and recrystallised from alcohol. Optically active carvoxime melts at 72°, but *i*-carvoxime, which is obtained by mixing equal quantities of the two optically active isomers, melts at 93°.

The phenylhydrazone melts at 109° to 110°, and the semi-carbazone at 162° to 163° (active varieties) or 154° to 155° (inactive form). The sulphuretted hydrogen compound mentioned above melts at 210° to 211°.

By reduction carvone fixes 2 atoms of hydrogen on to the ketonic group, and 2 atoms in the nucleus, with the formation of dihydrocarveol, $C_{10}H_{18}O$, whose corresponding ketone, dihydrocarvone, $C_{10}H_{16}O$, exists in small quantities in caraway oil.

G. Vavon[1] has examined the hydrogenation of carvone, in presenc of platinum black as a catalyst, and shown that it takes place in three entirely distinct phases. Carvone fixes successively three molecules of hydrogen, giving dextro-carvotanacetone, then tetrahydrocarvone, and finally carvomenthol.

By stopping the hydrogenation at a suitable moment, it is possible to obtain any one of these three bodies.

Carvotanacetone thus prepared has the following constants :—

Boiling-point	227° to 228° C.
D_4^{18}	0·937
n_D^{18}	1·4817
Molecular rotation	46·20
$[\alpha]_{578}$	+ 59·8°

Its oxime and its semi-carbazone melt respectively at 75° C. and 173° C. Tetrahydrocarvone boils at 218° to 219° C.

D_4^{20}	0·904
n_D^{20}	1·4555
Molecular rotation	46·25
$[\alpha]_{578}$	− 27°

Carvomenthol, obtained by the fixation of $3H_2$ by carvone, is a thick liquid boiling at 217° to 218° C.

D_4^{20}	0·908
n_D^{20}	1·4648
Molecular rotation	47·49
$[\alpha]_{578}$	− 24·7°

Its acetate is a liquid with pleasant odour, boiling at 230° to 231° C.

D_{20}^{4}	0·928
n_D^{20}	1·4477
Molecular rotation	57·07
$[\alpha]_{578}$	− 27·6°

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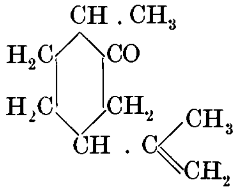
[1] *Comptes rendus*, **153**, 69.

The benzoate is a thick liquid.

Boiling-point (15 mm.)	185° to 186° C.
D_{4}^{20}	1·006
n_D^{20}	1·509
Molecular rotation	77·19
$[\alpha]_{578}$	12·9°

DIHYDROCARVONE.

Dihydrocarvone, $C_{10}H_{16}O$, is found to a small extent in oil of caraway, and can be prepared by the oxidation of dihydrocarveol by chromic acid in acetic acid solution. The ketone has the constitution :—



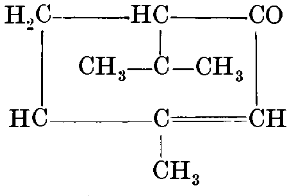
It is an oil having an odour resembling those of carvone and menthone. Its characters are as follows :—

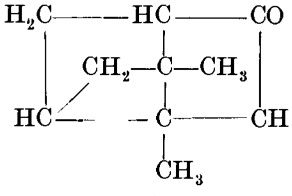
Boiling-point	221° to 222°
Specific gravity	0·930 „ 0·931
Refractive index	1·4711
Optical rotation	− 16°

It forms a characteristic dibromide, $C_{10}H_{16}Br_2O$, by the action of bromine in acetic acid, melting at 69° to 70° (optically active form) or 96° to 97° (racemic variety). Dihydrocarvoxime melts at 89° (active variety) or 115° to 116° (racemic variety).

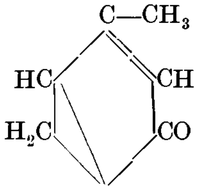
UMBELLULONE.

Umbellulone, $C_{10}H_{14}O$, is a ketone which was isolated from the oil of *Umbellularia californica*, by Power and Lees. It has been examined by Tutin [1] who assigned to it one of the following alternative constitutions :—





Semmler,[2] however, has carried out a very exhaustive examination of the ketone, and considers that its constitution is that of a bicyclic ketone of the thujone series, as follows :—



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[1] *Jour. Chem. Soc.*, **89** (1906), 1104.

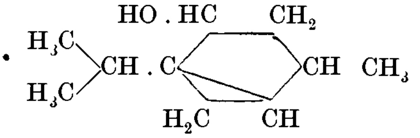
[2] *Berichte*, **40** (1907), 5017.

Umbellulone is a colourless liquid of irritating odour, recalling that of peppermint. It has the following characters :—

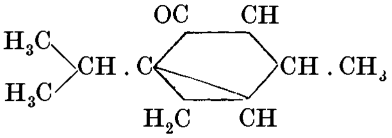
Boiling-point . . .	219° to 220° at 749 mm.
,, ,, . .	93° at 10 mm.
Specific gravity at 20° .	0·950
Refractive index . . .	1·48325
Optical rotation	– 36° 30

The normal semi-carbazone melts at 240° to 243° By reduction it yields dihydroumbellulol, $C_{10}H_{18}O$, a liquid of specific gravity 0·931 at 20° and optical rotation – 27° 30′.

This body, on oxidation, yields β-dihydroumbellulone, $C_{10}H_{16}O$, a ketone which yields a semi-carbazone melting at 150°. These two bodies have, according to Semmler, the following constitutions :—



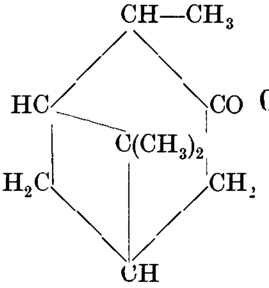
Dihydroumbellulol $C_{10}H_{18}O$.



β Dihydroumbellulone, $C_{10}H_{16}O$.

PINOCAMPHONE.

Pinocamphone, $C_{10}H_{16}O$, is the principal constituent of oil of hyssop, in which it occurs in its laevo-rotatory variety. It is a saturated ketone having the constitution :—



It has been prepared artificially by Wallach as a bye-product in the reduction of nitrosopinene, $C_{10}H_{17}NOH$. It is best prepared as follows. Five grams of nitrosopinene are dissolved in 40 c.c. of warm glacial acetic acid, and sufficient water added to produce a slight cloudiness. A large amount of zinc-dust is then added. After the reaction has become gradual, the mixture is heated on a water-bath under a reflux condenser for four hours. The liquid is then filtered, and the filtrate steam distilled. The distillate is exhausted with ether, the ether evaporated and the pinocamphone distilled in a vacuum. The characters of natural and artificially prepared pinocamphone are as follows :—

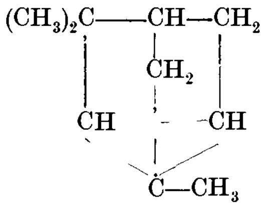
	Natural.	Synthetic.
Boiling-point	211° to 213°	211° to 213°
Specific gravity	0·966	0·963
Refractive index	1·4742	1·4731
Molecular refraction	44·4	44·44
Optical rotation	– 13° 42′	± 0°

Pinocamphone forms the following compounds suitable for its identification. The dibromide, $C_{10}H_{14}Br_2O$, is obtained by dissolving 5 grams of the ketone in 5 c.c. of glacial acetic acid. The theoretical amount of bromine (four atoms) is then added drop by drop, the vessel being kept cold by immersion in ice water. On standing in a cold place the dibromide solidifies, and can be recrystallised from petroleum ether. It then melts at 93° to 94°. By treatment with zinc and acetic acid, the dibromide is converted into the ketone again. The semi-carbazone exists in two modifications, one melting at 228° to 229° and the other at 182° to 183°. The oxime melts at 86° to 87°.

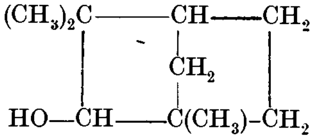
FENCHONE.

Fenchone, $C_{10}H_{16}O$, is found in fennel oil and in the oil of *Lavandula Stoechas*, in its dextro-rotatory form, and as laevo-fenchone in oil of thuja leaves. It can be extracted from these oils by treating the fraction boiling at 190° to 195° with nitric acid, or permanganate of potassium, and then steam distilling the unaltered fenchone.

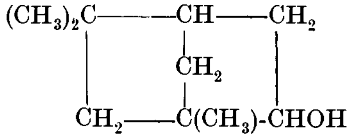
When the terpene α-fenchene (isopinene) is hydrated by means of acetic and sulphuric acids, it yields an isomer of fenchyl alcohol, which is known as isofenchyl alcohol (*q.v.*), and which on oxidation yields isofenchone, as fenchyl alcohol yields fenchone. The two ketones, fenchone and isofenchone, are sharply differentiated by isofenchone yielding isofenchocamphoric acid, $C_{10}H_{16}O_4$, on oxidation with potassium permanganate, which is not the case with fenchone. According to Aschan,[1] the hydrocarbon found in turpentine oil, and known as β-pinolene (or cyclofenchene—as he now proposes to name it), when hydrated in the usual manner, yields both fenchyl and isofenchyl alcohols, which on oxidation yield the ketones fenchone and isofenchone. According to Aschan the relationships of these bodies are expressed by the following formulæ :—



β-Pinolene.



Fenchyl alcoho .



Isofenchyl alcohol.

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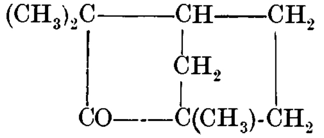
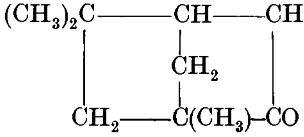
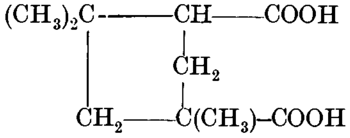
[1] *Annalen*, **387**, 1.



Fenchone.



Isofenchone.



Isofenchocamphoric acid.

Fenchone has the following characters:—

Boiling-point	192° to 193°
Melting-point	+ 5° ,, + 6°
Specific gravity	0·950
Refractive index	1·4630
Specific rotation	about ± 70°

The most characteristic derivative for the identification of fenchone is its oxime. Five grams of fenchone are dissolved in 80 c.c. of absolute alcohol and a solution of 11 grams of hydroxylamine hydrochloride in 11 c.c. of boiling water containing 6 grams of caustic potash, is added. After a time the oxime separates in the form of fine crystals which on recrystallisation from alcohol melt at 164° to 165° (active form) or 158° to 160° (inactive form).

The semi-carbazone melts at 182° to 183° (active form) or 172° to 173° (inactive form).

By reduction fenchone is converted into fenchyl alcohol, melting at 45°. The alcohol, however, has the opposite optical rotation to that of the ketone from which it is prepared.

By dehydration fenchone yields *m*-cymene.

THUJONE.

This ketone, of the formula $C_{10}H_{16}O$, isomeric with those above described, is found in the oils of thuja, tansy, wormwood, and sage. It is identical with the bodies formerly described under the names tanacetone and salvone. It is best prepared in a state of purity from oil of wormwood. According to Semmler, 200 c.c. of the oil, 200 c.c. of a saturated solution of sodium bisulphite, 75 c.c. of water, and 300 c.c. of alcohol are well shaken at intervals during a fortnight. The crystals formed, consisting of the compound of thujone with the sodium bisulphite, are separated, washed with alcohol-ether, and pressed. On treatment with caustic soda solution, the thujone, amounting to over 40 per cent. of the oil used, separates, and can be distilled with steam.

The hitherto unanswered question whether the chemically identical thujones isolated from various essential oils are also physically identical, or whether they are physically isomeric, has now been decided by Wallach in the last-named sense. He has succeeded in establishing the presence of two and possibly of three thujones, although with regard to the third the more probable view is, that it represents a mixture of the other two. His examination has, moreover, proved that thuja oil contains essentially α-thujone, and oil of tansy essentially β-thujone. Wormwood oil is very rich in β-thujone, but also contains some of the α-compound. Oils of artemisia and sage contain mixtures of α- and β-thujones. The formation of the semi-carbazones and their fractional crystallisation from methyl alcohol afford means for the separation and identification of the isomers.

α-thujone is laevo-rotatory, and yields two semi-carbazones, one dextro-rotatory, melting at 186° to 188°, and one, also dextro-rotatory, of the indistinct melting-point 110°. Pure α-thujone has the following properties:—

Boiling-point	200° to 201°
Specific gravity	0·9125
Refractive index	1·4510
Specific rotation	− 10° 23′

α-thujone is partially converted into β-thujone when heated with alcoholic potash solution, formic acid, or alcoholic sulphuric acid. The last-named then effects a further conversion into isothujone (*q.v.*).

β-thujone is dextro-rotatory, but is not the optical antipode of α-thujone. The semi-carbazone exists in a labile dextro-rotatory form of the melting-point 174° to 176°, which readily passes over into the second form, melting at 170° to 172°. When mixtures of the semi-carbazones of β-thujone or of α-thujone, or of both, are present, they give rise to complications which become even more pronounced owing to the fact that mixed crystals of uniform appearance are formed which can only be split up by very frequent recrystallisation. The ketone liberated from the semi-carbazone by means of phthalic anhydride has the specific rotatory power [α] + 76·16°. Its oxime melts at 54° to 55°, and is dextro-rotatory. β-thujone can also be converted into the isomeric α-thujone by boiling with alcoholic potash.

The various compounds of this ketone are closely analogous to those of the isomers already described.

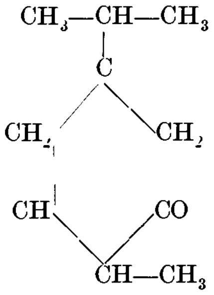
Thujone is easily converted into the isomeric ketones, isothujone and carvotanacetone. The former results by heating thujone with 40 per cent. sulphuric acid, whilst the latter is formed by heating thujone in a closed tube to 280°. The more interesting of these isomers is isothujone, for on reduction with sodium and alcohol, an alcohol, $C_{10}H_{19}OH$, results, which is isomeric with menthol, and which is sufficiently similar to this body in its properties to be termed thujamenthol. Thujamenthol on oxidation yields the ketone thujamenthone, which is isomeric with ordinary menthone. Carvotanacetone yields corresponding compounds carvomenthol and carvomenthone. The physical properties of the isomers, thujone (*i.e.* a mixture of α- and β-thujone), isothujone, and carvotanacetone are given by Wallach as follows:—

	Boiling-point.	Specific Gravity.	Refractive Index.
Thujone	200° to 201°	·912	1·4503
Isothujone	231° „ 232°	·9285	1·48217
Carvotanacetone	228°	·9373	1·48350

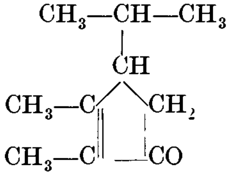
Tiemann gives the boiling-point of thujone (tanacetone) as 230° and of carvotanacetone as 230°.

Thujone is best identified by its tribromo-compound, $C_{10}H_{13}Br_3O$, melting at 121° to 122°. It is obtained by adding 5 c.c. of bromine (at once) to a solution of 5 grams of thujone in 30 c.c. of petroleum ether. The tribromo-compound separates on evaporation of the solvent and is washed with alcohol and recrystallised from boiling acetic ether.

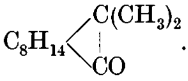
Thujone has the following constitution:—

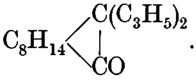


that of isothujone being as follows:—



These constitutions have recently received support from the work of A. Haller.[1] If they are correct, then thujone should be capable of yielding trialkyl substitution products, whilst isothujone should not be able to go beyond the dialkyl stage. By alkylation with the assistance of sodium amide, triallylthujone could be prepared, but no higher substitution product than dimethylisothujone could be prepared from isothujone. In the course of his work, Haller prepared the following alkyl derivatives of the two ketones:—

Dimethylthujone,  $C_8H_{14}{<}\begin{array}{l}C(CH_3)_2\\ \vert\\ CO\end{array}$. Boiling-point at 12 mm. 92° to 94° C.; specific gravity $\frac{15^\circ}{4^\circ}$ 0·916; $[\alpha]_D$ − 19·45°; does not combine with hydroxylamine.

Diallylthujone,  $C_8H_{14}{<}\begin{array}{l}C(C_3H_5)_2\\ \vert\\ CO\end{array}$. Boiling-point at 18 mm. 147·5° to 148·5° C. (corr.); specific gravity $\frac{20^\circ}{4^\circ}$ 0·9352; refractive index 1·4850.

Triallylthujone, $C_{19}H_{28}O$. Boiling-point at 21 mm. 173° to 175° C. (corr.); specific gravity $\frac{20^\circ}{4^\circ}$ 0·9467; refractive index 1·5016.

Dimethylisothujone, $C_{12}H_{20}O$. Boiling-point at 19 mm. 120° to 122° C. (corr.).

Allylisothujone, $C_{13}H_{20}O$. Boiling-point at 18 mm. 144° to 146° C. (corr.); specific gravity $\frac{20^\circ}{4^\circ}$ 0·9280; refractive index 1·4930.

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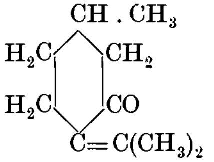
[1] *Comptes rendus*, **157**, 965.

PULEGONE.

Pulegone, $C_{10}H_{16}O$, is found in various essential oils, including those of *Mentha pulegium* and *Hedeoma pulegoides*. It can be extracted from essential oils containing it, in the usual manner, by means of its bisulphite compound. It is a colourless liquid having an odour recalling that of peppermint, and having the following characters :—

Boiling-point	221° to 222°
,, ,, at 15 mm.	100° ,, 101°
Specific gravity	0·940
,, rotation	+ 22·89°
Refractive index	1·4880

Its constitution is as follows :—



A crystalline oxime is obtained in the usual manner, but as the reaction causes some alteration of the pulegone, it in reality is the oxime of an isomeric ketone.[1] It is prepared in the following manner: 10 grams of caustic potash dissolved in 5 c.c. of water are added to a solution of 10 grams of pulegone in three times its volume of alcohol. The mixture is warmed to 80° and then poured into a solution of 10 grams of hydroxylamine hydrochloride in 10 c.c. of water. The mixture is now again heated to 80° for 10 minutes, and then, after cooling, poured into cold water. The oxime separates in a solid condition, and can be recrystallised from petroleum ether. It melts at 118° to 119°, or when repeatedly recrystallised at 123° to 124°.

The oxime thus obtained appears to be that of isopulegone.

The semi-carbazone, obtained in the usual manner, melts at 172°.

Bayer and Henrich[2] have prepared a bisnitrosopulegone, which is very useful for the identification of the ketone. A solution of 2 c.c. of pulegone in 2 c.c. of petroleum ether is cooled in a freezing mixture and 1 c.c. of amyl nitrite and a trace of hydrochloric acid are added. Fine needles of the bisnitroso compound quickly separate, which, when dried on a porous plate and washed with petroleum ether, melt at 81·5°.

By careful reduction pulegone is converted into the alcohol pulegol, $C_{10}H_{18}O$, or, by complete reduction into menthol, $C_{10}H_{20}O$.

When hydrolysed by means of formic acid, pulegone yields acetone and methyl-cyclohexenone, $C_7H_{12}O$. When this body is again condensed with acetone, it yields a body isomeric with, and very similar to, natural pulegone. This body may be termed pseudo-pulegone. A second isomer, isopulegone, was obtained by Tiemann and Schmidt, by oxidising isopulegol (a body which they obtained in the form of its acetate by heating citronellal (*q.v.*) with acetic anhydride). This isopulegone is probably a mixture of two stereoisomers which have not been separated. Isopulegone boils at 90° under a pressure of 12 mm., has a specific gravity 0·921 at 18°, refractive index 1·4690, and optical rotation + 10° 15′. It has the following constitution :—

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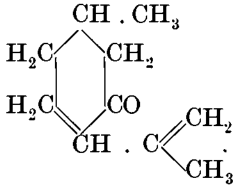
[1] *Annalen* **(1896)**, 347.

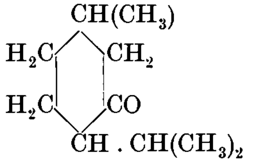
[2] *Berichte*, **28** (1895), 653.



The pulegone and the isopulegone series of compounds are very similar in their physical and chemical properties, but they differ sharply in the fact that pulegone yields menthol on reduction with sodium, whilst isopulegone does not.

MENTHONE.

Menthone, a ketone of the formula $C_{10}H_{18}O$, occurs with menthol in oil of peppermint. According to the early work of Moriya this body was described as optically inactive, but this has been shown to be incorrect. Atkinson describes it as an oily liquid, boiling at 206°, with a rotatory power of + 21°. Beckmann gives 208° as its boiling-point, and 26° to 28° as its optical activity. Its specific gravity is ·894. Oxidation of natural menthol produces laevo-menthone, but this is easily converted into dextro-menthone by the action of acids. This, on reduction, yields dextro-menthol. The various derivatives of the optically active isomers correspond closely, but complicated stereochemical relationships exist, which render the chemistry of their derivatives a very difficult question. The oximes of the two isomers do not correspond in their properties, that of dextro-menthone being a laevo-rotatory oil, whilst that of laevo-menthone is a solid, melting at 60° to 61°. The semi-carbazone melts at 184° in both cases. There are numerous bodies isomeric with, and closely similar to, those of the menthone series. Those of the thuja-menthol and carvomenthol series have already been mentioned. Menthone has the constitution—



menthol being, of course, the corresponding alcohol.

Four isomeric menthones may exist, with eight corresponding isomeric menthols (*vide supra*). But whichever menthone is converted into menthol, natural laevo-menthol is the predominating resulting compound.

Various specimens of menthone have been prepared and examined by different chemists, the characters of which fall within the following limits:—

Specific gravity	0·894 to 0·899
Optical rotation	– 26°
Refractive index	1·4495
Boiling-point	207° to 208°

Menthone has been prepared synthetically by Kötz and Hesse[1] from methyl hexanone. This body was condensed with ethyl oxalate by adding

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[1] *Annalen*, **342** (1905), 306.

an ice-cold mixture of the two in small quantities at a time to a cold solution of sodium ethylate. After fifteen hours the reaction mass is mixed with ice-cold dilute sulphuric acid, and the oxalic compound of methyl hexanone is extracted by means of ether. This product is methyl-1-hexanone-3-oxalic ester-4. When distilled at normal pressure this ester loses CO_2 and becomes methyl-1-hexanone-3-carboxylic ester, which when treated with methyl iodide and sodium yields methyl-1-hexanone-3-methyl-4-carboxylic ester-4. This ester on decomposition with alcoholic potash yields *d*-menthone.

Wallach[1] has synthesised *i*-menthone by condensing 1, 4-methylcyclo-hexanone with bromo-isobutyric ester; from the condensation product he prepared *i*-menthene, which was converted into *i*-menthenone, by means of its nitrosochloride, whence *i*-menthone resulted by reduction.

Beckmann[2] has examined the characters of the optically active menthones. The oxidation of natural *l*-menthol by chromic acid mixture yielded *l*-menthone $[\alpha]_D = -28{\cdot}5°$ which when treated with 90 per cent. sulphuric acid is converted into a *d*-menthone $[\alpha]_D = +28{\cdot}1°$, which, however, is not the optical antipode of the first: it behaves as a mixture of *d*- and *l*-menthone, but is more strongly dextro-rotatory than it would be if it were only a mixture of the two optical antipodes.

The reduction of *l*-menthone or inverted *d*-menthone yielded, together with ordinary menthol, a *d*-isomenthol melting at 78° to 81° C.; $[\alpha] = +2{\cdot}03$ which, on oxidation with chromic acid mixture, yielded an isomenthone, the specific rotatory power of which varied between $+30{\cdot}2°$ and $+35{\cdot}1°$.

The treatment of menthylamine by nitrous acid yielded a *d*-isomenthol still more strongly dextro-rotatory. A *d*-isomenthylamine hydrochloride, having a rotatory power of $[\alpha]_D = +17{\cdot}7°$, yielded a *d*-isomenthol having $[\alpha]_D = +25{\cdot}6°$.

Menthone can be prepared by the reduction of piperitone. For this, Smith and Penfold[3] give the following method:—

Pure piperitone was subjected to the action of purified hydrogen, in the presence of a nickel catalyst, for six hours, the temperature ranging between 175° to 180° C. The double bond in piperitone was readily opened out with the formation of menthone, but further action of the hydrogen under these conditions did not reduce the carbonyl group, even after continued treatment for two days. Under correct conditions, however, the reduction to menthol should take place. The ease with which menthone is formed in this way is of special interest, not only in connection with the production of this ketone, but also as a stage in the manufacture of menthol.

The reduction of piperitone to menthone cannot well be brought about by the action of sodium or of sodium-amalgam in alcoholic solution, because, with the latter particularly, a solid bimolecular ketone is formed at once. This is a finely crystallised substance, melts at 148° to 149° C., and has the formula $C_{20}H_{34}O_2$. Piperitone thus follows the rule with substances having a conjugated double bond, carvone for instance, also forms a bimolecular ketone on reduction, melting at 148° to 149° C.

Menthone was prepared from piperitone in almost quantitative yield, and had the characteristic peppermint odour of this substance. It

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[1] *Annalen*, **362** (1908), 261.

[2] *Berichte*, **42**, 846.

[3] *J. and Pro*. *Roy. Soc.*, N.S. Wales, liv. 45.

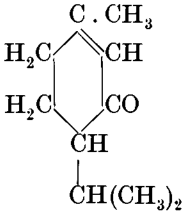
was colourless; boiled at 208° C., had specific gravity at 20° = 0·8978; optical rotation α_D − 0·15°, and refractive index at 20° = 1·4529. The oxime melted at 80° C., the more soluble semicarbazone at 156° C., while the least soluble melted at 187° to 198° C. Any unreduced piperitone can be removed from the menthone by the action of neutral sodium sulphite.

MENTHENONE.

Δ'-menthenone, $C_{10}H_{16}O$, has been isolated by Schimmel & Co.[1] from Japanese peppermint oil. It is an aromatic liquid having the following characters:—

Specific gravity	0·9382
Boiling-point	235° to 237° at 752 mm.
Optical rotation	+ 1° 30'
Refractive index	1·4844
Molecular refraction	46·58

Its constitution is—



It yields a semi-carbazone, which exists in two modifications, the α-modification, which is only slightly soluble in alcohol, melting at 224° to 226°, and the β-modification, which is easily soluble, melting at 171° to 172°.

With hydroxylamine, menthenone yields a normal oxime, and an oxaminoxime. The latter body is not very volatile, and the oxime can be separated by steam distillation, and, when recrystallised from alcohol, melts at 107° to 108°. The oxaminoxime melts at 164° to 165°.

CAMPHOR.

Camphor, $C_{10}H_{16}O$, occurs in the wood of the camphor tree (*Laurus camphora*) as dextro-camphor. This is the ordinary camphor of commerce, known as Japan camphor, whilst the less common laevo-camphor is found in the oil of *Matricaria parthenium.* Camphor can also be obtained by the oxidation of borneol or isoborneol with nitric acid. Camphor may be prepared from turpentine in numerous ways, and there are many patents existing for its artificial preparation. Artificial camphor, however, does not appear to be able to compete commercially with the natural product. Amongst the methods may be enumerated the following:—

1. Esters of borneol are obtained by the action of dry oxalic acid on turpentine under suitable conditions. From these, borneol is obtained by saponification and is oxidised to camphor. Some other acids produce a similar result, as, for example, salicylic and chlorobenzoic acids.

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[1] Schimmel's *Bericht*, October (1910), 79.

2. Pinene hydrochloride is prepared in the usual manner from turpentine, and this is allowed to react with acetate of silver. Isobornyl acetate is formed, which is hydrolysed, and the isoborneol oxidised to camphor. Acetate of lead is also used, as is also acetate of zinc.

3. The action of magnesium on pinene hydrochloride gives rise to bornyl esters, and camphor can be obtained from these in the usual manner.

4. Pinene hydrochloride is treated by one of the reagents which abstract HCl, and so converted into camphene (*q.v.*). This is heated with acetic and sulphuric acids, and so converted into isobornyl acetate. Camphor results in the usual manner.

Camphor forms a translucent mass, which crystallises well from alcohol. It has the following characters:—

Specific gravity at 18°	0·985
Melting-point	176° to 176·5°
Boiling-point	205° „ 207°
Specific rotation	± 44°

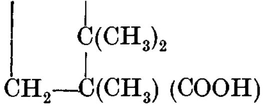
Optically inactive camphor melts at 179°.

Camphor is the ketone of the alcohol borneol, and forms a number of well-characterised crystalline derivatives. Amongst these are the semicarbazone, the phenylhydrazide, and the oxime, all characteristic of bodies containing the . CO . group. The semi-carbazone,

$$C_{10}H_{16} : N_2H . CO . NH_2,$$

melts at 236° to 238°. The hydrazide, $C_{10}H_{16} : N_2HC_6H_5$, results from the action of phenylhydrazine. The oxime, $C_{10}H_{16} . NOH$, is prepared by the action of hydroxylamine on camphor. It melts at 118°, and when reduced by means of sodium, yields the base bornylamine, $C_{10}H_{17}NH_2$.

When distilled with phosphorus pentoxide, camphor yields cymene, and with iodine, carvacrol. Both of these bodies are *para*-derivatives of benzene. On oxidation with nitric acid camphor yields many acids, of which the chief are camphoric acid, $C_{10}H_{16}O_4$, camphanic acid, $C_{10}H_{14}O_4$, and camphoronic acid, $C_9H_{14}O_6$. The constitution of these acids has an important bearing on that of camphor. Many formulæ have been suggested for camphor during the past few years, but that of Bredt is now universally accepted, and has received complete confirmation by Komppa's synthesis[1] of camphoric acid. This synthesis confirms the formula for camphoric acid as—



which is in accordance with Bredt's formula for camphor.

Camphor has the following constitution:—

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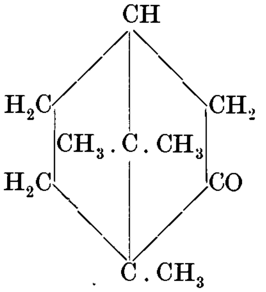
[1] *Berichte*, **36**, 1332.



Haller and Louvrier[1] have prepared a number of homologues of camphor by heating the ketone in benzene solution with sodamide and alkyl iodides. The following are the characters of a number of these :—

	Boiling-point.	Specific Gravity at 0°.	$[\alpha]_d$.
Monoethylcamphor . .	108° (14 mm.)	0·927	+ 45°
Diethylcamphor . . .	132° to 133° (14 mm.)	0·969	+ 91°
Methylethylcamphor . .	112° ,, 114° (11 ,,)	—	+ 99° 30′
Propylcamphor . . .	116° (11 mm.)	0·942	+ 60° 40′
Dipropylcamphor . .	157° (14 ,,)	—	+ 53° 50′
Benzylcamphor . . .	—	—	+ 147° 40′
Dibenzylcamphor . .	255° (12 mm.)	—	+ 103° 10′
Ethylbenzylcamphor . .	193° (11 ,,)	—	+ 91°

Rupe and Iselin[2] have prepared a number of homologues of methylene camphor by a general method depending on the reaction between chloromethylene camphor and various organo-magnesium compounds. Chloromethylene camphor itself can be prepared by the action of thionyl chloride on hydroxymethylene camphor ; the resulting compound is a colourless oil boiling at 113° at 12·5 mm. pressure, and having an optical rotation of + 180° in benzene solution. Ethylidene camphor,

$$C_8H_{14}(C : CH . CH_3)CO,$$

is prepared by the action of magnesium methyl bromide on an ethereal solution of chloromethylene camphor. It forms radiate crystals melting at 28° to 29° and boiling at 109° to 110° at 12 mm. It has an optical rotation + 178·5°. The corresponding propylidene camphor is prepared in a similar manner, and is a colourless oil, boiling at 121° to 122° at 13 mm. Its specific gravity is 0·9448 at 20°, and optical rotation + 173°. Butylidene camphor has a specific gravity 0·938 at 20°, and optical rotation + 161°. Amyildene camphor, the last of this series prepared, has a specific gravity 0·927 at 20°, and optical rotation + 156·6°. Aromatic substituted camphors were also prepared in the same manner, among which are the following : Benzylidene camphor is a colourless crystalline solid, melting at 98·5°, and having the formula

$$C_8H_{14}(C : CH . CH_2C_6H_5)CO.$$

It has the extraordinarily high specific rotation + 426·5°. Phenylethylidene camphor is a faintly greenish oil of specific gravity 1·025 at

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[1] *Comptes rendus*, **158** (1914), 754.

[2] *Berichte*, **49**, 25.

20°, and specific rotation + 129°. Phenyl-propylidene camphor has a specific gravity 1·0094 at 20°, and specific rotation + 128°. Phenyl-butylidene camphor has a specific gravity of 0·999 at 29°, and specific rotation + 113°. Cyclohexylmethylene camphor was prepared by the use of magnesium cyclohexyl bromide, and forms colourless prisms melting at 46° to 48°.

Alpha-naphthylidene camphor was similarly obtained in long transparent crystals melting at 98° to 99°, boiling at 253°, and having a rotation + 335·6°. An attempt was made to prepare a diphenyl derivative, but this was unsuccessful. A number of the above-described compounds were reduced with sodium amalgam in methyl alcohol, neutrality being maintained by the addition of 50 per cent. acetic acid. In this method the authors obtained iso-amyl camphor, a colourless, inodorous oil boiling at 140° at 14 mm., and having a specific gravity 0·9197 at 20°, and specific rotation + 66·8°. Phenyl-ethyl camphor forms colourless prisms melting at 60° to 61°, and having a specific rotation + 22·8°. Phenyl-propyl camphor is a colourless oil boiling at 208° to 210° at 15 mm., and having a specific rotation + 52·4°.

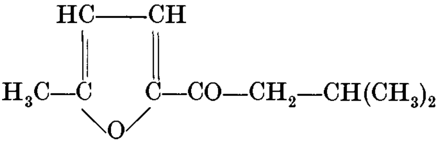
ELSHOLTZIONE.

The oil of *Elsholtzia cristata* contains a ketone, which has been examined by Asahina and Murayama, and which has the following constants :—

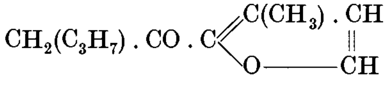
Boiling-point at 10 mm.	87° to 88°
„ „ „ 760 „	210°
Specific gravity	0·9817
Optical rotation	0°
Refractive index	1·4842

It has the formula $C_{10}H_{14}O_2$, and forms a semi-carbazone melting at 171° and an oxime melting at 54°.

This ketone has, according to Asahina and Murayama, the following constitution :—[1]



According to Asano,[2] however, its constitution is as follows :—



ACETOPHENONE.

Acetophenone, $C_6H_5 . CO . CH_3$, is a ketone occurring in oil of labdanum resin. It also occurs in the oil of *Stirlingia latifolia* which contains over 90 per cent. of the ketone.[3] It is a fragrant, crystalline substance melting at 20° and boiling at 200° to 202°. It is prepared artificially and is useful in synthetic perfumery. As found in commerce

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[1] *Jour. Pharm. Soc. Japan* **(1918)**, 1.

[2] *J. Pharm. Soc. Japan*, 1919, **454**, 999.

[3] *See Vol. I. p.* 172.

it is generally liquid, either in a state of superfusion, or because of traces of impurities. It can be prepared by distilling a mixture of calcium benzoate and calcium acetate, or by condensing benzene and acetyl chloride in the presence of aluminium chloride.

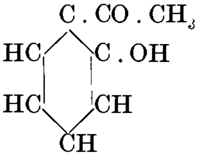
Anhydrous aluminium chloride in powder is placed in a capacious flask attached to a reflux condenser, and covered with dry benzene (30 grams). The flask is kept cold with ice, and acetyl chloride is allowed to drop slowly into the mixture. A vigorous reaction ensues, and much hydrochloric acid gas is evolved. After about one hour the reaction is finished, and the mass is transferred to a mixture of ice and water, when a brown oil separates. This mixture is extracted with benzene, the benzene extract is washed with dilute caustic soda, finally with water, and dried over calcium chloride, from which the liquid is decanted and distilled, and when the benzene has come over, the temperature of the vapour rises to 195°, the fraction 195° to 202° being collected as an almost colourless oil, which solidifies on chilling and is almost pure acetophenone. It forms an oxime melting at 56° to 60°, and a semi-carbazone at 185° to 187°. It is extremely powerful and gives good results in soap perfumery, and is a good auxiliary for such perfumes as new-mown hay, syringa, and the like.

METHYL-ACETOPHENONE.

Paramethyl-acetophenone, $CH_3 . C_6H_4 . CO . CH_3$, is a synthetic perfume ketone, having a powerful floral odour. It is prepared by the Friedel-Craft reaction in the same manner as acetophenone, by condensing toluene with acetic anhydride. It is a strongly odoriferous oil boiling at 220°, and having a specific gravity 1·0062. Its oxime melts at 88° and its phenylhydrazone at 97°.

OXY-ACETOPHENONE.

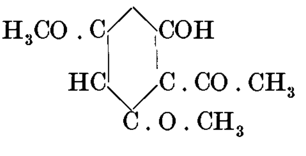
This body is a phenolic ketone of the formula $C_6H_4(OH) . CO . CH_3$. Its constitution is—



It is found naturally in the oil of *Chione glabra*. It boils at 160° to 165° at 34 mm., and has a specific gravity 0·850. It forms an oxime melting at 112° and a phenylhydrazone melting at 108°.

DIMETHYL-PHLORACETOPHENONE.

This ketone, of the formula $C_6H_2(CO . CH_3)(OH)(OCH_3)(OCH_3)$, is found in the essential oil of *Blumea balsamifera*. It is a crystalline substance melting at 82° to 83°, and having the constitution—



It yields an oxime melting at 108° to 110°, and a bromine derivative, $C_{10}H_{11}O_4Br$, melting at 187°.

BENZYLIDENE ACETONE.

Benzylidene acetone, $C_6H_5 . CH : CH . COCH_3$, is a crystalline body melting at 42°, having an intense floral odour. It results from the condensation of benzaldehyde and acetone under the influence of caustic soda. It has the following characters :—

Specific gravity	1·0377 at 15°
Boiling-point	260° to 262°
Melting-point	42°

Its oxime melts at 115° to 116°.

BENZOPHENONE.

This ketone, $C_6H_5 . CO . C_6H_5$, is diphenyl ketone. It is a fragrant crystalline body melting at 48° and boiling at 307°.

It is prepared artificially by the distillation of calcium benzoate, or by the condensation of benzene and benzoyl chloride in the presence of aluminium chloride.

It has not been found naturally occurring in essential oils.

TRIMETHYL-HEXANONE.

Masson [1] has isolated a ketone, of the formula $C_9H_{16}O$, from oil of labdanum. It has the following characters :—

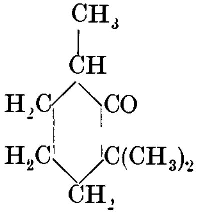
Boiling-point	178° to 179°
,, ,, at 10 mm.	66° ,, 67°
Specific gravity at 0°	0·922
Optical rotation	± 0°
Refractive index	1·4494 at 23°

It yields a monobromide melting at 41°, a semi-carbazone melting at 220° to 221°, and an oxime melting at 106°. When reduced with sodium and alcohol it yields a secondary alcohol, which forms large crystals melting at 51°. On oxidation by cold 3 per cent. solution of potassium permanganate it yields geronic acid, a keto-acid of the constitution—

$$CH_3 . CO . CH_2 . CH_2 . CH_2 . C(CH_3)_2 . COOH.$$

This acid boils at 190° to 191° at 31 mm., and yields a semi-carbazone melting at 164°.

The ketone itself is trimethyl-1, 5, 5-hexanone-6, of the constitution—



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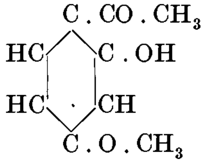
[1] *Comptes rendus*, **154** (1912), 517.

PAEONOL.

This ketone has been found in the essential oil of Pæonia Moutan. It is a crystalline body of the formula $C_9H_{10}O_3$. Its constitution is—



It is therefore *p*-methoxy-*o*-hydroxyphenyl methyl ketone.

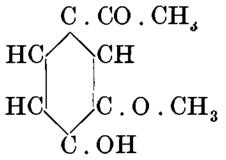
It yields an ethyl ether melting at 46·5°, and a phenylhydrazone melting at 170°.

Paeonol has been prepared synthetically by Hoesch;[1] he allowed 5 parts of resorcinmethyl ether to react with 3 parts of acetonitrile, with zinc chloride and ether. Chlorine was then passed through the mixture for four hours. The mixture was shaken with ether, and the aqueous solution steam distilled, when paeonol comes over with the steam, leaving the non-volatile isopaeonol in the flask.

Paeonol forms a nitro-compound $C_6H_9O_5N$, melting at 153° to 155°. Hydroxypaeonol, $C_9H_{10}O_4$, has also been found in essential oils of the *Xanthoirhœa* species. It melts at 79°.

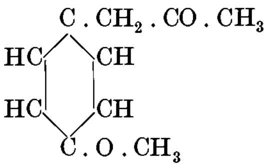
ACETOVANILLONE.

This body, which is found in the essential oil of *Apocynum andosaemifolium*, is isomeric with the last described ketone, being *m*-methoxy-*p*-hydroxyphenylmethyl ketone, of the constitution—



ANISIC KETONE.

Anisic ketone, $C_{10}H_{12}O_2$, is found in oil of fennel. It is a liquid boiling at 263°, and having a specific gravity 1·095 at 0°. Its oxime melts at 72°. On oxidation it yields anisic acid. Its constitution is as follows:—



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[1] *Berichte*, **48** (1915), 1122.

DIOSPHENOL.

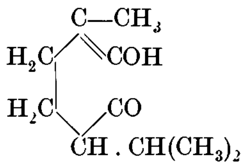
Diosphenol, $C_{10}H_{16}O_2$, or buchu-camphor as it is also called, is a phenolic ketone found in the essential oil of buchu leaves. It is a crystalline substance having the following characters:—

Melting-point	83° to 84°
Optical rotation	± 0°
Boiling-point	232°, with decomposition
,, ,, at 10 mm.	109° to 110°

It yields a phenylurethane melting at 41°, a semi-carbazone melting at 219° to 220°, and an oxime melting at 125°. The OH group appears to possess alcoholic as well as phenolic functions, forming acetic and benzoic esters, as well as direct combinations with alkalis.

On reduction by means of sodium amalgam and alcohol, it yields an alcohol, $C_{10}H_{18}O_2$, melting at 159°.

Diosphenol has the following constitution:—



It has been prepared artificially by Semmler and McKenzie[1] by oxidation of oxymethylene-menthone, $C_{11}H_{18}O_2$, a diketone, $C_{10}H_{16}O_2$, resulting, which is inverted by means of alkalis to diosphenol.

Cusmano[2] has also prepared it artificially by shaking dibromomenthenone with 2·5 per cent. solution of caustic potash, and when solution is effected, saturating the liquid with carbon dioxide.

JASMONE.

Jasmone, $C_{11}H_{16}O$, is a ketone found in essential oil of jasmin, and also in neroli oil. It is a dark-coloured liquid with a powerful jasmin odour, and having the following characters:—

Specific gravity	0·945
Boiling-point at 775 mm.	257° ,, 258°
Melting-point of oxime	45°
,, ,, ,, semi-carbazone	201° to 204°

SANTALONE

Santalone, $C_{11}H_{16}O$, is a ketone found in small quantity in sandalwood oil. It has the following characters:—

Boiling-point	214° to 215°
,, ,, at 15 mm.	88° ,, 89°
Specific gravity	0·9906
Optical rotation	− 62°
Melting point of oxime	75°
,, ,, ,, semi-carbazone	175°

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[1] *Berichte*, **39** (1906), 1158.

[2] *Atti R. Accad. d. Lincei* (5), **22**, ii. (1913), 569

Musk and Civet Ketones (Muskone and Zibethone).

Two ketones of unknown constitution have been isolated from natural musk. Of these, muskone, $C_{15}H_{28}O$ (or $C_{16}H_{30}O$), occurs to the extent of 0·5 to 2 per cent.[1] It is a thick, colourless oil with a very powerful odour of musk. It boils at 327° to 330° at 752 mm., and at 142° to 143° at 2 mm. It yields an oxime melting at 46° and a semi-carbazone melting at 133° to 134°.

Sack[2] has recently isolated a ketone from natural civet. The civet was boiled for some hours with alcoholic potash, the alcohol evaporated and the residue extracted with ether. The residue left on evaporating the ether was distilled with steam to remove skatole, again extracted with ether, the ether evaporated and the residue dissolved in alcohol. The alcohol was evaporated, and the residual ketone purified by conversion into its semi-carbazone, from which it was regenerated. It has the formula $C_{17}H_{30}O$, and its characters are as follows:—

Boiling-point	204° to 205° at 17 mm.
,, ,,	342° at 741 mm.
Melting-point	32·5°
,, ,, of oxime	92°
,, ,, ,, semi-carbazone	187°

The name zibethone has been proposed for this ketone.

Kaempferia Ketone.

The essential oil of *Kaempferia Ethelæ* contains a crystalline ketone of the formula $C_{24}H_{28}O_4$.[3] It forms large transparent diamond-shaped crystals melting at 102° and having a specific rotation + 198° 20′ in chloroform solution. The crystals are practically odourless, but in dilute alcoholic solution a distinct odour is perceived, which reminds one of crushed ivy leaves. It is a highly unsaturated compound, and combines readily with bromine. It does not form a bisulphite compound. It yields a hydroxylamine-oxime melting at 184°, which forms hard white crystals, and which when shaken with dilute hydrochloric acid is converted into the oxime $C_{24}H_{28}O_3 : NOH$, melting at 166°.

It forms a benzoyl derivative melting at above 260° with decomposition.

Gurjun Ketone.

A ketone exists in gurjin oil, which according to Semmler has the formula $C_{15}H_{22}O$, whilst Deussen and Philipp[4] consider its formula to be $C_{15}H_{24}O$. It has the following characters:—

Melting-point	43°
Boiling-point	163° to 166° at 10 mm.
Specific gravity at 20°	1·017
Refractive index	1·527°
Optical rotation	+ 123°

The last three figures apparently refer to the ketone in the superfused condition.

The semi-carbazone melts at 234°, and has a specific rotation + 317° in chloral hydrate solution.

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[1] *Jour. prakt. Chem.*, ii. **73** (1906), 488.

[2] *Chem. Zeit.*, **39** (1915), 538.

[3] *Chem. Soc. Trans.* **107** (1915), 314.

[4] *Annalen*, **369** (1909), 56; **374** (1910), 105.

7. PHENOLS AND PHENOLIC COMPOUNDS.

PHENYL-METHYL ETHER.

This ether, $C_6H_5 . O . CH_3$, known as anisole, is a mobile oil of very fragrant odour. It is used to some extent in synthetic perfumery. It is prepared by the action of methyl iodide on sodium-phenol, according to the following equation :—

$$C_6H_5ONa + CH_3I = C_6H_5 . O . CH_3 + NaI.$$

It boils at 172°.

PHENYL-ETHYL ETHER.

This ether, $C_6H_5 . O . C_2H_5$, is known as phenetole. It is a fragrant liquid boiling at 172°, and is prepared in a similar manner to the methyl ether.

DIPHENYL OXIDE.

Phenyl Ether.—Diphenyl oxide, $C_6H_5 . O . C_6H_5$, is a crystalline compound which has been known for many years, but which has suddenly come into considerable vogue in synthetic perfumery. It has been variously described as having an odour resembling orange oil, hyacinths, and geranium. As a matter of fact, it has a powerful odour of geranium leaves, and is the basis of most of the synthetic geranium oils. It can be prepared in numerous methods, of which the following are examples: On distilling copper benzoate, diphenyl oxide results directly, or by digesting diazo-benzene sulphate with phenol, diphenyl oxide results, according to the following equation :—

$$C_6H_5N : N . HSO_4 + C_6H_5OH = (C_6H_5)_2O + N_2 + H_2SO_4.$$

It also results by heating phenol with aluminium chloride.

Diphenyl oxide forms long crystals melting at 27° to 28° and boiling at 252° to 253°. As illustrating the manner in which valuable synthetic perfumes are overlooked, unless their discoverer happens to be an expert in odours, we quote the following from a work published in 1899: "Diphenyl oxide has an indescribable hyacinth-like odour, but has not found any practical application". To-day, it is manufactured in very large quantities, and, as stated above, forms the basis of all the synthetic geranium oils. It is readily soluble in alcohol, and most organic solvents, and is most useful in all blends where a geranium odour is required, Cresol yields similar oxides, having marked perfume odours, but these do not yet appear to be commercial articles. The three isomeric ethers have the following characters: their formula is $(C_7H_7)_2O$; the ortho-compound boils at 272° to 273°; the meta-compound boils at 284° to 286°; and the para-compound melts at 50°.

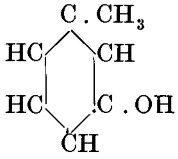
CRESOL COMPOUNDS.

Meta-cresol, C_7H_8O, is a crystalline substance, melting at 4° and boiling at 201°. It occurs to a considerable extent in coal-tar mixtures, and is present in very small amount in essential oil of myrrh. It forms a characteristic tribromide, melting at 82°.

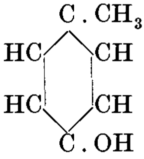
Para-cresol, which is also a constituent of coal-tar creasote, occurs in the essential oils of jasmin and cassie flowers. It is a crystalline substance melting at 36° and boiling at 199°. It can be identified in the following manner. Its alkaline solution is treated with dimethyl sulphate, which converts it with its methyl ether, a highly odorous liquid boiling at 175°, and which, on oxidation by permanganate of potassium, yields anisic acid melting at 180°. *Para*-cresol yields a benzoyl derivative melting at 70° to 71°.

Para-cresol methyl ether occurs naturally in oil of ylang-ylang and similar flower oils. It is also prepared synthetically, and forms a useful artificial perfume for compound flower odours. It is a liquid boiling at 175°, and, as stated above, yields anisic acid on oxidation.

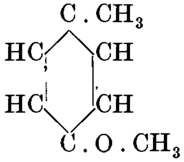
These three bodies have the following constitutions:—



m-cresol.

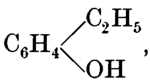


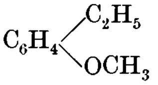
p-cresol.



p-cresol methyl ether.

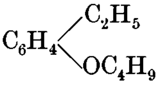
Phlorol Ethers.

Phlorol,  $C_6H_4\begin{cases}C_2H_5\\OH\end{cases}$, or *ortho*-ethyl phenol, has been identified in pine oil, and in the form of its methyl and isobutyl ethers, in oil of arnica. These two ethers have the formula—



$C_6H_4\begin{cases}C_2H_5\\OCH_3\end{cases}$

Methyl ether.



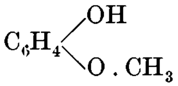
$C_6H_4\begin{cases}C_2H_5\\OC_4H_9\end{cases}$

Isobutyl ether.

Phlorol boils at 225° to 226°.

Guaiacol.

Guaiacol is the monomethyl ether of the diphenol, catechol, or *ortho*-dihydroxybenzene. Its constitution is—

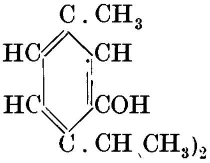


$C_6H_4\begin{cases}OH\\O \, . \, CH_3\end{cases}$

It has been found in pine oil.

Thymol.

Thymol, $C_{10}H_{14}O$, is the principal constituent of the oils of thyme and ajowan seeds. It is isopropyl-*meta*-cresol of the constitution—

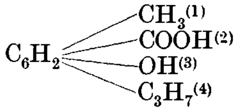


It is a colourless crystalline substance, having the characteristic odour of thyme oil, and possessing very powerful antiseptic properties. Its characters are as follows:—

Melting-point	50·5° to 51·5°
Boiling-point	232° at 752 mm.
Specific gravity at $\frac{24°}{4°}$	0·969
Refractive index	1·5227 (superfused)

It combines with chloral to form a compound melting at 131° to 134°. Its phenylurethane melts at 107°. It forms a nitroso-compound melting at 160° to 162°, when treated with nitrous acid.

If thymol be treated with sodium and a current of carbonic acid be passed through it, *o*-thymotic acid is formed, which when liberated by means of hydrochloric acid and purified by distillation, melts at 123°. Thymotic acid has the constitution—



$$C_6H_2\begin{cases}CH_3{}^{(1)}\\COOH^{(2)}\\OH^{(3)}\\C_3H_7{}^{(4)}\end{cases}$$

By oxidation it yields thymoquinone, $C_6H_2(O_2)(CH_3)(C_3H_7)$, melting at 48°.

Thymol frequently occurs associated with carvacrol, its *ortho*-isomer, and may be separated therefrom by fractional crystallisation of the phenylurethanes, that of carvacrol being much less soluble in petroleum ether than that of thymol.

Thymol forms a soluble compound with alkalis, and can be extracted from the oils in which it occurs by shaking with a 5 per cent. solution of caustic soda or potash.

Smith and Penfold[1] have shown that thymol can be prepared by the action of ferric chloride on piperitone.

60 grams of pure piperitone were added to a solution of 175 grams ferric chloride, 160 c.c. glacial acetic acid, and 500 c.c. of water. The whole was then heated on the sand bath to boiling. The reaction takes place according to the equation $2FeCl_3 + H_2O = 2FeCl_2 + 2HCl + O$, and was completed at the expiration of about one hour. The reaction product was then steam distilled, the phenol separated and absorbed in a 5 per cent. solution of sodium hydrate, the unabsorbed oil removed by ether, and the aqueous layer decomposed by hydrochloric acid. The phenol was finally distilled under reduced pressure when the thymol came over at 110° to 111° C. at 10 mm. In this way they obtained a 25 per cent. yield of the weight of piperitone taken; but, no doubt, methods can be devised whereby an almost theoretical yield could be obtained.

Phillips and Gibbs[2] have summarised the history of the preparation of thymol synthetically and gives the following interesting account thereof.

Starting with cuminal, nitro-cuminal was prepared, the nitro group entering the para position, meta to the aldehyde group. This compound when treated with phosphorus pentachloride was converted into nitro-cymyline chloride, which on reduction with zinc and hydrochloric acid

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[1] *J. and Proc. Royal Soc.* N.S. Wales, liv. 40.

[2] *Jour. Ind. Eng. Chem.* (1920), 733.

gave 3-aminocymene, and upon diazotisation and subsequent hydrolysis thymol resulted

Thymol has since been synthetised by a number of chemists, but only two of those syntheses need be considered in this connection because of their close relationship to the present method Dinesmann (D R P. 125,097 (1900)) obtained a patent for a process of making thymol from 2-brom-*p*-cymene This process consists in sulphonating 2-brom-*p*-cymene obtaining 2-brom-3- or 5-sulphonic acid, which, when heated with zinc dust and ammonia in an autoclave at 170°, gives cymene-3-sulphonic acid This compound on fusion with potassium hydroxide gives thymol

Recently a patent has been granted to Andrews (U S Patent 1,306,512, 1919) for a process for making thymol from cymidine (2-aminocymene). Cymidine is first acetylated, then nitrated, whereupon the nitro group enters meta to the methyl group The acetyl group is hydrolysed off and the amino group removed through diazotisation and subsequent reduction of the diazo compound with alkaline stannous chloride or with boiling alcohol The nitro compound thus obtained is then reduced to the corresponding amino compound, which on diazotisation and subsequent hydrolysis gives thymol

In the details given by Phillips and Gibbs in the publication referred to the following experimental procedure is outlined The *p*-cymene was isolated from a crude oil obtained from a sulphite spruce pulp mill The oil after standing over lime for about a week was subjected to steam distillation To the distillate about one-fourth its volume of sulphuric acid was added, and the mixture stirred in the cold by means of a mechanical stirrer. After two hours' stirring the dark acid was separated from the oil, a fresh quantity of sulphuric acid added and the stirring continued. This operation was carried on until a sample of the oil after being washed with water gave a very slight yellowish colour when shaken with sulphuric acid The oil was then washed with water, dried over calcium chloride and distilled over sodium, using a Glinsky stillhead. Practically all the material came over from 174° to 175° (759 6 pressure), leaving only a small amount of dark coloured oil in the flask

For the preparation of nitrocymene a method developed in the Colour Laboratory and described in the *Jour. of Ind and Eng Chem* in 1918, p. 453, was used The nitro group enters in the ortho position with respect to the methyl group The reduction of this compound to aminocymene or cymidine was accomplished by means of iron powder and hydrochloric acid in exactly the same way as nitrobenzene is reduced to aniline

The conversion of cymidine to cymidine sulphonic acid was effected as follows To 61 c c of concentrated sulphuric acid 160 grams of cymidine were added in small quantities at a time, stirring after each addition of the cymidine The cymidine sulphate was placed in an oven and heated for six hours at about 200° The mass on cooling was ground and dissolved in hot water. Upon making the solution distinctly alkaline with sodium hydroxide the cymidine which had escaped sulphonation separated as an oil and was recovered by steam distillation The residue in the flask was concentrated if necessary, boiled with animal charcoal, filtered, and acidified with hydrochloric acid Cymidine sulphonic acid separated out as a crystalline mass The yield was about 30 grams (32 per cent yield calculated on the 60 grams of cymidine actually used up), and the unused cymidine recovered amounted to 100 grams.

For the preparation of cymene-3-sulphonic acid from cymidine sulphonic acid the following modification of Widman's method was used: 22·9 grams of the cymidine sulphonic acid were suspended in about 400 c.c. of 95 per cent. alcohol, 20 c.c. concentrated sulphuric added, and diazotised in the cold in the usual manner. After diazotisation the solution was allowed to stand in the cold for an hour and then 10 grams of copper powder were added in small quantities at a time, allowing the rapid evolution of nitrogen to subside before making any further additions. The mixture was filtered and the filtrate distilled on the water-bath. The residue in the flask was diluted with water, boiled with barium carbonate, filtered, and the filtrate containing the barium salt of cymene-3-sulphonic acid was treated with sodium carbonate, and the sodium salt of the sulphonic acid obtained. This sodium salt was converted into thymol as follows: 30 grams of 98 per cent. sodium hydroxide were treated with a little water and heated in a nickel crucible, with stirring, to 280°. To this 10 grams of the sulphonate were added, with stirring. After all the salt had been added, the temperature was raised to 310°, and left there for about fifteen minutes, when the reaction was complete. The melt on cooling was dissolved in water, acidified with hydrochloric acid and steam distilled. The distillate was extracted with ether, dried over anhydrous sodium sulphate and fractionated after distilling off the ether. Nearly all of the product distilled over at the boiling temperature of thymol. The thymol obtained was identified by its phenylurethane derivative (m.p. 107°).

Mr. Max Phillips himself has taken out the following important patent for the preparation of thymol from para-cymene.

The process of converting para-cymene into thymol is preferably carried out as follows: The first step consists in converting cymene into cymidin by any known process, an example of a good method being: Pure para-cymene is slowly added to an equal weight of sulphuric acid (specific gravity 1·84), which is kept at or below 0°C. To this is slowly added the previously cooled nitrating mixture, consisting of 1 part nitric acid (specific gravity 1·42) and 2 parts sulphuric acid (1·84), the amount of nitric acid being used about 5 to 10 per cent. in excess of that necessary to substitute one nitro group into the cymene molecule. During the nitration the mixture is stirred efficiently and the temperature kept at or below 0° C. When all the nitrating mixture has been added, the mixture is stirred for one hour longer. The mixture is then poured into cold water, and the oily upper layer separated off. This is washed several times with water, with sodium carbonate solution, and again with water. The nitro-cymene thus obtained is then reduced to amino-cymene or cymidin by means of iron and hydrochloric acid in exactly the same way as that used in the industrial preparation of aniline from nitrobenzene.

The cymidin is now sulphonated, 100 parts by weight of cymidin being slowly added to 69 parts by weight of sulphuric acid (sp. gr. 1·84), contained in a shallow dish, and the solid crystalline mass of cymidin sulphate thus obtained is then converted into cymidin sulphonic acid by an identical method to that used in the so-called "baking process"[1] for the preparation of sulphanilic acid from aniline sulphate.

This produces 1-methyl-2-amino-4-isopropyl-3 or 5 sulphonic acid.

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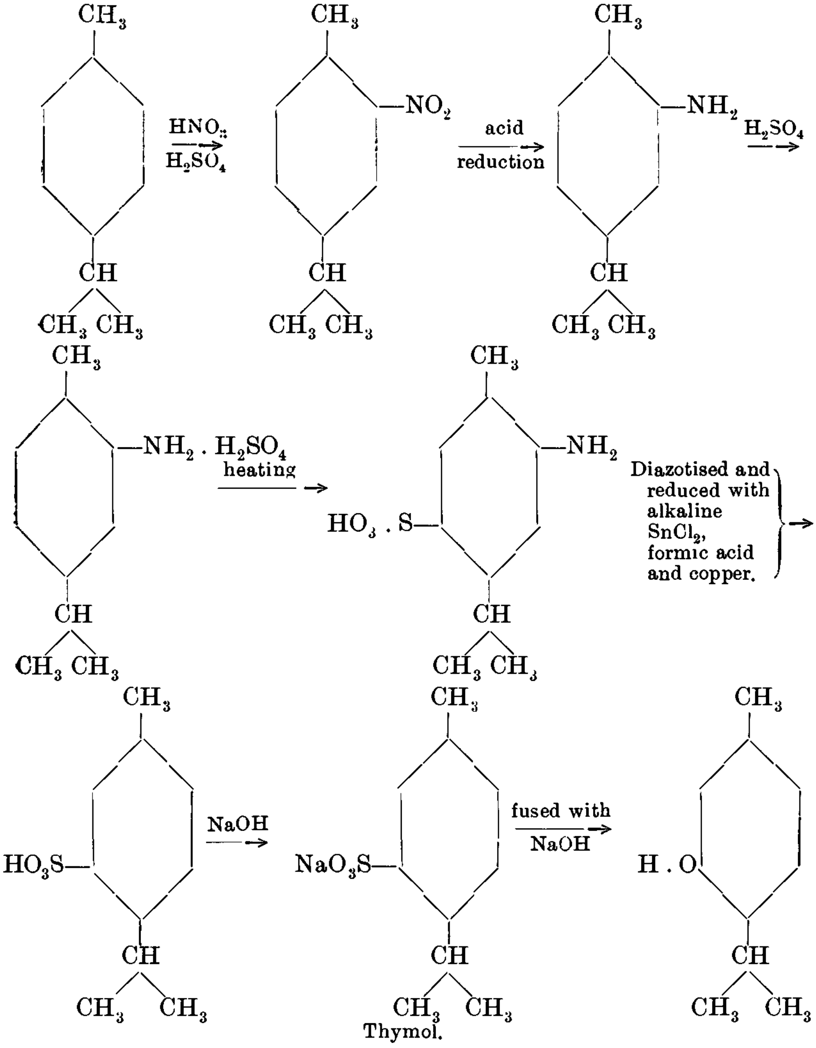
[1] *Zeitsch. angew. Chem.*, **9**, p. 685 (1896); *Berichte*, **13**, p. 1940 (1880); *Dingl. Polyt. Jour.*, **264**, p. 181 (1887).

The cymidin sulphonic acid is then diazotised in the usual manner by treating with sodium nitrite in acid solution and the diazo body reduced with alkaline tin chloride solution, or with formic acid and powdered copper, or with other relatively gentle reducing agents. The 3 or 5 cymidin sulphonic acid gives by the above process one and the same cymene sulphonic acid, viz., 1-methyl-3-sulphonic-4-isopropyl benzene.

The sodium salt of the cymene sulphonic acid is then fused with sodium hydroxide in the usual manner, and the hydroxyl group substituted for the sulphonic group. This gives 1-methyl-3-hydroxy-4-isopropyl-benzene or thymol.

The thymol can be separated by dissolving the product obtained by the sodium hydroxide fusion in water, acidulating with dilute sulphuric acid, and then steam distilling; or it may be extracted with a suitable solvent or in any other appropriate manner.

The reactions which take place in the process are conveniently expressed as follows:—



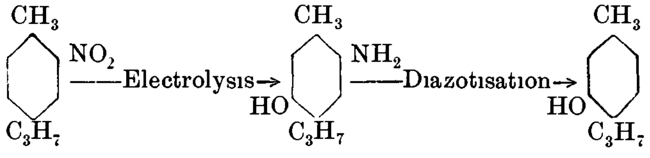
The latest patent for the preparation of artificial thymol is that of R. M. Cole (U S P 1,378,939, 24 May, 1921) His method consists essentially in the electrolytic reduction of nitro-cymene in the presence of sulphuric acid, and the subsequent diazotisation and reduction of the para-amidocymenol produced, by electric action, involving the use of stannous chloride

Apparatus suitable for the electrolytic reduction comprises a cylindrical tank with a lead lining, which also serves as the anode In this vessel is placed a container, sufficiently porous to permit the passage of ions from one chamber to another, but nearly impervious to the passage of molecules, and within the container is arranged a carbon or copper cathode in the form of a hollow perforated cylinder Within this latter cylinder is also arranged a stirrer or agitator, preferably of stoneware or lead-covered iron The anode chamber is charged with 30° Bé (sp gr. 1·26) sulphuric acid, and the cathode space with 25° Bé (sp gr 1·21) acid The strength of the acid in the anode chamber is maintained throughout the process by the addition of water in suitable quantities as the reaction proceeds The nitro-cymene is placed in the cathode space in a quantity approximately 50 per cent of the weight of 100 per cent acid

A current of density 5½ amperes per square decimetre of cathode space and a potential of 3 volts is used, and the temperature is maintained at between 75° and 85° C. During the electrolytic action, the nitro-cymene is kept in thorough emulsion in the aqueous acid solution by means of the agitator.

After the electrolytic action has continued for a suitable period, the contents of the vessel are allowed to cool, following which the unchanged nitro-cymene is separated for re-use, and the 1-methyl-2-amino-4-isopropyl-5-hydroxy benzol is filtered off from the remaining acid solution, which latter is strengthened for re-use The 1-methyl-2-amino-4-isopropyl-5-hydroxy benzol is then diazotised, and further reduced in an alkaline solution of stannous chloride, in the usual and well-known manner, with the resulting production of thymol (1-methyl-4-isopropyl-5-hydroxy benzol)

The reactions taking place in following out this process may be shown thus —



It is interesting to note that thymol, as well as its isomer carvacrol can be removed from its alkaline solution either by distillation by steam, or by repeated extraction by ether [1]

THYMOL-METHYL ETHER.

The methyl ether of thymol is found in the oil of *Crithmum maritimum*. It is a liquid of the constitution—

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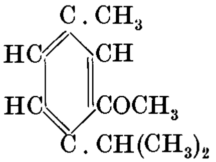
[1] *Berichte*, **32** (1899), 1517; and **15** (1882), 817.



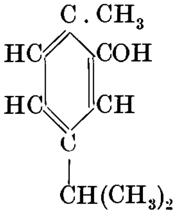
boiling at 214° to 216°, and having a specific gravity 0·954 at $\frac{0°}{4°}$.

On treatment with hydrobromic acid in acetic acid solution it yields thymol.

CARVACROL.

Carvacrol, $C_{10}H_{14}O$, is a phenol isomeric with thymol, with which it is frequently found associated, especially in certain types of thyme and origanum oils.

Carvacrol is isopropyl-*ortho*-cresol, of the following constitution :—



It results, artificially, from the treatment of carvone by potash or phosphoric acid, and by heating camphor with iodine.

Carvacrol is a colourless liquid, with a fragrant odour, solidifying, when quite pure, in the cold.

Its characters are as follows :—

Melting-point	+ 0·5° to + 1°
Boiling-point	236°
Specific gravity	0·981
Refractive index	1·5240
Optical rotation	± 0°

It yields a phenylurethane melting at 141°.

If carvacrol be treated, in alcoholic potash solution, with amyl nitrite, nitrosocarvacrol, $C_6H_2(CH_3)(OH)(C_3H_7)(NO)$, results. This body forms well-defined crystals melting at 153°.

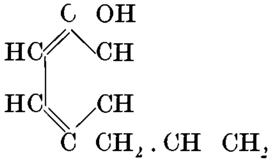
By heating carvacrol with alkalis, it is converted into isocuminic acid, $C_6H_3(C_3H_7)(OH)(COOH)$, melting at 93°. By oxidation with chromic acid mixture, thymoquinone results. This compound forms crystalline tables melting at 45° to 46°.

CHAVICOL.

Chavicol, $C_9H_{10}O$, is an unsaturated phenol, found in oils of betel nut and bay leaves. It is a colourless, highly odorous liquid, having the following characters :—

Specific gravity	1·035
Optical rotation	± 0°
Refractive index	1·5441
Boiling-point	237°

It is *para*-oxy-allyl-benzene, of the constitution—



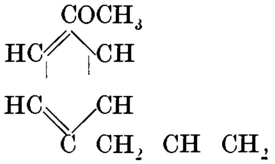
Like most phenols, it gives an intense blue colour with solution of ferric chloride By heating it with alcoholic potash and methyl iodide it is converted into methyl-chavicol or estragol, the characteristic constituent of tarragon oil

ESTRAGOL

Estragol, or methyl-chavicol, $C_{10}H_{12}O$, is a constituent of tarragon, anise-bark, bay, fennel, and other essential oils. It is a strongly odorous liquid having the following characters —

Boiling point . .	215° to 216° (corrected)
,, ,, at 12 mm .	97° to 98°
Specific gravity . .	0 972°
Refractive index . .	1 5220

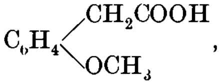
Its constitution is—



Methyl-chavicol (estragol, isoanethol methyl *p*-oxy-allyl-benzene) is isomeric with anethol, which by a system of cross-naming is also known as iso-estragol In common with other phenol ethers, containing the allyl group, estragol is converted into its isomer, anethol, which contains the propenyl group, by boiling with alcoholic potash.

This reaction serves as a means of identification of estragol. If it be heated for twenty-four hours on the water-bath, with three times its volume of a saturated alcoholic solution of potash, it is converted into anethol, which, after drying and recrystallisation from petroleum ether, melts at 22°, and boils at 232° to 233°

If 30 grams of estragol be shaken with 20 grams of potassium permanganate in 2000 c c of water, and 20 c c of acetic acid, the solution being kept cold, estragol yields homo-anisic acid which can be isolated by rendering the liquid alkaline with carbonate of sodium, filtering, liberating the acid by the addition of sulphuric acid, and extracting with ether.

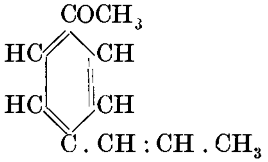
Homo-anisic acid,  $C_6H_4\begin{cases}CH_2COOH\\OCH_3\end{cases}$, forms well-defined crystalline tablets, melting at 85° to 86°

ANETHOL.

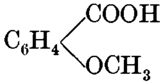
Anethol (isoestragol, methyl-*p*-oxy-propenyl-benzene) is the principal constituent of aniseed and star aniseed oil, and occur to a considerable extent in fennel oil. It is a crystalline solid, having the characteristic odour of aniseed oil, and possessing the following characters :—

Melting-point	22° to 23°
Boiling-point	233° ,, 234°
Specific gravity at 25°	0·985
Refractive index at 25°	1·5600

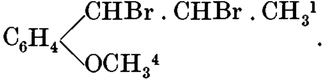
Its constitution is—



Anethol is the raw material from which most of the artificial hawthorn perfume is manufactured. This perfume consists of anisic aldehyde, known commercially under the name "aubepine".

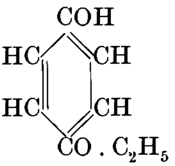
Anethol can be identified by oxidation to anisic acid,  $C_6H_4\begin{cases}COOH\\OCH_3\end{cases}$, melting at 184°. It is obtained in the following manner: 5 grams of the anethol containing oil or fraction are heated to 50° with a solution of 25 grams of bichromate of potassium and 50 grams of sulphuric acid made up to 100 c.c. with water. The mixture is well shaken, allowed to cool and the liquid decanted. The solid deposit is washed with water and finally recrystallised twice from boiling water when it will be found to melt at 184°.

Anethol dibromide, $C_6H_4 . OCH_3 . C_3H_5Br_2$, melting at 67°, is also a useful crystalline derivative by which anethol can be identified. It is obtained by the action of bromine in chloroform solution on anethol. The product is crystallised from petroleum ether, and then melts at 67°.

Its constitution is  $C_6H_4\begin{cases}CHBr . CHBr . CH_3{}^1\\OCH_3{}^4\end{cases}$.

HYDROQUINONE ETHYL ETHER.

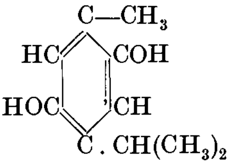
The ethyl ether of hydroquinone, *para* oxyphenetol, $C_8H_{10}O_2$, is found to a small extent in oil of star aniseed. It can also be prepared artificially by heating *para*-diazophenetol sulphate with dilute sulphuric acid, or by boiling hydroquinone with ethyl iodide and potassium hydroxide under a reflux condenser. Its constitution is—



It forms white colourless needles, melting at 66° and boiling at 246° to 247°.

THYMOHYDROQUINONE.

Thymohydroquinone, $C_{10}H_{14}O_2$, is a constituent of the essential oils of *Callitris quadrivalvis*, *Monarda fistulosa*, and *Thuja articulata*. It is a crystalline compound melting at 143° and boiling at 290°, or at 130° at 6 mm. pressure. Its constitution is—



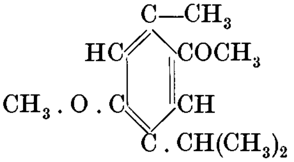
By oxidation with potassium permanganate, it yields thymoquinone (*q.v.*).

THYMOHYDROQUINONE DIMETHYL ETHER.

This phenolic compound, $C_{12}H_{18}O_2$, exists in the essential oil of *Eupatorium triplinerve*, and in arnica root oil. It is an oil having the following characters:—

Boiling-point	248° to 250°
„ „ at 12 mm.	118°
Specific gravity at 20°	0·9913
Refractive index	1·5134

Its constitution is—



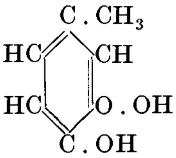
By treatment with hydriodic acid and amorphous phosphorus, it is converted into thymohydroquinone, which melts at 143°, and which, as described above, yields thymoquinone on oxidation.

THYMOQUINONE.

This body, although not a phenol or phenolic ether, is conveniently described here. It is a quinone, of the formula $C_6H_2(O_2)(CH_3)(C_3H_7)$, occurring in the essential oils of *Monarda fistulosa* and *Thuja articulata*. It is a crystalline body melting at 48° and boiling at 98° to 100° at 6 mm. By treatment with hydroxylamine it yields isonitrosothymol, $C_{10}H_{13}NO_2$, melting at 161°. This body, on oxidation with potassium ferrocyanide in alkaline solution, yields mononitrothymol, melting at 137°.

CREOSOL.

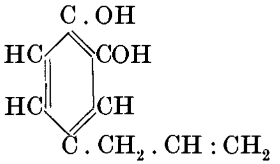
Creosol is a diphenol, of the constitution—



It occurs in oil of ylang-ylang. It is an odorous oil boiling at 220°.

ALLYL-PYROCATECHOL.

Allyl-pyrocatechol, $C_9H_{10}O_2$, exists in betel leaf oil. It is a crystalline body melting at 48° to 49° and boiling at 139° at 4 mm. It yields a dibenzoyl derivative melting at 71° to 72°. Its constitution is as follows:—



By methylation with dimethyl sulphate and potash, it yields methyl-eugenol, boiling at 248° to 249°; and which on oxidation yields veratric acid, melting at 179° to 180°.

PYROGALLOL DIMETHYL ETHER.

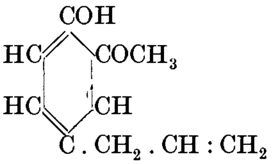
This phenolic ether, $C_6H_3(OH)(OCH_3)_2$, has been identified in the essential oil of an Algerian plant, whose botanical source is not identified. It is a crystalline body melting at 51°, and yields a benzoyl derivative melting at 107° to 108°.

EUGENOL.

Eugenol, $C_{10}H_{12}O_2$, is the characteristic constituent of the oils of cloves, cinnamon leaf, bay and pimento, and is also found in numerous other essential oils. It is a liquid of powerful clove odour, having the following characters:—

Specific gravity	1·070
Refractive index	1·5439
Boiling-point	252° at 750 mm.
„ „	123° „ 12 „
Optical rotation	± 0°

It has the following constitution:—



It is the raw material from which the bulk of the vanillin of commerce is obtained (see under *Vanillin*), for which purposes very large quantities are consumed.

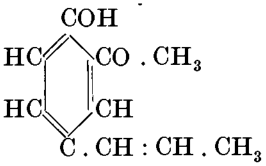
Eugenol yields a characteristic benzoyl derivative when treated with benzoyl chloride in the presence of caustic potash. Benzoyl-eugenol melts at 69° to 70°.

The diphenylurethane melts at 107° to 108°. By treatment with methyl iodide in the presence of caustic alkali, eugenol is converted into methyl-eugenol, which is characterised by its monobromo derivative melting at 79° to 80°.

For the manufacture of vanillin, eugenol is first isomerised to iso-eugenol, in which a rearrangement in the side chain has taken place.

ISOEUGENOL.

Isoeugenol, $C_{10}H_{12}O_2$, is found to a small extent in the essential oils of ylang-ylang and nutmeg, but is principally of importance in the manufacture of vanillin, eugenol being first isomerised into isoeugenol, which is then converted into vanillin. Isoeugenol has the following constitution:—



Its characters are as follows:—

Boiling-point	262°
Specific gravity	1·0880
Refractive index	1·5730

Isoeugenol, when cooled to a very low temperature, crystallises in fine needles, which melt at 34°, but it usually exists in a state of superfusion.

It is a liquid with a powerful carnation odour, and is indispensable in the compounding of perfumes of the carnation and "œillet" type.

There are several crystalline compounds useful for the identification of isoeugenol, amongst which are the following:—

Benzoyl-isoeugenol, melting at 105°, is prepared by the addition to 10 parts of isoeugenol of a dilute solution of caustic soda, and then of 15 parts of benzoyl chloride. The temperature should be kept low, and crystals of benzoyl-eugenol will separate.

If equimolecular proportions of isoeugenol and acetic anhydride are heated for four to five hours to 135°, and the mixture washed with dilute alkali, acetyl-isoeugenol results, which, when dissolved in benzene and precipitated by petroleum ether, crystallises in needles melting at 79° to 80°.

Isoeugenol, shaken with dimethyl sulphate and caustic potash, yields methyl-isoeugenol, which can be identified by its dibromide, melting at 101° to 102°.

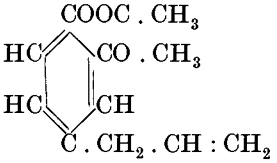
Isoeugenol yields a diphenyl-urethane, melting at 112° to 113°.

The conversion of eugenol into isoeugenol is a matter of considerable importance, especially in the manufacture of vanillin (*q.v.*). It can be effected by boiling eugenol with alcoholic potash for twenty-four hours, but the yield is not a satisfactory one. According to De Laire's patent (*France*, 209,149), 25 parts of caustic potash and 36 parts of amyl alcohol are heated, and any carbonate of potash present is separated by filtration. Five parts of eugenol are added and the mixture heated to 140° for sixteen to eighteen hours, the amyl alcohol being then removed by steam distillation. The isoeugenol is then liberated by the addition of dilute sulphuric acid and distilled in a current of steam.

There are several other methods for the isomerisation of eugenol, but they all, in the main, depend on the action of caustic alkalis at an elevated temperature.

ACETEUGENOL.

A very small amount of aceteugenol is present in essential oil of cloves. Its constitution is as follows:—



It also results from the action of acetic anhydride on eugenol. Its characters are as follows:—

Melting-point	29°
Boiling-point at 752 mm.	281°
„ „ „ 8 „	146°
Specific gravity (at 15°, superfused)	1·0842
Refractive index („ „ „)	1·5207

Acetisoeugenol is the corresponding derivative of isoeugenol, and melts at 79° to 80°.

METHYL-EUGENOL.

The methyl ether of eugenol, $C_{11}H_{14}O_2$, is found in calamus oil, cassie oil, betel oil, bay oil, and various other essential oils. It can be prepared artificially by the action of methyl iodide on eugenol sodium. Its constitution is identical with that of eugenol, except that the phenolic group, OH, has been replaced by the methoxy group, $O . CH_3$.

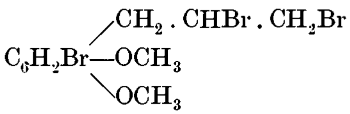
It is a useful adjunct in the manufacture of perfumes of the carnation type, modifying the odours of eugenol and isoeugenol to some extent.

Its characters are as follows:—

Specific gravity	1·042
Optical rotation	± 0°
Refractive index	1·5380
Boiling-point	248°

The principal derivative for identification purposes is veratric acid, $C_6H_3(COOH)(OCH_3)_2$, which is obtained by oxidising 6 grams of methyl-eugenol with a solution of 18 grams of potassium permanganate in 400 c.c. of water. When recrystallised from alcohol, veratric acid melts at 179° to 180°.

Monobrom-methyleugenol dibromide is also a useful derivative to prepare. Its constitution is—



$$C_6H_2Br\begin{array}{l}\diagup CH_2 . CHBr . CH_2Br\\ —OCH_3\\ \diagdown OCH_3\end{array}$$

It can be obtained by dissolving 50 grams of methyl-eugenol in 100 grams of absolute ether, and adding 30 c.c. of bromine drop by drop, the mixture being kept cold during the process. The crystalline compound, having the above formula, melts at 79° to 80°.

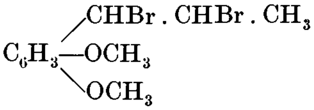
METHYL-ISOEUGENOL.

Methyl-isoeugenol, $C_{11}H_{14}O_2$, bears exactly the same relationship to isoeugenol as methyl-eugenol does to eugenol. It occurs naturally in the oil of *Asarum arifolium*, and can be obtained by the action of methyl iodide on isoeugenol sodium, or by isomerising methyl-eugenol by hot alcoholic potash.

Methyl-isoeugenol has the following characters :—

Boiling-point	263°
Specific gravity	1·062
Refractive index	1·5720

On oxidation it yields veratric acid melting at 179° to 180°, and by the action of bromine on the phenol-ether dissolved in absolute ether, a dibromide is obtained, which melts at 101° to 102°. It has the constitution—



$$C_6H_3\begin{array}{l}\diagup CHBr\,.\,CHBr\,.\,CH_3\\ -OCH_3\\ \diagdown OCH_3\end{array}$$

TASMANOL.

Robinson and Smith[1] have separated a phenol from the oil of *Eucalyptus linearis*, which they have named tasmanol.

The phenol was removed from the crude oil in the usual manner by shaking with aqueous sodium hydrate, washing the aqueous solution with ether to remove adhering oil, acidifying and extracting with ether. The residue, which contained a small amount of acetic and butyric acids, was washed with dilute sodium carbonate, extracted with ether, the ether removed and the phenol distilled. It boiled at 268° to 273° C. (uncor.) and at 175° under 25 mm. pressure. It was optically inactive, the specific gravity at 23° was 1·077, and the refractive index at 22° was 1·5269. Besides being soluble in alkalies the phenol is soluble in ammonia, partly soluble also in sodium carbonate but not in bicarbonate. It also dissolves slightly in boiling water. The reaction with ferric chloride in alcoholic solution is characteristic, the deep red colour which is first formed remaining persistent for days, after the alcohol has evaporated. The odour reminds one somewhat of carvacrol. It contains one methoxy group and appears to have two phenolic groups in the para position to each other.

AUSTRALOL.

Australol is a crystalline phenol obtained by Baker and Smith[2] from various eucalyptus oils, including those of *Eucalyptus hemiphloia* and *E. wooloiana*. It is a very caustic substance, resembling ordinary phenol in odour. Its characters are as follows :—

Melting point	62°
Specific gravity at 20°	0·9971 (superfused)
Refractive index at 20°	1·5195 („)
Boiling-point	115° to 116° at 10 mm.

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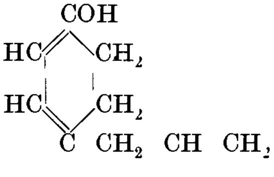
[1] *Jour. of Proc. Roy. Soc., N.S.W.*, **48** (1914), 518.

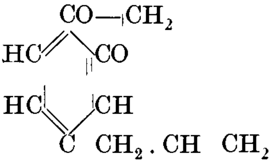
[2] *A Research on the Eucalypts*, 2nd. edition, p. 396.

It forms long thin prisms, which when melted tend to remain in the liquid condition, but when the liquid is sown with a crystal of the phenol it at once solidifies It forms a benzoyl compound, melting at 72° to 73°. It is apparently dihydro-para-allylphenol of the constitution—



SAFROL

Safrol, $C_{10}H_{10}O_2$, is the methylene ether of allyl-dioxybenzene, of the constitution—



It is found to a considerable extent in oils of sassafras, camphor, and *Ilicium religiosum.* When pure it is a white crystalline mass at low temperatures, melting at + 11°. At ordinary temperatures it forms a colourless oil of characteristic, pleasant odour, and having the following characters —

Specific gravity	1·105 to 1·107
Refractive index .	1·5360 „ 1·5400
Melting point .	+ 11°
Boiling point .	233°
„ „ at 4 mm.	91°
Optical rotation . .	± 0°

It is easily converted into isosafrol (containing the propenyl group) by the action of alcoholic potash. Safrol is used to an enormous extent for perfuming cheap soaps, and is also of great commercial value on account of the fact that on oxidation it yields heliotropin, an artificial perfume which is now largely employed (*q v.*).

Safrol, on oxidation in the following manner, yields homopiperonylic acid, melting at 127° to 128°. A mixture of 5 parts of safrol and 12·5 parts of potassium permanganate dissolved in water and 5 parts of acetic acid are heated to 70° to 80°, and the liquid rendered alkaline.

The liquid is filtered, and on extraction with ether yields some piperonal (heliotropin), melting at 37°. The residual liquid is boiled with magnesium carbonate, resinous matter extracted with ether, the liquid filtered and the acid set free by means of dilute sulphuric acid. Homopiperonylic acid crystallises out on evaporation, and forms fine needles melting at 127° to 128°.

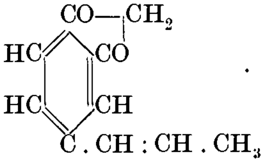
If chromic acid be used as the oxidising agent, piperonal and piperonylic acid, melting at 228°, are formed

Safrol yields a pentabromide, $C_{10}Br_5H_5O_2$, melting at 169° to 170° On reduction by nickel in a stream of hydrogen, safrol yields a dihydro product, $C_{10}H_{12}O_2$, boiling at 228°, and *meta*-propyl-phenol, boiling at 228° also.

ISOSAFROL.

Whilst safrol is the methylene ether of allyl-dioxy-benzene, isosafrol is the methylene ether of propenyl-dioxy-benzene, so that the two bodies are related to each other in the same way as eugenol and isoeugenol.

Isosafrol results from the isomerisation of safrol by heating with alcoholic potash, and this conversion is the preliminary step in the manufacture of heliotropine since isosafrol yields considerably more heliotropine on oxidation than safrol does. Isosafrol has the following constitution :—



Its characters are as follows :—

Specific gravity	1·1255
Boiling-point	254°
Refractive index	1·5780

Isosafrol yields piperonal (heliotropine) melting at 37° as the principal product of oxidation when potassium permanganate is used as the oxidising agent. If the oxidation be very energetic piperonylic acid, melting at 228°, is the principal reaction product.

With excess of bromine, isosafrol yields a penta-bromide, melting at 197°. If safrol, dissolved in carbon bisulphide be heated carefully with bromine, it yields monobrom-isosafrol dibromide, $C_{10}H_9Br_3O_2$, melting at 109° to 110°.

According to Hoering and Baum,[1] commercial isosafrol contains two geometric isomers, which they term α-isosafrol and β-isosafrol. They differ slightly in odour, α-isosafrol being intermediate in this respect between safrol and β-isosafrol. It is not probable that they yield different products on oxidation, nor is there the slightest reason to believe that heliotropine is any such corresponding mixture.

ASARONE.

Asarone, or 4-propenyl-1 . 2 . 5 . trimethoxybenzene, $C_{12}H_{16}O_3$, is the trimethyl ether of a triphenol, which is found occurring naturally in the essential oil of *Asarum arifolium*, and to a small extent in matico and acorus oils. It is an aromatic crystalline compound having the following characters :—

Melting-point	62°
Specific gravity	1·088
Refractive index	1·5719
Boiling-point	296°

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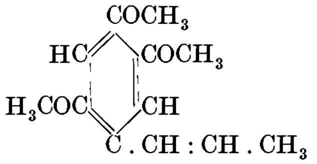
[1] *Berichte*, **42** (1909), 3076.

Its constitution is—



On treatment with bromine in carbon tetrachloride solution, it yields a dibromide in which two atoms of bromine have been fixed in the propenyl side chain, melting at 85° to 86°.

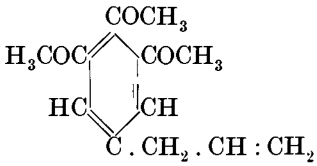
By oxidation asarone yields asarylic aldehyde, $C_6H_2(CHO)(OCH_3)_3$, melting at 114°, and finally asarylic acid, $C_6H_2(COOH)(OCH_3)_3$, melting at 144°. This acid is, of course, identical with trimethoxy-benzoic acid.

ELEMICIN.

Elemicin is isomeric with asarone. It is 4-allyl-1 . 2 . 6-trimethoxybenzene, and is found in the essential oil of Manila elemi. Its characters are as follows:—

Specific gravity	1·066
Boiling-point at 10 mm.	144° to 147°
Refractive index	1·5285

Its constitution is—



If elemicin be heated with alcoholic solution of potash, the allyl group is isomerised to the propenyl group, and iso-elemicin results.

Both bodies yield trimethylgallic acid, $C_6H_2(COOH)(OCH_3)_3$, melting at 169° on oxidation.

Elemicin has been synthesised by Manthora.[1]

By boiling allyl bromide and pyrogallol dimethyl ether with acetone and potassium carbonate, he obtained a dimethoxyphenyl allyl ether, which was converted into dimethoxyallyl phenol by heating to 220°. On methylation this yields trimethoxyallyl benzene, identical with elemicin.

MYRISTICIN.

Myristicin, $C_{11}H_{12}O_3$, is 4-allyl-6-methoxy-1 . 2-methylenedioxybenzene. It is found in oil of nutmeg and in parsley oil. It is a fragrant compound having the following characters:—

Specific gravity	1·1450
Refractive index	1·5403
Boiling-point	171° to 173° at 40 mm.
,, ,,	149° at 15 mm.

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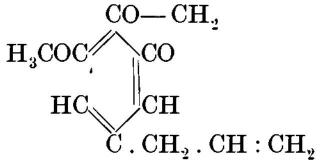
[1] *Annalen*, **414** (1917), 250.

Its constitution is—



On isomerisation with hot alcoholic potash it yields isomyristicin, which contains the propenyl group in the side chain, and is a solid body melting at 44° to 45°.

Myristicin and isomyristicin are distinguished by their reactions with bromine. Myristicin, when treated with two atoms of bromine, yields an oily liquid, whilst isomyristicin yields a crystalline body melting at 109°. If the isomers are dissolved in acetic acid, and treated with bromine until no more is absorbed, the mixture being kept cold all the time, the following compounds are obtained:—.

$$C_6Br_2(CH_2 . CHBr . CH_2Br .)(OCH_3)(O_2CH_2).$$

Dibromomyristicin dibromide. Melting point = 130°.

$$C_6Br_2(CHBr . CHBr . CH_3)(OCH_3)(O_2CH_2).$$

Dibromoisomyristicin dibromide. Melting point = 156°.

Both isomers yield myristic aldehyde on oxidation by means of potassium permanganate. This aldehyde has the formula

$$C_6H_2(CHO)(OCH_3)(O_2CH_2),$$

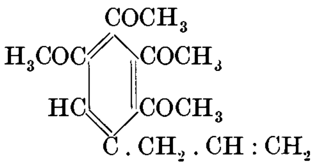
and melts at 131°. By further oxidation it yields myristic acid,

$$C_6H_2(COOH)(OCH_3)(O_2CH_2),$$

melting at 210°

ALLYL-TETRAMETHOXYBENZENE.

This phenol ether has been isolated from French oil of parsley. It is a crystalline compound of the formula $C_{13}H_{18}O_4$, which can be separated by freezing the oil and drying the crystals on porous plates for twenty-four hours, and recrystallising the product several times from alcohol. Its constitution is as follows:—



It has the following characters:—

Melting-point	25°
Specific gravity at 25°	1·087
Refractive index at 25°	1·5146

The corresponding propenyl isomer is unknown.

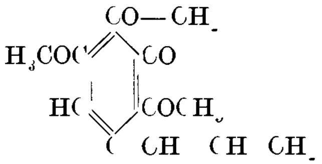
On oxidation with permanganate of potassium, this phenol ether yields tetramethoxy benzoic acid, $C_6H(OCH_3)_4COOH$, melting at 87°.

APIOL

Apiol, the principal constituent of oil of parsley, is an allyl-dimethoxy-methylene-dioxybenzene of the formula $C_{12}H_{14}O_4$ Its physical characters are as follows —

Melting point	30°
Boiling point	294°
,, ,, at 33 mm	179°
Specific gravity	1.1788 (superfused)
Refractive index	1.5380

Its constitution is as follows —



On heating apiol for twelve hours with alcoholic solution of potash, it is isomerised, the allyl group being changed into the propenyl group, isoapiol resulting Isoapiol, $C_6H(CH:CH.CH_3)(OCH_3)_2(O_2CH_2)$ is a crystalline compound having the following characters —

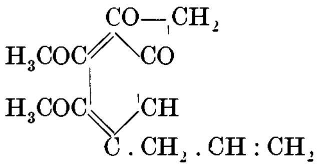
Melting point	55° to 56
Boiling point	303° ,, 304
,, ,, at 33 mm	180°

Apiol can be identified by its melting-point and its easy conversion into isoapiol, melting at 55° to 56°

If apiol, dissolved in carbon bisulphide, be treated with bromine in the same solvent, and the solvent evaporated, monobromapiol dibromide, $C_6Br(O_2CH_2)(OCH_3)_2(C_3H_5Br_2)$ melting at 88° to 89° results It can be obtained in a pure state by several crystallisations from absolute alcohol The corresponding isoapiol compound melts at 120° Both apiol and isoapiol yield apiolic aldehyde and apiolic acid on oxidation, a better yield being obtained if apiol be first isomerised to isoapiol Four grams of isoapiol are dissolved in 40 c c of acetic acid, and 5 grams of chromic acid dissolved in 100 grams of acetic acid are added After about two hours, 1000 c c of water are added, the mixture neutralised with caustic soda, and the liquid filtered On standing in a cold place, long needles of apiolic aldehyde $C_{10}H_{10}O_5$, separates, which when recrystallised from alcohol, melt at 102° and boil at 315° To convert isoapiol into apiolic acid, 30 grams of potassium permanganate are dissolved in 1600 c c of water and mixed with 8 grams of isoapiol suspended in 800 c c of water rendered alkaline and heated to boiling temperature The mixture is heated for an hour on the water-bath and then filtered and unaltered isoapiol extracted with ether The mixture is then acidified with sulphuric acid, the yellow precipitate formed is dissolved in boiling water with the addition of animal charcoal, and the filtrate allowed to cool, when apiolic acid, $C_{10}H_{10}O_6$, melting at 175°, separates

DILLAPIOL

Dillapiol, $C_{12}H_{14}O_4$, differs from apiol only by the orientation of its side chains It is found in East Indian, Japanese, and Spanish dill oils, and in certain types of matico oils, etc. It has the following constitution:—



Its physical characters are as follows;—

Boiling-point	285°
„ „ at 11 mm.	162°
Specific gravity at $\frac{13^\circ}{4^\circ}$	1·1644
Refractive index at 25°	1·5278

By boiling with alcoholic potash for six to eight hours, the allyl group is changed into the propenyl group, and iso-dillapiol results. This body is a crystalline compound, melting at 44° and boiling at 296°.

If dillapiol dissolved in glacial acetic acid be treated with excess of bromine, a precipitate is obtained, which, after several recrystallisations from alcohol, forms fine needles, melting at 110°. This body is monobrom-dillapiol dibromide of the formula,

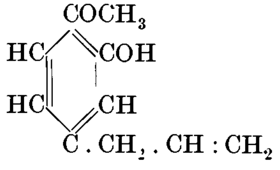
$$C_6Br(CH_2 . CHBr . CH_2Br)(OCH_3)(O_2CH_2).$$

Iso-dillapiol, which has also been found naturally in oil of *Piper acutifolium*, yields the corresponding bromide, melting at 115°.

On oxidation, in the manner described under apiol, there are obtained from both dillapiol and iso-dillapiol, dillapiolic aldehyde, melting at 75°, and dillapiolic acid, melting at 151° to 152°.

CHAVIBETOL.

This phenolic constituent of betel oil, $C_{10}H_{12}O_2$, is an allyl-guaiacol, of the constitution—



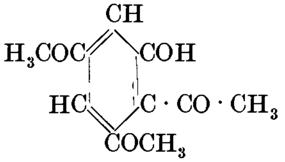
It is an oil having the odour of betel oil, and whose characters are as follows:—

Boiling point	254° to 255°
„ „ at 12 mm.	131° „ 133°
Specific gravity	1·069
Refractive index	1·5413
Melting-point	+ 8·5°

It yields a benzoyl compound, which crystallises in small plates melting at 49° to 50°. It also yields an acetyl derivative, boiling at 275° to 277°.

PHLORACETOPHENONE-DIMETHYL-ETHER.

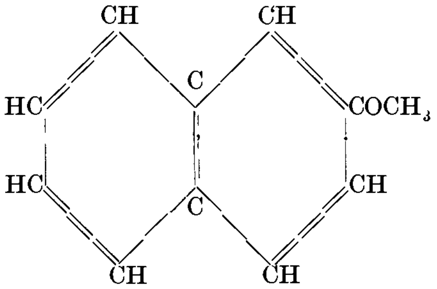
This ether, $C_{10}H_{12}O_4$, is a constituent of the oil of *Blumea balsamifera.* It is a colourless crystalline compound melting at 82° to 83°. Its constitution is as follows:—



It yields an oxime, melting at 108° to 110°, an acetyl derivative melting at 106° to 107°, a methyl ether melting at 103°, and a yellow crystalline monobromide melting at 187°.

β-NAPHTHOL-METHYL-ETHER.

This substance is an artificial perfume having a neroli-like odour, and was introduced into commerce under the name yara-yara, and is also known as nerolin. It is a crystalline compound melting at 72° and boiling at 274°. Its constitution is—



It can be prepared by digesting β-naphthol-sodium with the calculated quantity of methyl iodide in methyl alcohol solution; or by heating 1 part of β-naphthol, 3 parts of methyl alcohol, and 1 part of hydrochloric acid in an autoclave to 150°.

β-NAPHTHOL-ETHYL-ETHER.

This body corresponds with the methyl-ether just described, the CH_3 group being replaced by the C_2H_5 group. It is prepared in the same manner, substituting ethyl compounds for the methyl compounds. It was introduced into commerce under the name bromelia, and is, in common with the methyl-ether, known as nerolin. It is a colourless crystalline solid melting at 37° and boiling at 282°. Its specific gravity at 50° is 1·051. The ethyl-ether has a finer odour than the methyl-ether, and has a suggestion of pine-apple.

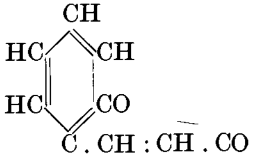
β-NAPHTHOL-BUTYL-ETHER.

This substance is an aromatic compound, similar to the ethel-ether, and is a useful fixative. It has been sold under the name Fragarol.

8. OXIDES AND LACTONES.

COUMARIN.

Coumarin, $C_9H_6O_2$, is, chemically, the δ-lactone of coumarinic acid (*o*-oxycinnamic anhydride), of the constitution—

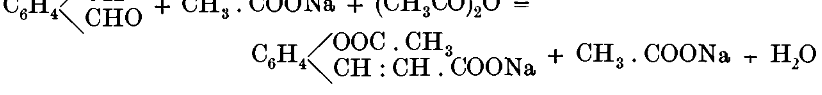


It is a white crystalline solid, melting at 67° to 68° and distilling at 290°. It is soluble in hot water, alcohol, ether, vaseline, and oils in general. It is the active odorous ingredient of the Tonquin bean (Tonca or Tonco bean), the seeds of at least two species of *Dipteryx* (N.O. *Leguminosæ*), in which it occurs up to 3 per cent. Coumarin possesses the characteristic odour of the Tonca bean, in which it was discovered in 1825 by Boullay.[1] It also occurs naturally in abundance in the dried leaves of *Liatris odoratissima* (deer's tongue, hound's tongue), an herbaceous plant common in North Carolina, 1 lb. of leaves yielding from 1½ to 2½ drachms of coumarin. It has also been found in the following plants, amongst others :—

Angræcum fragrans.
Myroxylon Pereiræ.
Cevatopetalum apetalum.
Ataxia Horsfeldii.
Cinna arundinacea.
Hierochloa alpina.
    ,, *australis.*
    ,, *borealis.*
Milium effusum.
Adiantum pedatum.
    ,, *peruvianum.*
    ,, *trapeziforme.*
Drynaria Wildenovi.
Phœnix dactylifera.
Aceras Winthrophora.
Nigritella angustifolia.
Orchis fusca.
Herniaria glabra.
Ruta graveolens.
Alyxia stellata.
Asperula odorata.
Galium trifolium.
Liatris spicata.
Prunus Mahaleb.
Melilotus officinalis.
    ,, *hamatus*
    ,, *albus.*
    ,, *leucanthus.*
    ,, *altissimus.*
Ageratum mexicanum.
Copaifera Salikounda.
Trifolium Melilotus.
Anthoxanthum odoratum.

Coumarin was first produced synthetically by Perkin.[2] He made it by heating salicylic aldehyde, $C_6H_4(OH)^1(COH)^2$, acetic anhydride, and sodium acetate. The whole solidifies to a crystalline mass, from which, on treatment with water, an oil separates containing coumarin and acetocoumaric acid. This acid on heating is decomposed into acetic acid and coumarin, so that the product of distillation is principally coumarin.

Perkin's synthesis proceeds according to the following equation :—



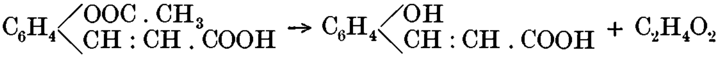
$$C_6H_4\left\langle\begin{matrix}OH\\CHO\end{matrix}\right. + CH_3 . COONa + (CH_3CO)_2O = C_6H_4\left\langle\begin{matrix}OOC . CH_3\\CH : CH . COONa\end{matrix}\right. + CH_3 . COONa + H_2O$$

---

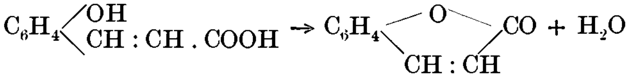
[1] *Jour. de Pharm.*, xi. 480.

[2] *Chem. Soc. Journ.*, xxi. 53, 181.

The sodium salt of aceto-coumaric acid on hydrolysis decomposes, yielding first an acid which loses water, forming coumarin, together with acetic acid—

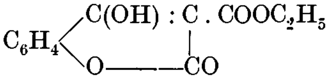


$$C_6H_4\begin{cases}OOC\,.\,CH_3\\CH:CH\,.\,COOH\end{cases}\rightarrow C_6H_4\begin{cases}OH\\CH:CH\,.\,COOH\end{cases}+C_2H_4O_2$$



$$C_6H_4\begin{cases}OH\\CH:CH\,.\,COOH\end{cases}\rightarrow C_6H_4\begin{cases}O\text{---}CO\\CH:CH\end{cases}+H_2O$$

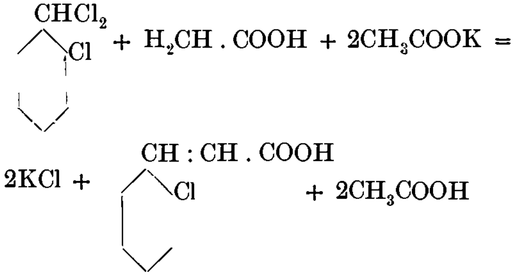
Anschütz[1] treated aceto-salicylic chloride with sodium-malonic ester, with the formation of ethyl acetate and β-hydroxy-coumarin-alpha-carboxylic ethyl ester—



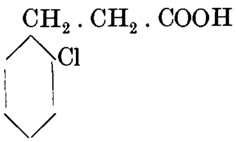
$$C_6H_4\begin{cases}C(OH):C\,.\,COOC_2H_5\\O\text{------}CO\end{cases}$$

This compound is heated with caustic potash solution, yielding beta-hydroxy-coumarin. From this body, coumarin is obtained by substituting a halogen atom for the OH group, and then reducing the product in alcoholic solution with zinc-dust.

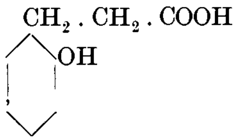
A synthesis of coumarin has been effected by Meyer, Beer, and Lasch.[2] Ortho-chlorbenzal chloride is heated with glacial acetic acid and potassium acetate—



yielding ortho-chlor-cinnamic acid. This is reduced to ortho-chlor-phenylpropionic acid—



On heating this under pressure, with a solution of caustic soda, ortho-hydroxy-coumaric acid results—



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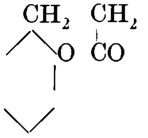
[1] *Annalen*, **202** (1909).

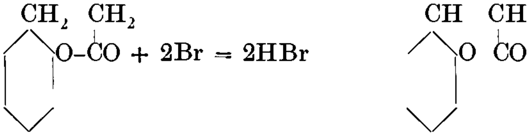
[2] *Monatshefte*, **34** (1913), 1665.

This acid forms needles melting at 81° C , and on boiling, yields hydrocoumarin—



which melts at 25° C , and boils at 272° C

By heating this lactone to 270° and 300°, and passing bromine vapour slowly over it, coumarin is produced—



Coumarin is sometimes adulterated with acetanilide, which should always be looked for , the ease with which it yields aniline, on heating with potash solution, renders it very easy of detection Some samples, otherwise pure, contain traces of unaltered salicylic aldehyde, which is revealed by the odour

Synthetic coumarin is largely used in the place of Tonca beans, and forms an extremely useful substance for fixing other odours Traces of fixed oil are useful in coumarin mixtures, as the coumarin odour appears to become more fixed in this way Foin coupé, or new-mown hay, is a favourite perfume in which coumarin is the chief ingredient The following table of solubilities of coumarin in alcohol of various strengths and in water has been compiled by Schimmel & Co —

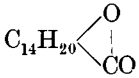
100 Parts of Alcohol		at 0° C	at 16° to 17° C	at 29° to 30° C
Of 90 volume per cent	dissolve	7 1 parts	13 7 parts	42 5 parts
,, 80 ,, ,,		6 0 ,	12 3 ,	38 3 ,
, 70 , ,,		4 4 ,,	9 1 ,	26 0 ,
, 60 ,, ,,		3 2 ,,	6 0 ,	16 0
,, 50 ,, ,,		1 7 ,,	3 4 ,	8·9 ,,
,, 40 ,, ,,		0 7 ,,	1 5 ,,	3 9 ,
,, 30 ,, ,		0 3 ,,	0 6 ,	1 7 ,
,, 20 , ,,		0 2 ,,	0 4 ,,	0·8 ,
,, 10 ,, ,,		0 15 ,,	0 25 ,,	0 5 ,,
100 parts of water		0 12 ,	0 18 ,,	0 27 ,,

On heating with concentrated solution of potash, coumarin is converted into *o*-coumaric acid, $HO\ C_6H_4\ CH\ CH\ COOH$, melting at 207° to 208°

ALANTOLACTONE

Alantolactone, $C_{15}H_{20}O_2$, also known as helenin, is a constituent of the essential oil of *Inula helenium* It is a crystalline compound, melting at

76° and boiling at 275° (or at 195° to 200° at 10 mm.). Its constitution is not known but it contains the following grouping :—



$$C_{14}H_{20}\Big\langle\begin{array}{l}O\\ |\\ CO\end{array}$$

By warming with dilute alkalis it is converted into the corresponding acid, alantolic acid, $C_{14}H_{20}(OH)(COOH)$, melting at 94°.

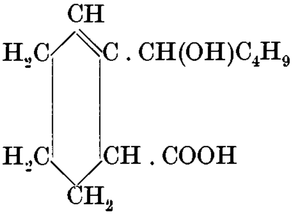
Alantolactone forms a hydrochloride melting at 117°, a hydrobromide melting at 106°, a dihydrochloride melting at 127° to 134°, and a dihydrobromide melting at 117°.

An isomeric compound, isoalantolactone, exists in the oil of *Inula helenium*. It is a crystalline body melting at 115°, and yielding isoalantolic acid with alkalis, melting at 237° to 239°.

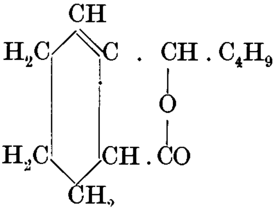
SEDANOLIDE.

Sedanolide, $C_{12}H_{18}O_2$, is the lactone of sedanolic acid. Both bodies occur in the essential oil of celery.

Sedanolide is a crystalline compound, melting at 88° to 89°. The relationships of the acid and its anhydride are shown by the following formulæ : —



Sedanolic acid.

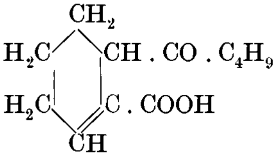


Sedanolide.

Sedanolide is therefore, probably, tetrahydrobutyl-phthalide.

SEDANONIC ANHYDRIDE.

The anhydride of sedanonic acid, $C_{12}H_{18}O_3$, is not a lactone, but an anhydride resulting from the elimination of a molecule of water from a monobasic ketonic acid. Sedanonic anhydride occurs in oil of celery. The acid, which melts at 113°, has the following constitution :—

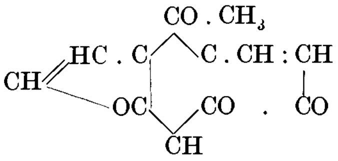


It is therefore *ortho*-valeryl-Δ'-tetrahydrobenzoic acid. The anhydride is formed by the elimination of a molecule of water from the two side chains.

BERGAPTENE.

Oil of bergamot contains about 5 per cent. of an odourless solid body known as bergaptene. This body has the formula $C_{12}H_8O_4$, and melts at

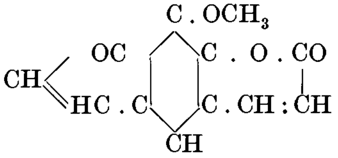
188°. It is the methyl ether of a phloroglucinol derivative, related to coumarin. Its constitution is as follows:—



By treatment with methyl iodide and alcoholic potash, it yields methyl-bergaptenic acid and its methyl ether.

Xanthotoxin.

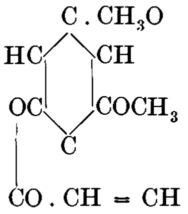
Xanthotoxin, $C_{12}H_8O_4$, is isomeric with bergaptene, and is present in the oil of *Fagara xanthoxyloides.* It is a solid compound, melting at 145° to 146°, and is a pyrogallol derivative, having the constitution—



It yields nitroxanthotoxin, $C_{12}H_7O_4 . NO_2$, melting at 230°, and a dibromide, melting at 164°.

Citraptene.

Citraptene, $C_{11}H_{10}O_4$, is the odourless solid constituent of the expressed oil of lemon. After repeated recrystallisations from acetone and methyl alcohol, it forms needles melting at 146° to 147°. By treatment with bromine in chloroform solution it yields a dibromide, $C_{10}H_{10}Br_2O_4$, melting at 250° to 260°. It appears to be a dimethyl-oxycoumarin of the constitution—



Cineol or Eucalyptol.

This body, $C_{10}H_{18}O$, has been described under several names, the best known being that now usually adopted, *viz.* cineol; also cajuputol (from its occurrence in oil of cajuput) and eucalyptol (from its occurrence in oil of eucalyptus). It is found in nature in very large quantities in the above-mentioned oils, as well as in many others, notably wormseed, lavender (English), and spike-lavender oils. It results also by the treatment of terpin hydrate with acids. Wallach and Brass, who first characterised it as a definite compound, give the following method for its preparation. A current of dry hydrochloric acid gas is passed into rectified wormseed oil. The resulting crystalline magma of cineol hydrochloride is pressed at low temperature to remove as much as possible of adhering liquid, and the crystals are treated with water and steam distilled. The crude cineol is again subjected to this treatment, when the pure body is obtained. When pure, cineol has the following characters :—

Specific gravity	0·930
Melting-point	+ 1°
Optical rotation	± 0°
Refractive index	1·4590
Boiling-point	176° to 177°

Scammel proposed its separation by means of a definite crystalline compound with phosphoric acid. This body has the composition $C_{10}H_{18}O . H_3PO_4$. The use of phosphoric acid is the basis of the British Pharmacopœial test for cineol in essential oils.

Cineol forms a number of crystalline derivatives, amongst which may be mentioned the hydrobromide, $C_{10}H_{18}O . HBr$, melting at 56°, and the compound with iodol, $C_{10}H_{18}O . C_4I_4NH$, which forms yellowish-green crystals, melting at 112°. It also forms a crystalline compound with resorcinol, which has been used as a basis for its quantitative determination. This compound consists of 2 molecules of cineol with 1 of resorcin, and forms needle-shaped crystals, melting at 80°.

Belluci and Grassi[1] have prepared compounds of cineol with the following bodies, in the proportion of 1 molecule of each constituent :—

Phenol	(melting-point + 8°)
o-Cresol	(„ „ + 50°)
m-Cresol	(„ „ − 5°)
p-Cresol	(„ „ + 1·5°)
Pyrocatechol	(„ „ + 39°)
Resorcinol	(„ „ − 15°)
Thymol	(„ „ + 4·5°)

add a compound of 2 molecules of cineol with 1 of hydroquinone, melting at 106·5.

Cocking has shown[2] that the compound with *o*-cresol melts, not at 50° but at 55·2°, and has prepared a method for the determination of cineol based on the preparation of this compound (*vide infra*). This method was criticised adversely in Volume I of this work. Further examination of the method has shown that this criticism is not altogether justified, and should be deleted, a fuller review of the method given on p. 282 taking its place.

According to all reliable observations, the oxygen atom in cineol does not possess alcoholic, ketonic, aldehydic, or acid functions. Apparently it is quite indifferent, which accounts for the isolated nature, chemically speaking, of the compound. In commerce, this body finds considerable employment under its name, eucalyptol.

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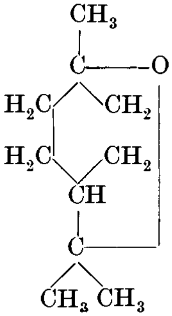
[1] *Chem. Zentral.*, **1** (1914), 884.

[2] *P. and E. O. R*, **11** (1920), 281.

Cineol has the constitution—



The quantitative determination of cineol has been fully dealt with in Vol. I. of this work under Eucalyptus Oil, but as this body occurs in various other oils, and its determination is a matter of considerable importance, details of its estimation are also dealt with here.

The earlier attempts in this direction gave distinctly too low results. The chief method adopted was a series of fractionations, retaining all those fractions distilling between 173° and 190°, cooling them to − 15°, filtering off the still liquid portion, retaining the crystals of cineol, refractionating the liquid portions and again freezing, subsequently weighing the crystallised cineol. An average loss of about 10 per cent., in the author's opinion, takes place in this process, assuming the oil to contain 50 to 60 per cent. of cineol. Scammel's process, above-mentioned, has been more successfully applied to the quantitative determination of cineol and yields the most satisfactory results so far, although an error of several per cent. is scarcely avoidable.

There is some diversity of opinion on this matter, some chemists maintaining that a very close result is obtained, others that very large errors occur.

To a known weight of oil from 1 to 1½ times its weight of phosphoric acid, of specific gravity 1·75, should be added, drop by drop, the oil being kept cold and continually stirred. The crystalline magma formed is pressed between filter paper, after as much as possible has drained off; and when the adherent terpenes and phosphoric acid have been removed as far as possible, the crystals are decomposed by hot water in a graduated tube. On cooling, the cineol is measured, and from its specific gravity (·930) the weight is easily calculated. The separated cineol should readily crystallise on cooling to − 3°, otherwise it must be regarded as impure and the process repeated. Oils rich in cineol yield a correspondingly high fraction distilling between 170° and 190°.

If the oil be first diluted with petroleum ether, before treatment with phosphoric acid, the results are rather more concordant in the hands of different analysts.

It has been assumed that the cineol and phosphoric acid enter into combination in molecular proportions, forming a solid compound of definite composition. Helbing and Passmore[1] have described a method in which the compound is weighed, and assume that the percentage of cineol in the phosphoric compound is 61·1 per cent. based on the formula $C_{10}H_{18}O \cdot H_3PO_4$.

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[1] *Pharmacological Record*, XXXV.

Baker and Smith in their *Research on the Eucalypts*[1] state, however, that correctly speaking no general formula can be given, as commercial phosphoric acid has not always the same concentration. They found that the mean cineol content in the perfectly dry powdery compound was 59·47 per cent. The theoretical mean for the cineol from the H_3PO_4 found was 59·56 per cent., thus being in very fair agreement. The results showed that 59·5 was approximately the amount of cineol in 100 parts of cineol-phosphate, and not 61·1 per cent. as was previously supposed.

Baker and Smith have devised an improved rapid method which they find works well with oils containing 20 per cent. and over. Eucalyptus oils which give a compound that cannot be satisfactorily pressed by the British Pharmacopœia method may be readily determined in this way and the decomposition of the cineol phosphate by long pressing (particularly in hot countries) is prevented.

The richest cineol oils give the best results when they are first diluted with the addition of one-third the volume of freshly distilled pinene (turpentine or the non-cineol portion of the more pronounced phellandrene oils. The method is to be applied in the following manner:—

If a preliminary test indicates from 60 to 80 per cent. of cineol, the oil is diluted as directed above; if about 60 per cent. or below it can be used directly.

Ten c.c. of the oil to be assayed are placed in a suitable vessel which is stood in a bath of ice and salt, and 4 c.c. of phosphoric acid are slowly added, a few drops at a time (3 c.c. if below 30 per cent.), incorporating the acid and the oil between each addition by stirring. The cineol phosphate is then allowed to remain in the bath for fully five minutes in order that the combination may be complete. A test tube containing 10 c.c. of petroleum ether, boiling below 59° C., is placed in the bath and when quite cold is added to the cake of cineol phosphate and well incorporated with the mass, using a flat-ended rod for the purpose. The mixture is at once transferred to a small Buchner funnel 5 cm. in diameter, upon which is placed a closely fitting filter paper. The non-combined portion is then rapidly sucked away by the aid of a filter pump. The thus dried cake is then transferred to a piece of fine calico, the calico folded over and the cake spread with a spatula to cover an area of about 6 cm. by 8 cm.. finally folded into a pad which is placed between several layers of absorbent paper and the whole strongly pressed for three minutes. The cake is then broken up with a spatula on a glazed tile or on glass, transferred to a measuring flask with graduated neck, decomposed with warm water, the cineol lifted into the neck of the flask, cooled, and when the separation is complete, the volume is measured. If the original oil were diluted, a correction is of course necessary. Baker and Smith have obtained very concordant results with the same sample and now use this method constantly.

Schimmel & Co. recommend the absorption of the cineol by a 40 to 50 per cent. solution of resorcin in water, and reading the unabsorbed portion in the neck of a Hirschsohn flask.

Ten c.c. of the oil containing cineol are mixed in a cassia flask of 100 c.c. capacity with so much 50 per cent. resorcinol solution that the flask is filled to about four-fifths. The mixture is shaken thoroughly

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[1] 2nd Edition, 1920, p. 359.

for five minutes, and the oil portions which have not entered into reaction are brought into the neck of the flask by adding resorcinol solution, and their volume determined. By subtracting the volume from 10 the cineol-content of the oil is obtained, which is then expressed in per cent. by volume by multiplication with 10.

Messrs. Schimmel & Co. have since modified the method by recommending the oil to be first fractionated and the portion boiling between 170° to 190° C. to be treated with the resorcin solution. In some cases this gives results fairly concordant with the phosphoric acid method usually adopted, as the following results will show:—

	Cineol by Direct Absorption with Resorcin Solution.	Cineol by Absorption with Resorcin after Fractionation.	Cineol by Phosphoric Acid Process.
Cajuput Oil, normal	62 per cent.	54 per cent.	52 per cent.
,, ,, abnormal	53 ,,	17 ,,	14 ,,
Eucalyptus Oil I.	82 ,,	68 ,,	65 ,,

C. T. Bennett[1] has, however, shown that this method is quite unreliable, only yielding accurate results in certain isolated cases.

In other cases, however, the results obtained are obviously too high. An oil which yielded 95 per cent. distilling between 170° to 190° C., all of which was absorbed by resorcin solution, had the following characters:—

EUCALYPTUS OIL II.

Specific gravity	0·924
Optical rotation	Nil
Cineol by phosphoric acid method	78 per cent.
,, ,, resorcin method	95 ,,

Other samples gave results as under:—

	Cineol by Direct Absorption.	Cineol by Absorption after Fractionation.	Cineol by Phosphoric Acid Process.
Eucalyptus Oil III.	100 per cent.	89 per cent.	70 per cent.
,, ,, IV.	Crystallised	97 ,,	75 ,,
,, ,, V	,,	92 ,,	73 ,,

It is evident that this modified method is not absolutely accurate, since other constituents besides cineol are undoubtedly included in the portion boiling between 170° and 190° C. A further objection is the separation of the solid crystalline double compound with oils rich in cineol.

The method has been criticised by H. G. Harding,[2] who states that a pure white oil from *Eucalyptus dives*, which contained no cineol, showed an absorption of 32 per cent. by the resorcinol test. Rectifying the oil and applying the test to the portion distilling between 170° and 190° does not entirely remove the difficulty, as the results are always slightly high,

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[1] *P. and E.O.R.* (1912), 269.

[2] *Analyst* (1914), 475.

owing to retention of other constituents by the resorcinol solution. His experiments show that the method is more reliable when the percentage of cineol does not exceed 40 to 50 per cent, oils containing a higher percentage requiring to be diluted Ordinary turpentine oil must not be used for dilution, as it is likely to produce serious errors By employing the fraction of turpentine distilling between 156° and 160° for dilution the error is minimised, and the following method is recommended 100 c c of the oil to be tested is distilled, the portion distilling between 170° and 190° collected, and this is diluted to 100 c c with the turpentine fraction. If a trial shows the percentage of cineol to be above 70 per cent, the cineol fraction is further diluted with the turpentine so that the percentage is not over 50 The temperature is noted, and 6 to 10 c c. is shaken with warm 55 per cent resorcinol solution After five minutes' shaking more solution is added so as to bring the oil into the graduated neck It is then cooled and the volume read

A method for the determination of cineol has recently been proposed by Dodge[1]

The process is based on the fact that the terpenes of the essential oils to be examined are readily oxidised at 0° C by a 5 to 6 per cent solution of potassium permanganate, whilst the eucalyptol remains unattacked Ten c c of essential oil are gradually added to 400 or to 100 c c of permanganate solution, according to whether the essential oil is more or less rich in terpenes When the reaction is finished, the solution is allowed to stand in the cold for twelve to eighteen hours, with occasional agitation, sulphurous acid or a mixture of sodium sulphite and hydrochloric acid is added and the oily portion of the residue is brought up into the neck of the flask, from which it is removed by means of a slender pipette This oil is washed with a little alkali, then transferred to a graduated tube where its volume is determined which indicates the percentage of eucalyptol

This method cannot be relied on, as the action of potassium permanganate is such as to react with some and not with other bodies present in various types of eucalyptus oil

The whole question of cineol determination in eucalyptus oil has recently been carefully studied by Turner and Holmes,[2] who consider that all methods so far published are either inaccurate or at best only approximate They suggest the following process —

The determination of cineol in cineol-bearing oils by means of arsenic acid is carried out as follows —

Deliver from a pipette 10 c c. of the oil into a glass dish (preferably a round-bottom one) of 50 c c capacity, which is imbedded in finely cracked ice Add 10 c c of concentrated arsenic acid (containing about 85 per cent arsenic acid), and stir until precipitation is complete When the mixture ceases to congeal further, allow to stand ten minutes in the ice *At this point* if the mixture forms a hard mass, indicating an oil rich in cineol, 5 c c of purified petroleum ether should be added, and the mass mixed well. Transfer immediately to a hardened filter paper by means of a pliable horn spatula, spread evenly over the surface of the paper, and lay a second hardened filter paper over the top Outside of the hardened filters place several thicknesses of absorbent or filter paper, and transfer the whole to an ordinary letter-press, bringing to bear all the pressure

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[1] *Jour Ind and Eng Chem.*, **4**, 592

[2] *P and E O R* **(1915)**, 21

possible for about one minute. Change the outside absorbent papers and press again, repeating the operation, if necessary, until the cineol arsenate is apparently dry and separates readily when touched with a spatula. The pressing is *not* complete when a hard mass remains which is broken up with difficulty. The method usually requires two changes of filter paper, pressing each time for about two minutes. If left too long in the press the compound may decompose. Now transfer completely the compound by means of the horn spatula to a glass funnel inserted into a 100 c.c. cassia flask with neck measuring 10 c.c., graduated in $\frac{1}{10}$ c.c. Wash the precipitate into the flask with a stream of hot water from a wash bottle, assisting the disintegration with a glass rod. Place the flask in boiling water and rotate until the compound is thoroughly broken up; add enough water to cause the cineol to rise into the neck of the flask, cool to room temperature, and read off the volume; on multiplying the latter by 10 the percentage of cineol in the oil is obtained.

In judging whether or not petroleum ether should be added, the following rule should be observed: Add enough petroleum ether to soften the cineol arsenate, so as to obtain a plastic mass; the quantity necessary never exceeds 5 c.c., and decreases with oils containing less than 80 per cent. of cineol. The object of adding petroleum ether is merely to soften the hard mass and to aid in the separation of non-cineol constituents of the oil; a large excess of petroleum ether will decompose the compound.

The above method is applicable directly to all oils containing above 50 per cent. of cineol; in oils containing lower proportions of cineol the precipitate is not solid enough to permit convenient handling; and if the cineol-content drops below 25 per cent. the separation of cineol arsenate is not quantitative. It was found that the addition of an equal volume of eucalyptol to such oils (*i.e.* mixing 5 c.c. of the oil with 5 c.c. of eucalyptol) successfully overcomes this difficulty; it then only becomes necessary to subtract from the volume of cineol, as observed in the neck of the flask, 5 c.c., and to multiply the difference by 10, in order to obtain the percentage of cineol in the oil.

A new method, based on the combination of cineol with ortho-cresol has recently been described by T. Tusting Cocking.[1] The method is a physical one and consists in determining the freezing-point of a mixture of eucalyptus oil and ortho-cresol in proportions corresponding to molecular weights of cineol and ortho-cresol. The apparatus required consists of: (*a*) A stout-walled test-tube about 15 mm. in diameter and 80 mm. in length, fitted with a wire loop for suspending it from the stirrup of a balance; (*b*) a small wide-mouthed bottle fitted with a cork bored to take the test-tube; (*c*) a thermometer graduated in fifths of a degree; and (*d*) a couple of pipettes to introduce the liquids into the tube.

The determination is carried out as follows:—

The tube is suspended from a balance and into it is accurately weighed 3 grams of the oil and 2·1 grams of melted ortho-cresol. It is then removed from the balance, inserted through the bored cork into the wide-mouthed bottle, stirred with the thermometer and the freezing-point noted. The tube is then gently warmed until the contents are completely melted, stirred vigorously with an up-and-down motion until solidification begins and the freezing-point again noted. This is

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[1] *P. and E.O.R.* (**1920**), p. 281.

repeated until concordant figures are obtained. It is found that in nearly all cases with the mixtures of high cineol content the first figure noted is two to three degrees lower than the subsequent ones. This is due to the rapid crystallisation which takes place before the two liquids are properly mixed. In order to obtain accurate results with weaker cineol mixtures it is necessary to introduce a minute crystal of the double compound (to which the name "cresineol" has been given by the author) to promote crystallisation, as the solubility of the compound in the terpene and excess cresol is so great that only a small quantity of cresineol separates out.

Pure ortho-cresol melting at 30° should be employed, and the results obtained with mixtures of known cineol content were as follows :—

Percentage of Cineol in Mixture.	Freezing-points. Terpene Mixture.	Freezing-points. Sesquiterpene Mixture.
100	55·2° C.	55·2° C.
95	53·4° C.	53·6° C.
90	51·2° C.	51·7° C.
85	48·5° C.	49·7° C.
80	45·8° C.	47·7° C.
75	43·2° C.	45·7° C.
70	40·6° C.	43·8° C.
65	37·4° C.	41·2° C.
60	34·2° C.	37·4° C.
55	29·0° C.	33·6° C.
50	25·4° C.	29·8° C.
45	22·2° C.	26·2° C.

The greatest difference recorded is equivalent to 6 per cent. of cineol, and, by taking the mean, the maximum error is reduced to ± 3 per cent.

The effects on the freezing-point of other essential oil constituents were compared by mixing ortho-cresol with mixtures of cineol and camphor, geraniol, geranyl acetate, terpineol and terpinyl acetate. The results showed that camphor has the same effect as sesquiterpenes, geraniol gives a result 2·3 per cent. lower, terpineol 1 per cent. higher and the two esters 3·1 to 3·3 per cent. higher than sesquiterpenes.

As compared with the B.P. phosphoric acid process the results were from 4·4 per cent. higher in the case of 80 per cent. oils to 10·5 per cent. higher in the case of cajuput oil indicating 50 per cent. by the B.P. process.

This method has been examined carefully and it appears to be more accurate than the phosphoric acid method as set on in the British Pharmacopœia and likely to give practically identical results in different hands and under different atmospheric conditions.[1]

It should be emphasised, however, that, as the cresol method gives higher results than the B.P. method, a minimum of 60 or even 65 per cent. cineol should be required if the new method is made official in the British Pharmacopœia.

The value of Cocking's method was not fully appreciated when volume I. of this work was published. It appears, on investigation, to have much to recommend it.

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[1] See *P. and E.O.R.*, 1921, pp. 44-46.

DICITRONELL-OXIDE.

Spornitz[1] has isolated from Java citronella oil a compound of the formula $C_{20}H_{34}O$, which is an oxide having the following characters:—

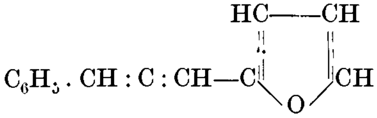
Boiling-point at 12 mm.	182 to 183°
Specific gravity at 20°	0·9199
Optical rotation	—4°
Refractive index	1·49179

CARLINA OXIDE.

The essential oil of *Carlina acaulis* contains an oxide, $C_{13}H_{10}O$, which has the following characters:—

Boiling-point at 20 mm.	167° to 168°
Specific gravity at $\frac{17^\circ}{17^\circ}$	1·066
Optical rotation	± 0°
Refractive index	1·5860

On oxidation with potassium permanganate it yields benzoic acid, and on reduction with sodium and alcohol, it is converted into the tetrahydroderivative $C_{13}H_{14}O$. The constitution of this oxide is probably—[2]



It is possible, however, that the chain joining the benzene and furfurol rings may be differently arranged.

COSTUS LACTONE.

Semmler and Feldstein have isolated a lactone from costus root oil, which they named costus lactone. It is an oil of the formula $C_{15}H_{20}O_2$, having the following characters:—

Boiling-point at 13 mm.	205° to 211°
Specific gravity at 21°	1·0891
Optical rotation	+ 28°
Refractive index	1·53043

Dihydro-costus lactone, $C_{15}H_{22}O_2$, is also present in the oil.

ANGELICA LACTONE.

E. Böcker and A. Hahn have recently isolated a crystalline lactone of the formula $C_{15}H_{16}O_3$ in the last runnings of angelica root oil. From 200 grams they obtained 10 grams of a lactone which, when recrystallised from ethyl ether and light petroleum, melted at 83°. It boils without decomposition at 250°. The lactone is an unsaturated body; when brominated in a glacial acetic acid solution it yields a dibromide, which when recrystallised from glacial acetic acid, melts with decomposition at 143° to 145°.

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[1] *Berichte*, **47**, 2478.

[2] Semmler, *Berichte* (**1909**), 2355.

ASCARIDOL.

Ascaridol is the principal constituent of the oil of *Chenopodium ambrosoides*, var. *anthelminticum*.

It is an oxide having the following characters :—

Specific gravity	1·003
Optical rotation	– 4° 14′
Refractive index	1·4731
Boiling-point at 5 mm.	83°

When ascaridol is treated with a solution of ferrous sulphate, care being taken to avoid any rise of temperature, it fixes the elements of water with the formation of a glycol, $C_{10}H_{18}O_3$, melting at 62·5° to 64° C. and yielding a benzoate melting at 136° to 137° C. The glycol possesses the following characters :—

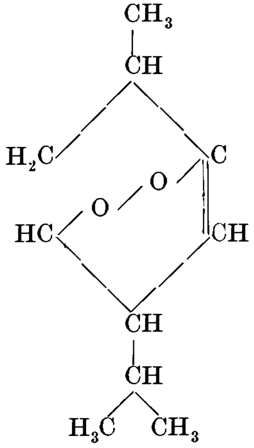
Specific gravity	1·0981
Optical rotation	± 0°
Refractive index	1·4796
Molecular refraction	48·63

It yields a dibenzoate (melting-point, 116·5° to 117·5° C.) when it is heated for two hours at 150° C. with benzoic anhydride.

On oxidation the glycol yields a dibasic acid, $C_{10}H_{16}O_5$, called ascaridolic acid (melting-point, 116·5° to 117° C.), and another solid acid, melting at 186° to 187° C., to which Nelson attributes the formula $C_{10}H_{16}O_6$.

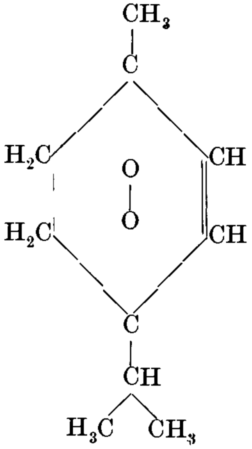
Nelson regards ascaridol as a peroxide possessing the constitution I (*see below*).

O. Wallach[1] has also examined the constitution of ascaridol. He considers it to be an oxide having the formula II—



I.

Nelson.



II.

Wallach.

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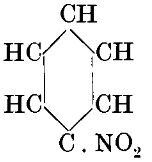
[1] *Ann. Chem.*, **392**, 49.

9. NITROGEN COMPOUNDS.

NITROBENZENE.

Nitrobenzene, $C_6H_5NO_2$, also known as oil of mirbane, is an artificially prepared benzene derivative, having a coarse, but powerful odour resembling that of oil of almonds. Its coarse odour renders it quite unsuitable for fine perfumery, but it finds considerable employment in the manufacture of cheap soaps, polishes, and other articles where more or less rancid fats are used, as it covers the bad odour of the fat and gives the product a coarse almond perfume.

Nitrobenzene is an oily liquid, resulting from the direct nitration of benzene, having the following constitution :—



Its characters are as follows :—

Solidifying-point	+ 5°
Boiling-point	209°
Specific gravity	1·2200 at melting-point
,, ,, at 15°	1·2060
Refractive index	1·5520

On reduction with iron and acetic acid, nitrobenzene yields aniline.

ARTIFICIAL MUSK.

There are a number of nitro-compounds known under the name of artificial musk, all of which may conveniently be grouped together here. The natural odorous constituents of musk appear to be, in the main, ketonic compounds free from nitrogen, so that the term artificial musk must be understood to mean artificially prepared bodies, having musk-like odours, but not having any direct chemical relationship with natural musk perfume.

For many years attempts have been made to artificially imitate the odour of musk. To a certain extent successful experiments were made by Margraff and Elsner.[1] Rough pieces of amber, ground to powder and mixed with sand, are distilled in an iron retort ; the oil which distils over is separated from the fœtid liquor and succinic acid which accompanies it, and after being rectified at a gentle heat with about six times its volume of water, is gradually added to and digested with $3\frac{1}{4}$ parts by weight of fuming nitric acid, artificial cold being employed to prevent any portion of the oil carbonising. A resinous matter of a yellowish colour forms, which, after being dried, is the product which is required. It is said to be also formed by digesting for ten days an ounce of fœtid animal oil, obtained by distillation, and half an ounce of nitric acid, then adding a pint of rectified spirit, and digesting for one month. Another artificial musk has been patented in England[2] by Schnaufer & Hupfeld, of Frank-

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[1] *Jour. für Praktische Chemie*, 1842.

[2] No. 18,521, 18 December, 1888.

furt. The specification of this patent states that "3 parts of metaxylol, 2 parts of isobutyl alcohol, and 9 parts of chloride of zinc are heated in a digestor to from 220° to 240°, until the pressure, which at the commencement is from 25 to 29 atmospheres, sinks to below 6 atmospheres. The resulting hydrocarbon, corresponding to the formula $C_{12}H_{18}$, is collected, and the fraction which distils over at from 190° to 230° is nitrated with HNO_3, or with HNO_3 and H_2SO_4, whilst being cooled. The product of the reaction is poured into water, whereupon a reddish-brown oil separates, which is washed several times with alkaline water. The formula of this oil is $C_{12}H_{17}NO_2$, and in a concentrated condition it possesses a sweet smell, whilst in a dilute solution it gives off a penetrating and enduring musk-like odour."

The complete specification states that "aromatic hydrocarbons containing the isopropyl, isobutyl, or isoamyl group, on treatment with fuming nitric acid or a mixture of strong nitric acid (40° to 44° B.) and sulphuric acid (66° B.), produce derivatives which, in very dilute alcoholic solution, furnish a liquid possessing an odour resembling tincture of musk in the highest degree". Only one example of the process is given in the provisional specification, but of course the process may be carried out with the other well-known homologues. "The hydrocarbons may be produced in the ordinary way, but we produce them by the following operation: Toluene or xylol is heated in a digester with isopropyl or isobutyl, or isoamyl alcohol in molecular quantities, with the addition of from four to five times the quantity of chloride of zinc, to the boiling-point of the hydrocarbon, or to about 40° or 50° above the boiling-point of alcohol, until the pressure, which at the commencement was equal to about 26 atmospheres, sinks to a little above 2 or 3 atmospheres. The product of the reaction is subjected to fractional distillation.

"By the above process the following hydrocarbons are obtained:—

1. From toluene:—
    Methylisopropyl-benzene.
    Methylisobutyl-benzene.
    Methylisoamyl-benzene.
2. From xylol:—
    Dimethylisopropyl-benzene.
    Dimethylisobutyl-benzene.
    Dimethylisoamyl-benzene.

"To produce the 'musk-substitute':—

"We add to the above-mentioned hydrocarbons, which during the operation should be kept thoroughly cool, a little more than the molecular quantity of fuming nitric acid or nitro-sulphuric acid. The acid should be gradually run in and the whole then allowed to stand undisturbed for from one to two hours, the resulting mass being then poured into water in order to get rid of the excess of acid. The well-washed substances thus obtained are then subjected to distillation by means of steam, whereupon simultaneously formed bodies, which smell like nitro-benzol and overpower the musk odour, readily distil over, whilst the pure substances remain behind."

The artificial musk which was the first to achieve marked success was that manufactured under the patent of Albert Baur (English patent No. 4963 of 1889). The provisional and complete specifications of this patent are as follows:—

Provisional Specification.—I, Albert Baur of Gispersleben, in the Empire of Germany, Doctor, do hereby declare the nature of this invention to be as follows:—

The object of this invention is to produce a compound or material, or series of compounds or materials, having the properties of musk.

To this end I purpose to make a nitrated hydrocarbon of the $C_{11}H_{16}$ group, and proceed as follows:—

Toluene is mixed with a haloid combination of butane and boiled with addition of chloride or bromide of aluminium. Water is added to the product and it is then distilled with steam, and that portion which distils over at a temperature between 170° and 200° C. is taken and treated with fuming nitric acid and fuming sulphuric acid. The resulting product is washed with water and crystallised from alcohol.

The product may be dissolved in alcohol, and on addition of a small quantity of ammonia or sal-ammoniac will exhibit all the essential properties of a tincture of musk.

Complete Specification.—I, Albert Baur of Gispersleben, in the Empire of Germany, Doctor, do hereby declare the nature of my invention and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

The object of this invention is to produce a compound or material, or series of compounds or materials, having the properties of musk.

To this end I make a nitrated hydrocarbon of the $C_{11}H_{16}$ group, and proceed as follows:—

Toluene is mixed with a haloid combination of butane and boiled with addition of chloride or bromide of aluminium. Water is added to the product and it is then distilled with steam, and that portion which distils over at a temperature between 170° and 200° C. is taken and treated with fuming nitric acid and fuming sulphuric acid. The resulting product is washed with water and crystallised from alcohol.

The product may be dissolved in alcohol, and on addition of a small quantity of ammonia or sal-ammoniac will exhibit all the essential properties of a tincture of musk.

For carrying the invention into practice, 5 parts of toluene are mixed with 1 part of butyl bromide, or butyl chloride or butyl iodide, and to these may be added gradually whilst boiling $\frac{1}{5}$ part of aluminium chloride or aluminium bromide; this results in the development of hydrobromic acid, or hydrochloric acid or hydriodic acid respectively, and a product of reaction is obtained from which by the action of steam the hydrocarbon $C_{11}H_{16}$ and unchanged toluene are distilled. By the admission of steam the hydrocarbon is carried along and may be obtained in a condenser as a colourless oil floating on the water. The oil removed and dried by means of chloride of calcium is fractionated, and in this manner the necessary hydrocarbon for the production of artificial musk is obtained, 100 parts of the former giving a like quantity of musk preparation. Three parts of fuming nitric acid of 1·52 specific weight and 6 parts of fuming sulphuric acid are mixed together, and to this mixture is carefully added whilst cooling 1 part of the hydrocarbon aforesaid. Each drop causes a violent reaction. As soon as all the hydrocarbon is added, the whole mixture is heated up to a temperature of about 100° C. After cooling, the nitro product is precipitated by pouring into cold water of about 5 to 6 times the volume, and is separated from superfluous acid by washing with cold water. The nitro product separates first as a heavy viscid oil, which after some time hardens into a firm crystalline substance.

The raw nitro product is then purified by recrystallisation from alcohol of 90 per cent. strength. The purified product crystallises out in yellowish-white needles, possessing a strong smell of musk.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is—

The process for producing artificial musk substantially as described.

The original scientific account of the preparation of this body stated[1] that *meta*-isobutyl toluene was heated on a water-bath for twenty-four hours, with five times its weight of a mixture of sulphuric and nitric acids. The product was subjected to a repetition of the same treatment, so as to convert it into trinitro-butyl toluene, which crystallises from alcohol in white needles melting at 96° to 97°. It is insoluble in water, but soluble in organic solvents. Even in very dilute solutions this compound has a

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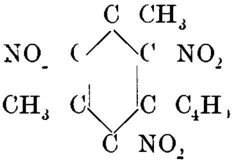
[1] *Comptes rendus*, cxi. 238.

strong odour of musk, and for many purposes can replace the natural product. The homologues of isobutyl toluene behave similarly, and trinitro-isobutyl metaxylene has an exactly similar odour. In a later communication[1] Baur stated that his previous view was incorrect, and that the "artificial musk" was the trinitro-derivative of *tertiary* butyl xylene, and not of isobutyl xylene, owing to the occurrence of an intra-molecular change during the reaction. Tertiary butyl xylene is easily prepared by the interaction of tertiary butyl chloride and xylene in the presence of aluminium chloride as follows:—

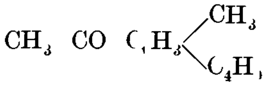
$$C_4H_9Cl + C_6H_4(CH_3)_2 = C_4H_9 \; C_6H_3 . (CH_3)_2 + HCl.$$

The mono- and dinitro products have no musk odour and therefore the nitration of the hydrocarbon should be carried as far as possible. The constitution of this artificial musk, or "xylene musk" as it is often called, is probably—



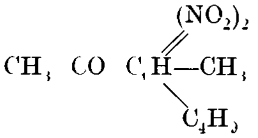
This is the most common form of artificial musk of commerce. It melts, when pure, at 110° to 113°.

Still later[2] Baur has shown that if an acetyl group is introduced into the butyl toluene molecule, and the methyl ketone thus formed is nitrated, artificial musk (ketone musk) is produced. One part of butyl toluene, 10 parts of carbon disulphide, and 6 parts of aluminium chloride are cooled in a flask and 6 parts of acetyl chloride are run in quickly. After distillation on a water-bath, the residue is poured on to ice and treated in the usual manner. The acetyl derivative is obtained as an oil with a pleasant aromatic odour, boiling at 255° to 258°, of the formula—



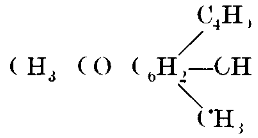
$$CH_3 . CO . C_6H_3 \begin{cases} CH_3 \\ C_4H_9 \end{cases}$$

By nitrating this ketone a dinitro derivative—



$$CH_3 . CO . C_6H \begin{cases} (NO_2)_2 \\ —CH_3 \\ C_4H_9 \end{cases}$$

is obtained in needles melting at 131°, and having a strong musk odour. In this compound one of the nitro groups of the original artificial musk, trinitro-butyl toluene, has been replaced by the acetyl group. Which group has been so replaced is uncertain. A quite similar body is obtained from butyl xylene, the resulting ketone—



$$CH_3 . CO . C_6H_2 \begin{cases} C_4H_9 \\ —CH_3 \\ CH_3 \end{cases}$$

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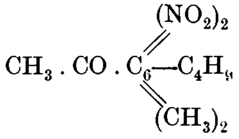
[1] *Berichte*, xxiv. 2832.

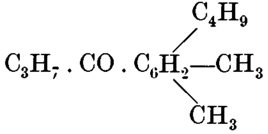
[2] *Ibid.*, xxxi. 1344.

melting at 48°, and yielding a dinitro derivative—



$$CH_3 . CO . \overset{(NO_2)_2}{\underset{(CH_3)_2}{C_6}} — C_4H_9$$

melting at 136°, and having a strong musk odour. These bodies are known as "ketone musk". Instead of using acetyl chloride, either butyryl chloride or valeryl chloride may be used, and higher homologues produced. Butyl-xylyl-propyl ketone—



$$C_3H_7 . CO . \overset{C_4H_9}{\underset{CH_3}{C_6H_2}} — CH_3$$

melts at 50° and boils at 290°. It forms a dinitro derivative, melting at 128°, with a powerful musk odour. The corresponding butyl-xylyl-butyl ketone is an oil boiling at 185° to 190° at 14 mm., and its dinitro derivative melts at 151°, and has also a powerful musk odour.

There are also, although not much met with, an aldehyde and a cyanide musk. The former is dinitro-tertiary-butyl-xylyl-aldehyde, $C_6(CH_3)_2C(CH_3)_3(NO_2)_2CHO$, melting at 112°, and the latter is dinitro-tertiary-butyl-xylyl-cyanide, $C_6(CH_3)_2CN . C(CH_3)_3(NO_3)_2$, melting at 110°.

Musk ambrette, which is usually regarded as the finest of all the artificial musks is a nitro-compound of the methyl ether of butyl-*meta*-cresol, usually described as dinitro-butyl-*meta*-cresol methyl ether. It should melt at 85°.

Some of the artificial musks of commerce are mixtures of two or more of the bodies above described, a fact which is easily demonstrated by fractionally crystallising the specimen, when the fractions will show altered melting-points. The principal adulterant of artificial musk is acetanilide. This can, of course, be easily detected by the phenyl-isocyanide reaction or by dissolving it out with hot water.

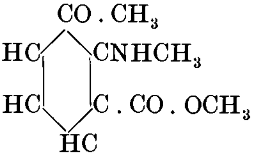
DAMASCENINE.

Damascenine, $C_{10}H_{13}NO_3$, is a nitrogenous compound of an alkaloidal nature, which is present in the oil of *Nigella damascena* to the extent of about 9 per cent. It can be extracted from the oil by shaking it with dilute hydrochloric acid, rendering the aqueous liquid alkaline and extracting the alkaline liquid with petroleum ether.

Damascenine has the following characters:—

Melting-point	26°
Boiling-point	270° at 750 mm.
,, ,,	157° ,, 10. ,,

It yields salts with the usual alkaloidal reagents, such as platinum, gold, and mercuric chlorides. Its constitution is—



It is, therefore, the methyl ester of 2-methylamino-3-methoxybenzoic acid.

It has been prepared synthetically by Ewins [1] in the following manner: Meta-oxybenzoic acid is converted with the aid of dimethyl sulphate into *m*-methoxybenzoic acid, which is then nitrated, and from the nitration products 2-nitro-3-methoxybenzoic acid is separated. This is reduced to 2-amino-3-methoxybenzoic acid which on heating with methyl iodide, yields 2-methylamino-3-methoxybenzoic acid. On warming this with freshly precipitated silver chloride it yields damascenine hydrochloride.

HYDROCYANIC ACID.

Hydrocyanic acid, HCN, also known as prussic acid, or formo-nitrile, is the product of decomposition of numerous glucosides found in a very large number of plants, usually together with some other volatile compound, so that essential oils containing hydrocyanic acid do not, for practical purposes, exist in the first instance as such in the plant, but are only developed on the decomposition of the glucoside.

Hydrocyanic acid is one of the most powerful poisons known. It is a colourless liquid, boiling at 26·5°, of specific gravity 0·700.

It can be detected and estimated in essential oils by the following method:—

Hydrocyanic acid may be approximately estimated by dissolving 1 gram of oil in 5 c.c. of alcohol, and adding 50 c.c. of water. Then add ammonio-silver nitrate solution and shake well. Acidify slightly with nitric acid, and collect, wash, and dry the silver cyanide precipitated. Ignite and weigh the silver, 4 parts of which correspond to practically 1 of hydrocyanic acid.

For an exhaustive examination of the various processes proposed for the determination of hydrocyanic acid, the reader is referred to a series of papers by Runne in the *Apotheker Zeitung*.[2]

ALLYL CYANIDE.

Allyl cyanide, $CH_3 . CH : CH . CN$, occurs in some of the oils of the mustard type. It is a liquid of specific gravity 0·8365 boiling at 120° to 123°, and yields, on boiling with alcoholic potash solution, crotonic acid, melting at 72°.

BENZYL CYANIDE.

Benzyl cyanide, $C_6H_5 . CH_2CN$, or phenyl-aceto-nitrile, is a constituent of cress oil, and probably of neroli oil. It is a strong smelling liquid boiling at 231·5°, and having a specific gravity 1·0146 at 18°. On boiling with alcoholic potash it yields phenyl-acetic acid, which can be identified by its melting-point, 77°, and by the analysis of its silver salt.

PHENYL-PROPIONITRILE.

Phenyl-propionitrile, $C_6H_5 . CH_2 . CH_2 . CN$, is present in nasturtium oil. It is a powerfully smelling oil, boiling at 261°. On hydrolysis by alcoholic potash it yields phenyl-propionic acid, melting at 47°.

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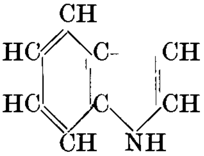
[1] *Jour. Chem. Soc.*, 101 (1912), 544.

[2] *Apotheker Zeitung*, 24 (1900), 288, 297, 306, 314, 325, 333, 344, 356.

INDOL.

Indol, C_8H_7N, is the mother substance of the indigo group of compounds. It exists in various essential oils including neroli oil and oil of jasmin flowers. It is a crystalline compound, melting at 52° and boiling at 253° to 254°. Its odour is powerful and disagreeable, being distinctly fæcal in character. Its constitution is as follows:—



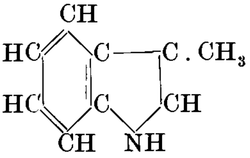
Indol is prepared artificially by numerous methods, most of which have been patented.

Indol can be isolated from, and determined in, essential oils in the following manner: The oil is mixed with 10 per cent. of picric acid and heated to 60°. Excess of petroleum ether is then added. A picric acid compound of indol separates in long red crystals, which are washed with petroleum ether and decomposed by caustic alkali, and the free indol extracted by ether, and the residue left on evaporation of the ether steam-distilled, when pure indol passes over.

Indol, in alcoholic solutions, turns a pine shaving, moistened with hydrochloric acid, a cherry-red colour. When shaken with a solution of oxalic acid, indol gives a red coloration.

SKATOL.

Skatol, C_9H_9N, is β-methyl-indol, of the constitution—



It is found in civet and in the wood of *Celtis reticulosa*. It forms crystals melting at 95° and boiling at 265° to 266°. It yields a hydrochloride, $2(C_9H_9N) . HCl$, melting at 167° to 168°, and a picric acid compound melting at 172° to 173°. Skatol yields a blue colour with a solution of dimethyl-aminobenzaldehyde.

Skatol is a foul-smelling compound, but when used in very minute amount is useful in the manufacture of flower blossom perfumes.

10. SULPHUR COMPOUNDS.

DIMETHYL SULPHIDE.

Dimethyl sulphide, $(CH_3)_2S$, is a foul-smelling liquid, found in minute quantity in the essential oils of peppermint and geranium. It boils at 37°.

Vinyl Sulphide.

Vinyl sulphide, $CH_2 = CH_2S$, has been identified in the oil of *Allium ursinum*. It is an evil-smelling liquid of specific gravity 0·912. It boils at 101°.

Diallyl Disulphide.

Diallyl disulphide, $(C_3H_5)S.S(C_3H_5)$, is a light yellow oil of garlic odour, found to the extent of about 60 per cent. in oil of garlic. It is a liquid of specific gravity 1·023, and boils at 80° to 81° at 16 mm. pressure.

Allyl-propyl Disulphide.

Allyl-propyl disulphide, $(C_3H_5)S . S . (C_3H_7)$, exists to the extent of about 5 per cent. in garlic oil. It is a bright yellow oil of foul odour, having a specific gravity 1·023 and boiling at 66° to 69° at 16 mm. pressure.

Diallyl Trisulphide.

Diallyl-trisulphide, $(C_3H_5)S . S . S . (C_3H_5)$, is probably the compound of the formula $C_6H_{10}S_3$ isolated from garlic oil by Semmler.[1] It boils at 112° to 122° at 16 mm., and has a specific gravity 1·0845.

Butyl Isothiocyanate.

Secondary butyl isothiocyanate, $CH_3 . CH_2 . CH(CH_3) . N : C : S$, has been isolated from the oils of *Cardamine amara* and *Cochlearia*. It is a liquid with a powerful, irritating sulphur odour, having a specific gravity 0·9415 and boiling at 159° to 160°. Warmed with alcoholic solution of ammonia, it yields a thiourea, melting at 135° to 136°.

The artificial cochlearia oil of commerce is not identical with secondary butyl isothiocyanate, but consists of isobutyl isothiocyanate. It is a liquid boiling at 162° and yields a thiourea, melting at 93·5°.

Allyl Isothiocyanate.

Allyl isothiocyanate, $CH_2 : CH . CH_2N : C : S$, also known as "artificial mustard oil," is the principal constituent of natural oil of mustard. This body results from the hydrolysis of the glucoside sinigrin under the influence of the ferment myrosin, according to the equation—

$$\underset{\text{Sinigrin.}}{C_{10}H_{16}NS_2KO_9} + H_2O = \underset{\text{“Mustard oil.”}}{SCNC_3H_5} + \underset{\text{Glucose.}}{C_6H_{12}O_6} + KHSO_4,$$

It can be prepared artificially by the action of allyl iodide on an alcoholic solution of thiocyanate of potassium, the latter body being isomerised to the isothiocyanate under the influence of heat.

Allyl isothiocyanate is a colourless liquid, gradully becoming yellow on keeping, and having an intensely irritating odour of mustard. Its characters are as follows:—

Specific gravity	1·023
Refractive index	1·5285
Boiling-point	152°
,, ,,	30° to 31° at 5 mm.

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[1] *Arch. Pharm.*, ccxxx. 434.

When treated with alcoholic solution of ammonia, it yields thiosinamine (allyl thiourea), of the formula $C_3H_5 . NH . CS . NH_2$. This body melts at 74°. The formation of this body forms the basis for a method of its determination, which, with other methods, will be found fully described under "Oil of Mustard" (Vol. I, p. 474).

Crotonyl Isothiocyanate.

Crotonyl isothiocyanate, $C_4H_7 . N : C : S$, has been found in Indian rape-seed oil. It is an oil of odour somewhat similar to that of the corresponding allyl compound, and having the following characters :—

Boiling-point	175° to 176°
Specific gravity	0·994
Optical rotation	+ 0° 3′ (probably due to impurities)
Refractive index	1·52398

Benzyl Isothiocyanate.

Benzyl isothiocyanate, $C_6H_5 . CH_2 . N : C : S$, has been found in *Tropæolum* oil, probably resulting from the decomposition of the glucoside, glucotropæolin, $C_{14}H_{18}KNS_2O_9$, It has the characteristic odour of the plant, and yields a thiourea melting at 162°.

Phenyl-ethyl Isothiocyanate.

Phenyl-ethyl isothiocyanate, $C_6H_5(C_2H_4)N : C : S$, has been found in the oils of reseda root, nasturtium, and some varieties of *Brassica*. It is an oil of powerful odour, yielding a thiourea, melting at 137°. The latter body, when treated with silver nitrate and baryta water, yields phenyl-ethyl-urea, melting at 111° to 112°.

Oxybenzyl Isothiocyanate.

Para-oxybenzyl isothiocyanate, $C_6H_4 . OH . CH_2NCS$, is a liquid of intense odour, occurring in the essential oil of white mustard. It is also known as acrimyl thiocarbimide. It is produced by the hydrolysis of the glucoside sinalbin, $C_{30}H_{42}N_2S_2O_{15}$. It can also be obtained artificially by the action of carbon bisulphide on *p*-oxybenzylamine, and treating the resulting compound with mercurous chloride.

11. ACIDS.

Formic Acid.

Formic acid, $H . COOH$, is found in traces in a number of essential oils. It is a colourless corrosive liquid or crystalline solid, having the following characters :—

Melting-point	8°
Boiling-point	101°
Specific gravity	1·223

It can be prepared artificially in various ways; for example, by distilling oxalic acid with glycerine, when at about 130° formic acid comes over according to the equation—

$$C_2H_2O_4 = HCOOH + CO_2.$$

To prepare it in a completely anhydrous condition the 90 per cent. acid may be dehydrated by means of phosphorus pentoxide.

ACETIC ACID.

Acetic acid, $CH_3 . COOH$, occurs in traces in the free state in many essential oils, but principally in the form of esters, of which it is the usual acid constituent.

It is a crystalline solid, or a liquid at ordinary temperatures, having the following characters:—

Melting-point	16·7°
Boiling-point	118°
Specific gravity	1·0514 at 20°

It can be obtained by the oxidation of ethyl alcohol, either chemically or by fermentation under the influence of the organised ferment *Mycoderma aceti.*

PROPIONIC ACID.

Propionic acid, $C_2H_5 . COOH$, has been found in lavender and a few other oils in traces. It is a liquid of rancid odour having the following characters:—

Congealing-point	− 24°
Boiling-point	141°
Specific gravity	1·017

BUTYRIC ACID.

Butyric acid, $C_3H_7 . COOH$, is an oily liquid having an odour of rancid butter. It has been found in the oils of *Eucalyptus globulus*, *Heracleum giganteum*, and in nutmeg, niaouli, and other essential oils. It has the following characters:—

Congealing-point	− 6°
Boiling-point	162° to 163°
Specific gravity	0·9587 at 20°

Its constitution is $CH_3 . CH_2 . CH_2 . COOH$. Isobutyric acid, which has the constitution $(CH_3)_2CH . COOH$, exists in Spanish hop oil, arnica root oil, and a few others. It is a liquid of specific gravity 0·949 at 20°, boiling at 155°.

VALERIANIC ACID.

The isomeric valerianic acids have the formula $C_5H_{10}O_2$. Normal valerianic acid does not appear to be found in any essential oils. Isovalerianic acid, $(CH_3)_2CH . CH_2 . COOH$, is found in valerian and other oils; it is a liquid boiling at 174°, of specific gravity ·947. Another isomer, also found in champaca and coffee oils, is methyl-ethyl-acetic acid, $(C_2H_5)(CH_3) . CH . COOH$. This is an optically active liquid, boiling at 175°, of specific gravity ·941 at 21°.

CAPROIC ACID.

Caproic acid, $C_5H_{11}\,.\,COOH$, has been found in lemon-grass, palmarosa, and several other essential oils. It is a liquid having the following characters:—

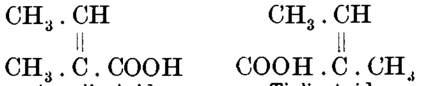
Congealing point	$-2°$
Boiling-point	205°
Specific gravity	0·928 at 20

HIGHER FATTY ACIDS.

The fatty acids of higher molecular weight than caproic acid are of little interest or importance so far as essential oils are concerned, and for their characters, the reader is referred to standard works on general organic chemistry.

ANGELIC AND TIGLIC ACIDS.

These two acids, of the formula $C_5H_8O_2$, are geometrical isomerides. They are both unsaturated, and belong to the acrylic acid series. Tiglic acid forms crystals melting at 64·5° and boiling at 198·5°, whilst angelic acid melts at 45° to 46° and boils at 185°. They have the following constitutions:—



$$\begin{array}{cc} CH_3\,.\,CH & CH_3\,.\,CH \\ \| & \| \\ CH_3\,.\,C\,.\,COOH & COOH\,.\,C\,.\,CH_3 \end{array}$$

Angelic Acid. Tiglic Acid.

These two acids occur chiefly as esters in Roman chamomile oil. Tiglic acid is also found as geranyl tiglate in geranium oil.

TERESANTALIC ACID.

Teresantalic acid, $C_{10}H_{14}O_2$, is a hydro-cyclic acid, found in sandalwood oil. Its characters are as follows:—

Boiling-point at 11 mm.	150° (approximate)
Melting-point	157°
Specific rotation	$-70°\ 24'$

CITRONELLIC ACID.

Citronellic acid, $C_9H_{17}\,.\,COOH$, is the acid corresponding to the alcohol citronellol, and is present in the essential oil of *Barosma pulchellum*. It has the following characters:—

Boiling-point	257° to 263°
„ „ at 5 mm.	143° „ 144°
Specific gravity	0·939
Optical rotation	$+5°\ 2'$
Refractive index	1·45611

It forms a crystalline amide melting at 81° to 82°, which can be obtained by converting the acid into its chloride, and then acting on this with aqueous ammonia.

BENZOIC ACID.

Benzoic acid, $C_6H_5\,.\,COOH$, is the simplest acid of the benzene series. It is found either free or in the form of esters in vetivert, jasmin, ylang-

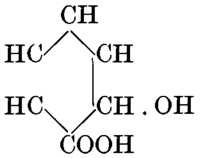
ylang, neroli, and numerous other essential oils. It is a crystalline body with a slight aromatic odour, having the following characters:—

Melting-point	121° to 121·5°
Boiling-point	249°

It is prepared artificially on a large scale, usually by hydrolysing the chlorination product of toluene.

SALICYLIC ACID.

Salicylic acid, $C_6H_4(OH)COOH$, is ortho-hydroxy-benzoic acid of the constitution—



It is the acid constituent of the ester forming almost the whole of wintergreen and birchbark oils, and is a crystalline solid melting at 159°. Commercially pure samples, however, rarely melt at above 157°. It is prepared artificially on an enormous scale by heating sodium phenol, under pressure, with carbon dioxide.

PHENYL-ACETIC ACID.

This acid, $C_6H_5 . CH_2COOH$, is a sweet-smelling substance, especially recommended for sweetening soap perfumes. It occurs in neroli oil, and has a sweet honey-like odour. It is formed by converting toluene into benzyl chloride which is converted into benzyl cyanide, which is digested with dilute sulphuric acid, and so converted into phenyl-acetic acid. It is a crystalline body, melting at 76° to 76·5° and boiling at 266°. It has been isolated from oil of neroli.

CINNAMIC ACID.

This acid, of the formula $C_6H_5CH : CHCOOH$, occurs in a number of essential oils in the free state. It is prepared artificially by heating benzal chloride with sodium acetate. It has a sweet odour. It is a crystalline substance, melting at 133° and boiling at 300°.

HYDRO-CINNAMIC ACID.

This acid, $C_6H_5 . CH_2 . CH_2COOH$, has a sweet and powerful odour, and can be used to advantage in many rose odours. It is recommended especially for perfuming powders and sachets. It is a crystalline compound, melting at 47° and boiling at 280°. It can be obtained by the reduction of cinnamic acid by means of sodium.

PARA-METHOXY-CINNAMIC ACID.

This acid, $CH_3O . C_6H_4 . CH : CH . COOH$, is methyl-*p*-coumaric acid, and is present in kaempferia oil. It is a crystalline solid melting at 171°.

Anisic Acid.

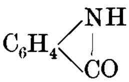
Anisic acid is *p*-methoxy-benzoic acid, $C_6H_4 . COCH_3 . COOH$. It is found in aniseed oil, and also in Tahiti vanillas. It is a crystalline body melting at 184°.

Veratric Acid.

Veratric acid, $(CH_3O)_2 . C_6H_3 . COOH + H_2O$, is present in the essential oil of sabadilla seeds. It melts at 179° to 181°.

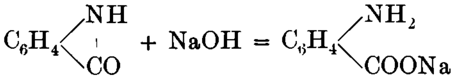
Anthranilic Acid.

Anthranilic acid, or *o*-amidobenzoic acid, $C_6H_4 : (NH_2)(COOH)$, is the acid constituent of the ester found in neroli, petit-grain, jasmin, and mandarin oils. It is a solid crystalline substance melting at 145°. It is prepared artificially, and then converted into synthetic methyl anthranilate. To prepare anthranilic acid, *o*-nitrobenzaldehyde is reduced by tin and hydrochloric acid to anthranil,



$$C_6H_4\left\langle\begin{array}{l}NH\\ \mid\\ CO\end{array}\right.$$

the internal anhydride or lactame of anthranilic acid. This is converted into anthranilic acid by boiling with alkalis:—

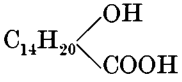


$$C_6H_4\left\langle\begin{array}{l}NH\\ \mid\\ CO\end{array}\right. + NaOH = C_6H_4\left\langle\begin{array}{l}NH_2\\ \\ COONa\end{array}\right.$$

Methylanthranilic acid, which has been found as an ester in similar oils, melts at 179°, and forms an acetyl derivative melting at 186°.

Alantoic Acid.

Alantoic acid, $C_{15}H_{22}O_3$, is present in oil of elecampene, both as free acid and in the form of its lactone. Its constitution is—



$$C_{14}H_{20}\left\langle\begin{array}{l}OH\\ \\ COOH\end{array}\right.$$

It is a crystalline compound melting at 94°, and can be obtained by hydrolysing alantolactone.

Eudesmic Acid.

Eudesmic acid, $C_{14}H_{18}O_2$, is found in the form of its amyl ester in the oil of *Eucalyptus aggregata*. It is a crystalline compound melting at 160°. It is monobasic and unsaturated, and yields a dibromide melting at 102° to 103°.

Costic Acid.

Costic acid, $C_{15}H_{22}O_2$, is a free acid isolated from costus root oil. It is an unsaturated bicyclic acid of specific gravity 1·0501. It forms a methyl ester, boiling at 170° to 175° at 11 mm.

CHAPTER III.

THE ANALYSIS OF ESSENTIAL OILS.

In general, the analysis of essential oils merely involves the application of the ordinary principles of analytical chemistry to this special group of bodies, which possess many features in common. Of course, many special processes have to be used in certain cases, to which attention will be drawn where necessary. The present chapter will be devoted to the details of a few methods which are in very common use in the analysis of these bodies, and which are absolutely necessary in order to form an opinion on the purity of very many oils. Particular processes are mentioned as required under the essential oils or compounds concerned. These remarks may be prefaced by saying that the obtaining of the results of an analysis of an essential oil is not always as difficult a matter as the interpretation of the same when obtained.

The adulteration of essential oils is now practised to a considerable extent in a very scientific manner, the adulterants being so chosen that the final mixture shall have, as far as possible, as many of the ascertainable characters of a pure oil as possible.

Specific Gravity.

The first thing to be done in examining an essential oil is to determine its specific gravity. For this purpose hydrometers are useless. Approximate accuracy is useless in this work, and hydrometers are only capable of yielding approximate results. Besides, one frequently has far too little oil at one's disposal to use a hydrometer. For ordinary work a specific gravity bottle is generally used, holding from 10 to 50 c.c. There are two points to be noted in connexion with this. The graduated bottles sent out by apparatus firms seldom contain the exact quantity they are supposed to do. It is therefore advisable to check the contents of the bottle, and to use the necessary correction when calculating a specific gravity. Secondly, the counterpoise of a 50 c.c. bottle should be about 60 mgs. less than its apparent weight when empty on account of the air contained in the bottle. A consideration of the laws of hydrostatic pressure will show that if this be not so the specific gravity as determined will be the ratio

$$\frac{\text{weight of oil} - \cdot 06 \text{ gram}}{\text{weight of water} - \cdot 06 \text{ gram}}$$

instead of the correct ratio

$$\frac{\text{weight of oil}}{\text{weight of water}}.$$

This correction of ·06 gram is not absolutely accurate, but is sufficiently so for all practical purposes and may be omitted in most cases.

It is essential that great care should be taken that the temperature be accurately determined when taking the specific gravity. The bottle filled with oil takes some time to assume the exact temperature of the water in which it is immersed, especially if these differ much at first. Hence it is always advisable not to depend only on an observation of the temperature of the water, but to use a very small bulbed thermometer with which the actual temperature of the oil itself in the bottle can be taken. Specific gravities are usually expressed as the ratio of the weight of a volume of the oil to that of an equal volume of water, both at 60° F., or approximately 15·5° C. This is written $\frac{d15\cdot5^\circ}{d15\cdot5^\circ}$. Any variation in temperature can thus easily be expressed. For example, the specific gravity of, say, otto of roses at 30°, as given in the *British Pharmacopœia*, is intended to be interpreted as $\frac{d30^\circ}{d15\cdot5^\circ}$, that is, with the water to which it is compared at 15·5°. Wherever the specific gravity of an oil is referred to in this work, it is to be understood as referring to $\frac{d15\cdot5^\circ}{d15\cdot5^\circ}$, except when otherwise quoted.

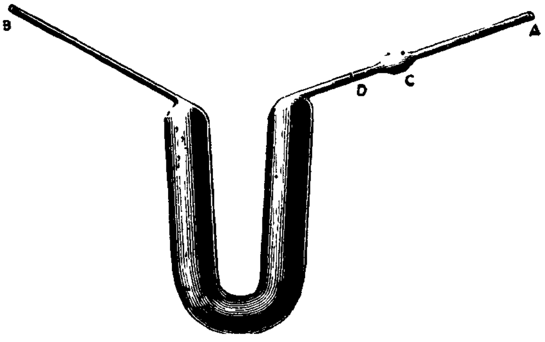


FIG. 3.

Frequently one has less than 50, and sometimes even less than 10 c.c. of an oil at one's disposal. The specific gravity should then be determined in a Sprengel tube. The above diagram shows the most convenient form of tube for general use. With a very small knowledge of glass-blowing they can be made in five minutes out of a few inches of glass-tubing. The only important point is to choose a piece of thick walled tubing, otherwise it is impossible to draw out satisfactory capillaries. The oil should be sucked into the tube through the opening, B, by means of a small india-rubber tube fixed on to the end, A, up to the small glass bulb C. The tube is then placed in a beaker of water at the desired temperature, the bent arms serving to support it on the side of the beaker. Owing to its small content, from 2 to 5 c.c., it very rapidly acquires the temperature of the water, and by gently tilting the end, A, upwards, the oil runs out at B until it just reaches the graduation mark, D. Taking care to wipe off the last drop of oil exuding at B, the tube is again levelled, when the liquid flows back into the bulb, so obviating any possibility of loss. It is then carefully wiped and suspended by a copper wire loop to the hook on the balance and weighed, and the specific gravity calculated from the weight of the oil and the weight of the corresponding volume of water. The accuracy of these tubes depends on the fineness of the capillaries and the rapidity with which their contents assume the exact temperature of the water in which the tube is immersed.

It is rarely that any greater degree of accuracy than that attained in the above methods is required. If, however, scientific accuracy is necessary in specific gravity determinations, the usual standard of comparison, at whatever temperature the determination may be made, is water at its maximum density temperature, namely 4°. If no correction is made for the weight of the air contained in the bottle or tube, accuracy to the fourth place of decimals is ensured by reducing the observed weighings to vacuum weighings. This can be done by the equation—

$$d\frac{t^\circ}{4^\circ} = \frac{m}{w}(\mathrm{Q} - \mathrm{L}) + \mathrm{L},$$

where m is the observed weight of the substance, w that of the water, Q the density of water at t° (compared with water at 4°), and L is taken as 0·0012, which is approximately the density of air over a reasonable range of temperature.

For practical purposes the alteration in specific gravity of essential oils may be taken as 0·00075 for every degree centigrade, so that to correct a specific gravity observed at 20° it is usual to add $0·00075 \times 5$ to correct it to 15°, and so on.

OPTICAL METHODS.

1. *Refraction.*

The author and several other chemists have for some years past persistently advocated the use of the refractometer in the examination of essential oils. Although this determination was regarded as of little use by many chemists, it is now generally recognised that it is indispensable. But its value is only to be properly estimated by a very careful consideration of the results obtained.

The refractive index of a given sample of oil is in many cases of very little value in indicating adulteration. There are certain well-recognised exceptions, where the oil and the adulterant have refractive indices which vary very widely. Such, for example, is the case with otto of roses and geraniol, or aniseed oil and petroleum. But the chief value of this determination lies in a careful examination of the various fractions obtained when an oil is distilled *in vacuo*. Here a consideration of the boiling-points, specific gravity, optical rotation, and refractive index of the various fractions will lead to most important indications. For example, an oil of peppermint adulterated with, on the one hand, a small quantity of copaiba or cedar-wood oil, and, on the other hand, with a small quantity of glyceryl acetate, would give a refractive index not much different from that of the genuine oil. But when distilled *in vacuo* and the residues or high boiling fractions examined, the high index in the one case would at once suggest the presence of sesquiterpene bodies, whilst in the other case the very low index would indicate bodies belonging to the open-chain series.

Experience alone will enable one to make the best use of these indications, but it is important that as many figures should be available as possible. All determinations recorded in this volume are made on instruments of the Pulfrich or the Zeiss Abbé types.[1] Of these the Pulfrich instrument is the more elaborate, but the Zeiss Abbé refractometer, which is illustrated below, is the most useful instrument for ordinary work. Its great advantage lies in the fact that it requires only a few drops of fluid for a determination, and gives results which are accurate to one or two points in the fourth place of decimals. The author has made a very large number of determinations with it, and finds it to be absolutely reliable. Refractive indices between 1·3 and 1·7 can be determined by it, which figures cover the range found in essential oils. The following is the method of using this instrument:—

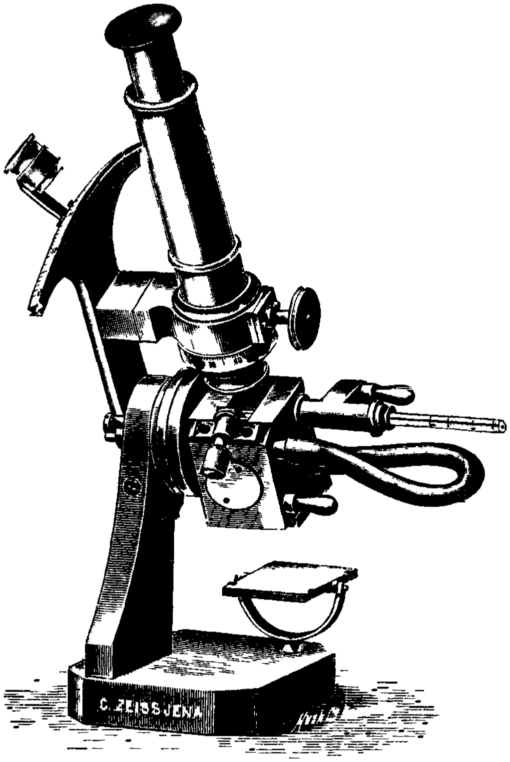


FIG. 4.—The daylight which falls upon the mirror passes through the double prism, closed for the purpose of measurement, into the telescope; the arrows indicate the direction of the circulation of hot water round the prisms to retain a constant temperature. The magnifier is fitted with a reflector, not shown in the figure.

The method of measurement is based upon the observation of the position of the border line of the total reflection in relation to the faces of a prism of flint-glass, into which the light from the substance under investigation enters by the action of refraction.

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[1] An instrument of the Zeiss Abbé type is now made in England, and is fully equal in every respect to the German instrument

The refractometer is mainly composed of the following parts:—

1. The double Abbé prism, which contains the fluid and can be rotated on a horizontal axis by means of an alidade.
2. A telescope for observing the border line of the total reflection which is formed in the prism.
3. A sector rigidly connected with the telescope, on which divisions (representing refractive indices) are engraved.

The double prism consists of two similar prisms of flint-glass, each cemented into a metal mount and having a refractive index n_d = 1·75; the fluid to be investigated (a few drops) is deposited between the two adjoining inner faces of the prisms in the form of a thin stratum (about 0·15 mm. thick). The former of the two prisms, that farther from the telescope (which can be folded up or be removed), serves solely for the purpose of illumination, while the border line is formed in the second flint prism.

The border line is brought within the field of the telescope by rotating the double prism by means of the alidade in the following manner: Holding the sector, the alidade is moved from the initial position, at which the index points to n_d = 1·3, in the ascending scale of the refractive indices until the originally entirely illuminated field of view is encroached upon, from the direction of its lower half, by a dark portion; the line dividing the bright and the dark half of the field then is the "border line". When daylight or lamplight is being employed, the border line, owing to the total reflection and the refraction caused by the second prism, assumes at first the appearance of a band of colour, which is quite unsuitable for any exact process of adjustment. The conversion of this band of colour into a colourless line, sharply dividing the bright and dark portions of the field, is effected by a compensator.

The compensator, which finds its place in the prolongation of the telescope tube beyond the objective, *i.e.* at a point between the objective and the double prism, consists of two similar Amici prisms, of direct vision for the D-line and rotated simultaneously, though in opposite directions, round the axis of the telescope by means of the screw head. In this process of rotation the dispersion of the compensator passes through every value from zero (when the refracting edges of the two Amici prisms are parallel and on different sides of the optical axis) up to double the amount of the dispersion of a single Amici prism (the refracting edges being parallel and on the same side of the axis). The above-mentioned dispersion of the border line, which appears in the telescope as a band of colour, can thus be rendered innocuous by rotating the screw head, thereby giving the compensator an equal, but opposite, dispersion. The opposite equal dispersions will then neutralise each other, with the result that the border line appears colourless and sharply defined.

The border line is now adjusted upon the point of intersection of the crossed lines by slightly inclining the double prism to the telescope by means of the alidade. The position of the pointer on the graduation of the sector is then read off by the aid of the magnifier attached to the alidade. The reading supplies the refractive index n_d of the substance under investigation itself, without any calculation.

As the refractive index of fluids varies with the temperature, it is of importance to know the temperature of the fluid contained in the double prism during the process of measurement.

If, therefore, it be desired to measure a fluid with the highest degree of accuracy attainable (to within 1 or 2 units of the fourth decimal of n_d) it is absolutely necessary to keep the fluid, or rather the double prism containing it, to a definite known temperature and to keep it constant.

The refractive index of a substance is, of course, a relative expression, as it refers to a second substance, which, in ordinary determinations, is always the air. The term refractive index indicates the ratio of the velocities with which light traverses the two media respectively. This is, as is easily demonstrated by a consideration of the wave theory of light, identical with the ratio of the sine of the angle of incidence, and the sine of the angle of refraction, thus—

$$n = \frac{V}{V^1} = \frac{\sin i}{\sin r},$$

where V and V^1 are the velocities of light in the two media, i is the angle of incidence, and r the angle of refraction.

To correct a refractive index determined for *air/liquid* to the absolute index *vacuum/liquid*, the observed value should be multiplied by 1·00029. This correction is, however, too small to be of the slightest value in practice.

The molecular refraction is a constant frequently quoted for individual chemical compounds, and is of considerable value as evidence of constitution. since it is generally true that the molecular refraction of a compound is composed additively of the refractive powers of the atoms contained in the molecule. The molecular refraction is the value obtained by multiplying the refractive power by the molecular weight.

The refractive power is a value which attempts to correct the effects of temperature, pressure, and concentration of the substance, all of which cause the refractive index, $n_{,,}$, to vary with the slightest alteration of the conditions. The most accurate expression for the refractive power is that of Lorenz and Lorentz, which is

$$\frac{n^2 - 1}{(n^2 + 2)d},$$

where n is the observed refractive index and d is the density of the substance. The molecular refraction then becomes

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d},$$

where M is the molecular weight of the compound.

Brühl found that the increase of CH_2 in all the homologous series of fatty compounds corresponds to a difference of 4·57 in the molecular refraction for the red hydrogen line. By deducting n times this value from the molecular refraction of an aldehyde or ketone of the formula $C_nH_{2n}O$, he found 2·328 to be the value for intra-radical oxygen. Similarly the values of other groupings have been determined which may be summarised as follows:—

	Atomic Refractions for the Sodium Line.
Carbon	2·494
Hydrogen	1·051
O' (hydroxyl oxygen)	1·517
O'' (intra-radical oxygen) . . .	2·281
O (simple ether oxygen)	1·679
Cl	5·976
Br	8·900
I	14·120
= double linkage between carbon atoms	1·700
≡ triple linkage between carbon atoms .	2·220 (for hydrogen red line)

To indicate the value of this constant in deciding the constitution of a compound, the case of geraniol, $C_{10}H_{18}O$, may be examined. Calculated from the above values the molecular refraction would be the sum of the atomic refractions, as follows:—

Carbon	2·494 × 10 =	24·940
Hydrogen	1·051 × 18 =	18·918
Oxygen (hydroxyl)	1·517 =	1·577
		45·375

But by experimental determination the molecular refraction is found to be 48·71, which is 3·235 in excess of the value calculated from the atomic refractions. Two double bonds between carbon atoms would account for 3·414 in excess, so that it is evident that geraniol contains two such double linkages. No alcohol of the formula $C_{10}H_{18}O$ with two double linkages can contain a ring, so that geraniol must belong to the open chain series, a conclusion entirely supported by its chemical characters.

The refractive indices of most essential oils have been given under each oil in Volume I.; if a temperature correction is required, as it frequently is, the addition of 0·0004 for each degree centigrade by which it is necessary to reduce the temperature, and a similar subtraction for a rise of 1°, should be made. This figure varies slightly, but unless accuracy to the fifth place of decimals is required, it is sufficiently accurate for practical purposes.

2. *Polarimetry.*

The polarimeter is an instrument with which the essential oil chemist cannot possibly dispense. The hypothesis, first seriously enunciated by Le Bel and van t'Hoff, that substances which contained an asymmetric carbon atom (*i.e.* a carbon atom directly united to four different atoms or radicles) were capable of rotating the plane of polarisation of a beam of polarised light, has now become a fundamental theory of organic chemistry. The majority of essential oils contain one or more components containing such a carbon atom, and so possess the power of effecting this rotation. In general, the extent to which a given oil can produce this effect is fairly constant, so that it can be used, within limits, as a criterion of the purity or otherwise of the oil.

Without discussing the theories of the polarisation of light it will be desirable to briefly illustrate the fundamental principles upon which their application depends. Ordinary light consists of transverse vibrations in numerous planes in which is no polarity or *two-sidedness*, if the expression is justifiable; whilst plane polarised light consists of vibrations in one plane only. This may be roughly illustrated in the following manner; If a string, fixed at its ends, be plucked, it will vibrate in a certain plane dependent on the direction of the plucking. If the string be passed through a slit, just wider than it is itself, in a piece of cardboard, so that the slit is in the direction of the vibrations, these will not be interfered with; but if the slit be turned round, the vibrations will be interfered with, and when it is at right angles to the direction of the vibrations, they will be totally suppressed. Light waves (for convenience, the expression, a ray of light, is more general) may be plane polarised in several ways, so that the vibrations in the one plane may be similarly interfered with, and upon this depends the use of the polarimeter. This instrument, of which the theory is described fully in the following pages, is constructed on several different principles, of which by far the most useful for all general purposes is the Laurent half-shadow instrument. In the annexed diagram, A is a small telescope, B is a magnifying glass used to read the graduation on the dial and vernier, C is one of the verniers, D is a dial graduated to half degrees, E is the analysing Nicol's prism (a specially prepared prism of calc-spar, capable of polarising light) which is fixed to the graduated dial and telescope, F is the groove in which tubes containing the liquids to be examined are inserted, H is a pointer attached to the polarising Nicol's prism, G is the fixed Laurent plate (*vide infra*), and J is a plate of bichromate of potassium.

This apparatus can only be used with sodium light, as for quantitative results light of definite refrangibility must be used. A Bunsen lamp of convenient construction, into the flame of which a little common salt can be introduced on a platinum wire, is placed about 4 or 5 inches from the end J. The light is further sifted by means of the bichromate plate, so that light approximately corresponding to the D line of the spectrum falls on to the polariser, and that which passes through is plane polarised. The plate G is a special contrivance, half of which is made of quartz or gypsum, and the other half of plain glass; the thickness of this is carefully graduated, and the result—the optical theory of which need not here be discussed—is that when the analyser is in a certain position with reference to the polariser and plate, the two halves of this plate appear equally illuminated. By adjusting the prisms by means of the movable pointer, H, and the screw, E, which govern the delicacy of the instrument, the zero marks on the dial and on the vernier are made to correspond when the position of equal illumination is attained. A slight rotation of the analyser in either direction by means of the projecting screw handle at once causes the two halves of the field to become unequally illuminated. Having set the instrument at zero, a tube containing an optically active liquid is inserted in the groove, F. It will now be found that the analyser

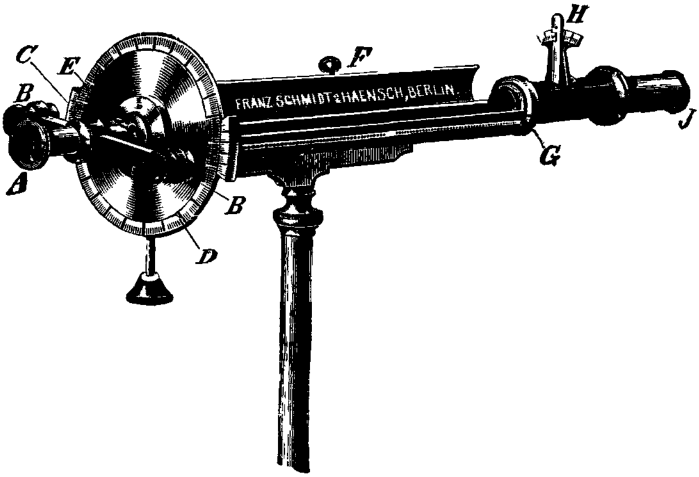

FIG. 5.

has to be rotated a certain number of degrees either to the right or the left in order to restore the position of equal illumination of the two halves of the field. This is the angle through which the plane of polarisation has been rotated. The beginner will find a little difficulty in using this instrument; for example, when examining oils with high rotations or when the dial has been rotated too far, and has been taken beyond the range of sensitiveness; half an hour with some one who understands the instrument will explain its use far better than pages of printed matter. The rotation of the dial in the direction of the movement of the hands of the clock, as the observer sees it, is conventionally termed dextro-rotation, and conversely. In general, the *optical rotation* is expressed for a column of 100 mm. The specific rotatory power is a different figure, and is expressed by the symbol $[\alpha]$, and, taking the decimetre as the unit of length for this purpose, is the observed rotation in the decimetre tube divided by the specific gravity of the liquid. It is to be noted, however, that the expression $[\alpha]$ is very frequently used to mean the observed rotation for 100 mm. The molecular rotation refers of course only to pure compounds and not to mixtures, and need not be discussed here, otherwise than to mention that it is the product of the specific rotary power and the molecular weight. In the sequel, the optical rotation will be understood to refer to the rotation produced by a column 100 mm. long, unless otherwise mentioned.

The theory of the half-shadow polarimeter is, briefly, as follows: The light, of approximately constant refrangibility, falls on the polarising Niçol's prism, which is a rhomb of calc-spar cut obliquely by a plane perpendicular to the principal section. The cut faces are polished and cemented together again by a thin film of Canada balsam. Calc-spar is a doubly refracting substance, and in the ordinary way the incident ray is divided by the spar into two rays, the ordinary and the extraordinary, the former following the ordinary laws of refraction, the latter behaving abnormally. Two rays, then, will be found to emerge. But the refractive index of the balsam is greater than that of the spar for the extraordinary ray, and less than that tor the ordinary ray, both of which are plane polarised. According to the usual laws of refraction, total reflection can only occur in passing from a more to a less refracting medium. Hence the extraordinary ray will always be transmitted, but by arranging the angle of incidence properly the ordinary ray can be totally reflected. Hence only the extraordinary ray now falls on to the Laurent plate, and it is in a plane polarised condition. This plate is made of quartz or gypsum over one-half of the field, and plain glass over the other. It is a doubly refracting substance and refracts the incident ray as ordinary and extraordinary rays. The thickness is so adjusted that it introduces a retardation of $\frac{1}{2}\lambda$ (where λ is the wave length of the light used) between the two rays. Consequently, the light emerges plane polarised from the crystalline plate, but the planes of polarisation of the rays emerging from the two halves will be inclined at an angle 2α, if α is the inclination of the incident single polarised ray to the optical axis of the quartz. Hence when this plate, with its two polarised rays, is viewed through the analysing Nicol, the two halves will be in general unequally illuminated, except when the principal plane of the Nicol be parallel to the optical axis of the crystalline plate. In this position we have the zero point of the instrument. The insertion of an optically active liquid destroys this condition by rotating the plane of polarisation, and the angle through which it is necessary to rotate the analyser in order to restore the "equal shadows" measures the rotation of the plane of polarisation.

Another simple instrument, known as the *Biquartz* polariser, depends on a rather different principle. Here two semicircular plates of quartz are placed in juxtaposition, each cut at right angles to its axis, one possessing *dextro-* and the other *laevo*-rotatory power. The two plates are of the same thickness, and produce equal rotations in opposite directions. The incident light in this case is white, and the lights of different refrangibilities are rotated through different angles. Hence when viewed by an analysing Nicol, waves of different refrangibilities will be quenched in the two halves, and they will in general appear of different colours. When the principal plane of the analyser, however, is parallel to the direction of the incident vibrations, the two halves will always be of the same colour, dependent on the complementary colours which are quenched. By suitably adjusting the thickness of the plate, the brilliant yellow may be quenched, and the delicate grey-violet tint, known as the tint of passage (Biot's *teinte sensible*), appears when both halves have the same colour. This point, the zero point of the apparatus, is easily fixed. for the slightest rotation to the right or left renders one-half of the field blue and the other red. Having set the instrument, it is found that when an optically active substance is introduced, the tint of passage disappears, and the analyser must be rotated in order to restore it, according to the optical activity of the substance.

To most observers it is easier to obtain equal illumination in the two halves of the field than to correctly obtain the tint of passage, hence the popularity of the former apparatus.

The angle of rotation is, of course, directly proportional to the thickness of the layer of active substance through which the polarised light passes. The expression optical rotation or rotatory power is universally understood to be the observed angle of rotation produced by a column of 100 mm. of the optically active substance. If tubes of other lengths be used, the optical rotation becomes $\alpha = \frac{a}{l}$, where a is the observed angle, and l is the length of the tube in decimetres. If, as is usually the case, this is observed with sodium light the optical rotation is expressed by the symbol, α_d.

It is usual to express this value as for the temperature 20°. A slight correction may be made for difference in temperature, but as it has no appreciable effect on the results obtained, it may be regarded as negligible if the observation be made at any temperature between 15° and 20°.

The expression "specific rotation" is symbolised by $[\alpha]_d$, and indicates the optical rotation divided by the specific gravity: $[\alpha]_d = \frac{\alpha}{\text{specific gravity}}$.

If expressed for white light instead of sodium light, it is expressed by $[\alpha]_j$.

For solid substances the substance is dissolved in a neutral solvent, and the specific rotation is calculated from the formula—

$$[\alpha]_d = \frac{100\alpha}{pld}.$$

Where α is the observed angle, p is the percentage of active substance, l is the length of the tube in decimetres, and d is the specific gravity of the solution.

But, since the specific rotation of dissolved substances vary with the concentration and the nature of the solvent, these data should always be given when the specific rotation is quoted.

MELTING- AND SOLIDIFYING-POINTS.

Many oils possess the property of becoming solid at temperatures slightly below the ordinary, and a determination of the solidifying- or melting-points becomes an important criterion of purity in these cases. The melting-point is not usually the same as the solidifying-point, on account of the peculiar properties of bodies, included under the term superfusion, etc. In addition, the temperature recorded differs somewhat with the method used in the determination. For general work the following apparatus gives the best results in a convenient manner:—

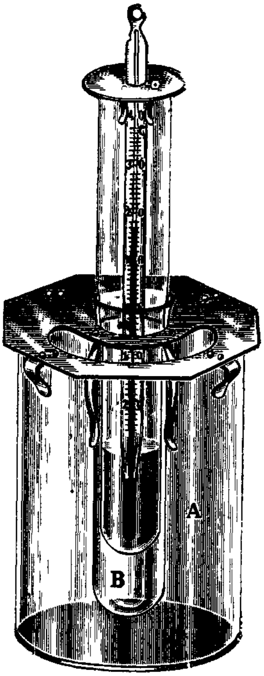

FIG. 6.

Here the outer vessel contains a sufficient quantity of the freezing mixture, such as a mixture of ice and salt, or a solution of one of the usual salts. The longer test tube acts as an air cover to the inner tube in which the thermometer is placed. A small quantity of the oil—just enough to cover the bulb of the thermometer—is placed in this tube, and in certain cases the platinum stirrer is used. The melting-point is determined by freezing the oil and then removing the freezing mixture and allowing the temperature to rise slowly, and noting the temperature at which liquefaction takes place. The solidification-point is determined by cooling the oil down without disturbing it until the temperature is clearly below the point of solidification. A slight agitation of the stirrer will now usually induce solidification, if not, the introduction of a crystal of the compound solidifying—anethol, for example, in the case of aniseed oil—will do so. A disengagement of heat occurs on solidification, which causes the thermometer to rise. The maximum reading during the process of solidifying may be regarded as the solidifying-point.

Boiling-point and Distillation.

The determination of the temperature at which an oil begins to boil is often of importance, as is also the percentage of the oil which distils within definite limits of temperature. The results obtained in distillation processes must, however, be interpreted very carefully, as the *quantitative* results depend so largely on the exact conditions of distillation. For ordinary purposes, an ordinary Wurtz flask is useful for determining the temperature at which the liquid first boils, but when an examination of any of the fractions or any estimation of the quantity boiling between given temperatures is needed, a fractional distillation flask is better. These flasks are illustrated above.

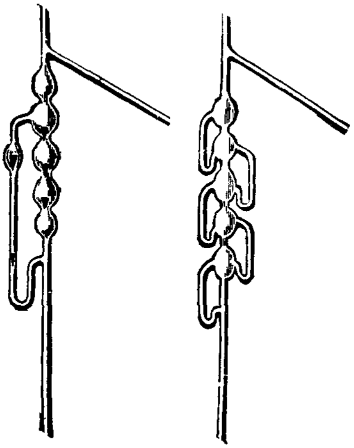

Fig. 7.—Fractionating columns.

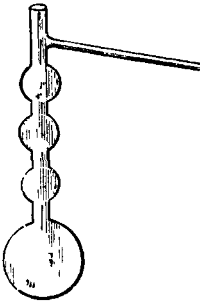

Fig. 8. Fractionating flask.

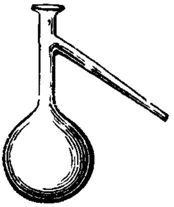

Fig. 9. Wurtz flask.

It is often advisable to distil or fractionate an oil under reduced pressure, especially when the constituents decompose when boiled at atmospheric pressures.

The value of fractional distillation in the examination of essential oils cannot be overestimated. The various fractions may be examined and their specific gravities, optical rotations, and refractive indices determined. The combination of these figures will often give the experienced analyst the most useful information and save him many hours' needless work. Experience alone, however, will teach the chemist to make the fullest use of the results so obtained. In most cases distillation under reduced pressure is necessary on account of the risk of decomposing the various constituents of the oil. The use of a Bruhl receiver (or any similar contrivance), which is easily obtained from any apparatus maker, saves the necessity of breaking the vacuum when collecting the different fractions.

But by applying the process of fractional distillation to a sample, and determining the characters of numerous fractions, the actual number of available determinations may be, and frequently is, so largely increased that there is practically no chance of the adulterator being able to standardise his oils to meet *all* these figures. This proposition, of course, fails where it is possible to use a substance obtained from a cheaper source which is identical with one contained naturally in the oil, and which is added in such amount as not to materially exceed, in the total, the amount naturally occurring in the essential oil in question.

In fractionally distilling an oil, in order to compare it with oils of known purity similarly treated, it should be remembered that the details of the process should be as constant as possible for all the samples examined. Thus the size of the distilling flask, the nature of the condensing apparatus, and the rate of distillation are of the highest importance. Experience alone will tell whether it is better to distil the oil at normal pressure or under reduced pressure. Then again, in some intances it is advantageous to separate the fractions according to their temperature, noting the quantities collected. In others, it is better to collect definite amounts and note the variations in temperature.

The Determination of Esters.

Esters, or salts of alkyl radicles, such as linalyl acetate, etc., are frequently the most important constituents of essential oils. Their importance is especially noteworthy in such cases as lavender, bergamot, peppermint, and wintergreen oils, and their estimation is very frequently necessary. The principle upon which this depends is the fact that most esters are decomposed by solution of caustic alkali (preferably in alcohol) according to the equation—

$$R\bar{A} + KOH = R.OH + K\bar{A},$$

where R is the alkyl, and $\bar{A}$ the acid, radicle.

Strictly speaking the amount of free acids present in an essential oil should be determined, and the acid value deducted from the saponification value, the difference being the ester value.

In many cases the amount of free acids is negligible, but in a number of cases this is not the case, and with oils of lavender, bergamot, geranium, and similar oils, the deduction for the free acids becomes of importance.

To use this principle for the estimation, from 2 to 5 grams of the oil, according to the magnitude of its ester content, are exactly weighed into a small flask capable of holding about 150 to 250 c.c., and from 25 to 35 c.c. of solution of caustic potash in alcohol are added. The strength of this should be approximately half-normal. The whole is then boiled in the water-bath under a reflux condenser for an hour. It is then diluted with water and the excess of potash is estimated by titration with seminormal sulphuric acid, using phenol-phthalein as an indicator. To determine the amount of potash originally employed, it is best to perform a blank experiment with the same quantity of potash solution, merely omitting the oil, so that the blank and the oil have been treated in an exactly similar way. The difference in the two titrations gives the amount of potash used in decomposing the esters. Care should be taken that the number of c.c. of $\frac{N}{2}$ potash absorbed does not exceed the number of c.c. unabsorbed, as otherwise the percentage of esters tends to be underestimated. If any free acids are present these will have neutralised some of the potash, and it is then necessary to determine by a preliminary titration how much is used for this purpose, and to deduct the result from the total quantity of potash used.

The number of milligrammes of KOH used to saponify 1 gram of the oil (minus that required for the free acids) is termed the ester number. From this figure, which is now known, the percentage of esters present in a given oil may be rapidly calculated from the formula—

$$\frac{M \times A}{560} = \text{percentage of ester,}$$

where M is the molecular weight of the ester, and A the ester number. (This is assuming, as is usually the case, that the ester is a combination of a monobasic acid with a monatomic alcohol.)

As the free acids present in essential oils consist in the main of acetic acid, they are, when necessary, calculated in terms of acetic acid; in the same way the esters are conventionally calculated from the alkali required for their hydrolysis, in terms of the principal ester present, for example, linalyl acetate in the case of lavender and bergamot oils, and geranyl tiglate in the case of geranium oil.

The molecular weights of the esters commonly found in essential oils are as follows:—

Geranyl, linalyl, and bornyl acetates	M = 196
Menthyl acetate (for peppermint oil)	M = 198
Geranyl tiglate (for rose-geranium oil)	M = 236
Santalyl acetate (for sandalwood oil)	M = 262
Sabinyl acetate (for savin oil)	M = 194

The Detection of Artificial Esters in Essential Oils.—The custom of valuing certain essential oils, such as lavender, bergamot, geranium, petit-grain, etc., by the determination of their ester-content, has led to the use of scientific adulterants in the form of artificial esters which have been deliberately employed for the purpose of misleading the analyst. Of course, the ester determination is not a true criterion of value, as most of this class of oils owe their perfume value to various other bodies as well. The first compounds of this nature employed for adulteration were ethyl succinate and ethyl oxalate.[1] For the detection of these in lavender oil the following test was proposed by Guildemeister and Hoffman:—

"Two grams of the oil are saponified; the portion insoluble in water separated by shaking with ether, and the aqueous solution neutralised with acetic acid. The solution is diluted to 50 c.c. and 10 c.c. of cold saturated solution of barium chloride added. It is then warmed for two hours on a water-bath and allowed to cool. If a crystalline deposit is formed, the oil is to be considered adulterated, as the acids contained in normal lavender oil, acetic and butyric acids, give soluble barium salts."

It is evident that this test will only detect those acids whose barium salts are insoluble. A more comprehensive test is therefore needed, as several other esters have since been employed for adulteration purposes. Glycerin acetate, prepared by the acetylation of glycerine, was first de-

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[1] Schimmel's *Report*, April, **1897**, 25.

tected in peppermint oil by Bennett.[1] The acetic radical was overlooked in the preliminary experiments since the oil itself contained acetic esters. By fractionation a substance of high molecular weight and low refractive index was separated, and this proved to be triacetin or glycerin acetate. Ethyl citrate was detected later by the same worker[2] in a sample of lavender oil.

The high saponification value of these two bodies render them particularly suitable for adulteration, a small proportion being sufficient to materially raise the ester value.

The following esters are amongst those used as adulterants:—[3]

	Boiling-point.	Specific Gravity.	Per Cent. Linalyl Acetate Indicated by Addition of 1 per Cent.
Acetine	261° to 264°	1·19	2·00
Monacetine	Decomposes	1·21	1·62
Diacetine	260° to 265°	1·184	2·22
Triacetine	258° ,, 260°	1·165	2·62
Ethyl Citrate	286° ,, 289°	1·140	2·13
,, Laurinate	270° ,, 310°	0·866	0·75
,, Oleate	330° ,, 345°	0·680?	0·64
,, Phthalate	290° ,, 293°	1·124	1·77
,, Succinate	212° ,, 218°	1·044	2·26
Methyl Phthalate	271° ,, 275°	1·195	2·02

It is not easy to outline a general method which will detect this adulteration of ester-containing oils. As a general rule, however, the synthetic esters may be partially separated by fractional distillation, and by comparing the physical characters of the last fractions with those obtained from oils of known purity, an indication of the presence of abnormal constituents may usually be obtained. By saponifying the high-boiling ester-containing portion with alcoholic potash, neutralising with acetic acid, evaporating the alcohol and extracting the oily matter by shaking with ether, abnormal potassium salts may be detected in the aqueous portion by evaporating to dryness, dissolving in water, and applying the usual chemical reagents such as barium chloride, calcium chloride, ferric chloride, etc.

The table on next page shows the reactions of the more common acids with these reagents.

The natural esters present in essential oils are usually those of acetic, butyric, and valerianic acids, and in the case of geranium oil, tiglate acid.

The detection of phthalic acid by fusion with resorcin has been found to be unreliable as a fluorescein reaction is frequently obtained with pure oils.

Denigè's test for citric acid in the saponification liquor is as follows:—

Ten c.c. of the neutral solution of the potassium salt is shaken with 1 to 1·5 grams lead peroxide; 2 c.c. of a solution of mercuric sulphate is added (prepared by dissolving 5 grams HgO in 20 c.c. concentrated H_2SO_4 and water to 100 c.c.). The solution is filtered and a 2 per cent.

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[1] *Chemist and Druggist*, **62**, 591.

[2] *Ibid.*, **69**, 691.

[3] *P. and E.O.R.*, July, **1912**, 170.

solution of $KMnO_4$ is added until it is no longer decolorised. A white or pale yellow flocculent precipitate indicates the presence of citric acid.

	$BaCl_2$.	$CaCl_2$.	$FeCl_3$.
Benzoate . . .	nil	nil	Buff ppt.
Butyrate . .	,,	,,	nil
Cinnamate . .	White ppt.	White ppt	Buff ppt.
Citrate	,,	White ppt. on boiling	Green colour
Formate . . .	nil	nil	Red ,,
Oleate . . .	White ppt.	White ppt.	Brown ppt.
Oxalate . .	,,	,,	Green ,,
Phthalate . . .	nil	nil	Brown ,,
Succinate . . .	,,	,,	,, ,,
Tartrate . . .	White ppt.	White ppt. ?	Green colour Brown ppt. on heating.
Valerianate . . .	,,	,,	Brown ppt.

The following methods for the determination of a number of artificial esters are reproduced, for the sake of completing the subject here, from Volume I of this work :—

Terpinyl acetate in the absence of esters of high molecular weight, or ethyl esters of the fatty acids of coconut oil, is indicated by a difference to be observed in the apparent ester value by different times of saponification. This ester is far more resistant to the action of caustic alkali than is linalyl acetate, and requires two hours at least for complete saponification. Hence, if the oil shows a difference in the saponification value in thirty minutes and in two hours, which amounts to more than from 1 to 2, terpinyl acetate is almost certainly present. The following table[1] shows the effect of this partial-saponification on the two esters and on adulterated oils :—

Time of Saponification.	5 mins.	15 mins	30 mins.	45 mins.	1 hr	2 hrs.
Linalyl Acetate E. No.	191·5	217·5	**223·2**	223·7	**223·1**	224·7
Terpinyl ,, ,,	108·2	166·8	**209·7**	233·4	**245·8**	262·7
Bergamot Oil ,,	80·3	94·5	**97·3**	97·5	**97·8**	98·5
,, ,, + 5% Terpinyl Acetate ,,	82·5	94·8	**101·2**	102·1	**104·7**	107·2
,, ,, + 10% ,, ,, ,,	79·9	96·4	**102·8**	105·2	**108·3**	112·5
,, ,, + 25% ,, ,, ,,	78·8	100·6	**108·1**	116·4	**119·0**	126·8

Fractional saponification, with the use of varying amounts of caustic alkali, will also reveal the presence of terpinyl acetate.

The following table will indicate the differences observed when about 2·5 grams of the oil are saponified (1) with 20 c.c. of $\frac{N}{2}$ alkali for two hours, and (2) with 10 c.c. of $\frac{N}{2}$ alkali, diluted with 25 c.c. of alcohol for one hour :—

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[1] Schimmel's *Report*, October, 1910, 60.

Oil.	20 c.c. × 2 hours.	10 c.c. (and 25 c.c. Alcohol) × 1 hour.	Difference.
Bergamot (1)	100·5	98·6	1·9
Bergamot (2)	108	105·5	2·5
„ with 5 per Cent. Terpinyl Acetate	117	102·5	14·5
„ with 10 per Cent. Terpinyl Acetate	121	104·0	17·0

The table on next page represents the behaviour on fractionation at 3 mm. pressure of two samples of bergamot adulterated with terpinyl acetate and a sample of pure bergamot oil.

The author[1] has recommended the examination of the last 10 per cent. left on evaporation of the oil on a water-bath, since the heavy artificial esters accumulate in this fraction. The refractive index of this 10 per cent. should not be below 1·5090, and the saponification value should not exceed 190. The following figures (see p. 317) represent nine samples of adulterated oil, all sold as genuine bergamot oil.

Glyceryl acetate, which is an artificial ester commonly used in the adulteration of bergamot oil, is detected fairly easily on account of its high solubility in dilute alcohol. The test is carried out as follows:[2] Ten c.c. of bergamot oil and 20 c.c. of 5 per cent. alcohol are well shaken in a separating funnel, and after the solutions have separated and become clear the watery solution is run off and filtered. Ten c.c. of the filtrate are exactly neutralised with deci-normal alkali, and then 5 c.c. of semi-normal alkali run in, and the whole saponified under a reflux condenser for one hour. In the case of pure bergamot oil 0·1 or at most 0·2 c.c. of semi-normal alkali will have been used up by the saponification, whilst each 1 per cent. of glyceryl triacetate present in the oil will be represented by practically 0·5 c.c. of semi-normal alkali.

Glyceryl acetate is so easily washed out with ordinary hot distilled water, that an adulterated oil when washed several times with hot water will show a distinctly lower ester value and refractive index than the original unwashed oil.

Pure oils of lavender, bergamot and similar oils show practically no reduction either in refractive index or ester value by such treatment.

Hall and Harvey[3] prefer to determine glyceryl acetate in essential oils by a method in which the glycerol is separated and weighed. This method is as follows:—

A quantity, if possible not less than 10 grams, of the oil to be examined is mixed with about 50 c.c. of ·830 alcohol and saponified with N/2 alcoholic potash; it is then digested on the water-bath for a period of one hour; the solution is neutralised by means of N/2 HCl, and evaporated to dryness upon the water-bath in order to remove the alcohol; about 20 c.c. of water is added and the oily proportion extracted by methylated ether, the water solution being run in a 6-oz. round-bottomed flask; the ether extract should again be washed with a further quantity of about 10 c.c. of water, which is then added to that already in the flask

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[1] *P. and E.O.R.*, **1911**, 14. [2] Schimmel's *Bericht*, April, **1911**, 151.
[3] *P. and E.O.R.*, **1913**, 6.

Fraction.	I.			II.			Pure Bergamot Oil.		
	Per Cent.	α_D.	$n_{D20°}$.	Per Cent.	α_D.	$n_{D20°}$.	Per Cent.	α_D.	$n_{D20°}$.
1. to 40°	2	+ 36° 35′	1·47225	10·6	+ 52° 34′	1·47235	18·6	+ 58° 16′	1·47303
2. 40 ,, 50°	38·8	+ 60° 5′	1·47274	28·5	+ 64° 47′	1·47264	18·9	+ 68° 51′	1·47245
3. 50 ,, 68°	9·1	− 11° 32′	1·46030	3·9	+ 8° 35′	1·46664	5·6	+ 17° 15′	1·46545
4. 68 ,, 72°							21·4	− 15° 20′	1·45781
5. 72 ,, 78°				8·7	− 11° 20′	1·46001	20·2	− 11° 16′	1·45331
6. 78 ,, 82°	12·1	− 8° 56′	1·45871	14·8	− 6° 12′	1·45991	—	—	—
7. 82 ,, 88°	20·1	− 3° 42′	1·46011	19·5	− 2° 16′	1·46229	—	—	—
8. 88 ,, 91°	5·4	− 1° 30′	1·46387	—	—	—	—	—	—
9. Residue	12·5	—	—	14 0	—	—	15·3	—	—

	1.	2.	3.	4	5.	6.	7.	8.	9
Specific Gravity	0·885	0·884	0·884	0·8855	0·886	0·886	0·886	0·885	0·878
Optical Rotation	+ 16°	+ 16° 30′	+ 16° 30′	+ 18°	+ 23°	+ 17°	+ 20°	+ 26°	+ 27°
Refractive Index at 20°	1·4660	1·4660	1·4662	1·4658	1·4660	1·4660	1·4681	1·4675	1·4691
Apparent Esters as Linalyl Acetate . .	39 °/₀	39·5 °/₀	41 °/₀	39 °/₀	38·8 °/₀	39·5 °/₀	40 °/₀	41 °/₀	34 °/₀
Fixed Residue	6·5 °/₀	6·3 °/₀	4·2 °/₀	6·4 °/₀	6·1 °/₀	7·2 °/₀	4·5 °/₀	6·9 °/₀	4 °/₀
„ „ Saponification Value of .	257	225	160	239	236	252	172	242	162
„ „ of Saponified Oil . . .	5·3 °/₀	5 °/₀	4·1 °/₀	4·9 °/₀	4·7 °/₀	5·4 °/₀	4·2 °/₀	5·4 °/₀	4 °/₀
Refractive Index of last 10 per cent. . .	1·5040	1·5042	1·5085	1·5042	1·5040	1·5050	1·5070	1·5050	1·5091
Increase in Ester Value in one hour . .	—	—	3·8 °/₀	—	—	—	4·1 °/₀	—	—

All these were adulterated with ethyl citrate except Nos. 3 and 7, which contained terpinyl acetate, and No. 9, which was adulterated with lemon terpenes.

and the whole evaporated to a syrupy condition. This residue contains the glycerol originally present as glyceryl acetate which is estimated in the usual way by the triacetin method, the amount of glyceryl acetate being calculated therefrom.

Schimmel & Co. have proposed to detect esters of fixed acids by an estimation of the amount of volatile acids obtained by distilling the acidified saponification residues, and comparing this figure with the amount of acid indicated by the saponification value.

In this determination about 2 grams are saponified in the usual manner, and the saponification residue rendered slightly alkaline, and evaporated to dryness on a water-bath. The residue is dissolved in 5 c.c. of water and acidified with 2 c.c. of dilute sulphuric acid. This liquid is now distilled by passing a current of steam through it, and when no further acid comes over the distillate (about 300 c.c.) is titrated with decinormal alkali, using phenolphthalein as indicator. The alkali consumed in this neutralisation is nearly identical with that used in the direct saponification, if all the esters present are those of volatile acids, as is the case, with pure bergamot oil. The distillation value should not be more than 5 to 10 below the direct saponification value (*i.e.* milligrams of KOH per 1 gram of oil). When esters of non-volatile acids have been used as adulterants the difference is enormous. For example, an oil containing 2 per cent. of ethyl citrate yielded a direct saponification value of 109·1 and a distillation value of 92·8, and one containing 5 per cent. of ethyl succinate gave a direct value of 127·6 and a distillation value of 91·5.

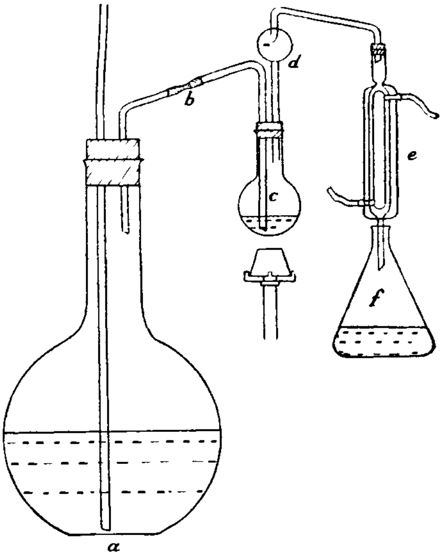

FIG. 10.

Umney[1] has made a critical study of this method, and recommends the following apparatus to be used in the process :—

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[1] *P. and E.O.R.*, **1914**, 116.

(*a*) A 3 litre Jena glass flask.

(*b*) A rubber connection, the removal of which, of course, immediately cuts off the steam supply.

(*c*) A long-necked CO_2 flask of Jena glass and 150 c.c. capacity.

(*d*) The most suitable splash head for the operation.

(*e*) A Davies' condenser.

(*f*) A 500 c.c. Erlenmeyer flask.

The results obtained, unless the special precautions described be adopted when calculated as percentages of ester in the oil, are considerably too high. Whilst some of the causes may be apparent to many, nevertheless the following is a list constructed to include the more important of these causes, and will serve to indicate in what manner the necessary amendments should be made:—

1. The use of methylated spirit (unpurified by further distillation) in the preparation of the standard potash solution employed by some experimenters in the saponification of the oil.
2. The use of hydrochloric acid in neutralising the excess of alkali after saponification.
3. The employment of water in the steam generating flask which has been insufficiently boiled to free it from carbon dioxide and other impurities.
4. The sulphuric acid, used to acidulate before distillation, may be advantageously replaced by phosphoric acid. This modification, whilst in many cases not absolutely essential, is desirable on account of the fact that sulphuric acid is liable to become reduced by certain constituents of oils, particularly of old oils, which frequently contain substances of a resinous nature. In such cases the volatile acid products of the reduction pass over along with the true acids of the oil undergoing examination.

The relations which the abnormal results obtained bear to the above outlined conditions are clearly shown by the figures on next page.

It is evident that, in order to obtain accurate results, the method of working must be clearly and minutely adhered to, especially so in view of the fact that the determination of ester by the method of steam distillation is a very valuable indication as to the purity of an oil, serving to detect the fraudulent addition to oils of such esters as diethyl succinate, triethyl citrate, and diethyl oxalate, the free acids of which are non-volatile in steam. It will not detect glyceryl acetate, terpinyl acetate, nor the esters of coconut oil fatty acids.

The method yielding reliable results and including modifications, devised to remove the sources of error above-mentioned, is as follows:—

About 2 grams of the oil (bergamot or lavender) is accurately weighed into a carbon dioxide flask, and 15 c.c. neutralised alcohol added along with a few drops of phenolphthalein solution, and the whole is just boiled on the steam-bath. The acid number is ascertained by titration with deci-normal alcoholic potassium hydroxide, 25 c.c. semi-normal alcoholic potash (made with 90 to 96 per cent. spirit, preferably distilled over potash) is now added, and the whole boiled under a reflux condenser for one hour, the excess of potash, after saponification and addition of 40 c.c. of carbon dioxide-free water, being neutralised by means of semi-normal sulphuric acid. This titration gives the figure from which the ester percentage is calculated.

Method.	Percentage of Ester found.
1. Oil saponified by solution of potash in unpurified methylated spirit. Excess of alkali neutralised by hydrochloric acid and the acids liberated, previous to distillation by sulphuric acid	47·28
2. As 1, but the excess of alkali after saponification neutralised by sulphuric acid	43·51
3. As 2, but the methylated alcoholic potash replaced by a solution of potash in 96 per cent. (60 o.p.) alcohol .	41·38
4. As 2, methylated alcoholic potash (the spirit being previously purified by distillation over potash) being used instead of the solution of potash in unpurified spirit	41·45
5. As 2, the methylated alcoholic potash being replaced by a solution of potash in absolute alcohol purified by distillation over potash	41·00
6. A "blank" experiment, employing for distillation the residue resulting from the evaporation of 25 c.c. of the alcoholic potash used in 5, previously neutralised by means of sulphuric acid	1·5 c.c. deci-normal sodium hydroxide was required for the neutralisation of the distillate
7. Ester found in 5 less the amount of ester equivalent to the volume of deci-normal sodium hydroxide used up in the blank experiment	39·69

A few drops of semi-normal alcoholic potash are added, and the liquid allowed to evaporate on the steam-bath.

To the residue is added 10 c.c. of dilute phosphoric acid, prepared by mixing about 3·5 c.c. of 88 per cent. acid with 100 c.c. of carbon dioxide-free distilled water.

The carbon dioxide flask is now immediately attached to the apparatus, and the distillation is commenced.

It should here be noted that the distilled water in the steam generating flask must have been allowed to become entirely free from carbon dioxide by at least half an hour's preliminary boiling.

The whole apparatus must be thoroughly cleansed and freed from air by allowing steam from the generator to blow through for a few minutes before attaching the carbon dioxide flask.

Distillation is allowed to proceed, the water in the generator being kept boiling as quickly as possible, and the volume of liquid in the smaller flask being kept at about 10 c.c. by means of a small flame.

The time taken for the collection of the required 250 c.c. of distillate is usually about thirty minutes.

The distillate is collected in a 500 c.c. Erlenmeyer flask having a mark upon it to indicate the level of 250 c.c. Phenolphthalein solution and a sufficient excess of deci-normal sodium hydroxide solution are added to the distillate and the excess of alkali determined by titration.

The best general method for the detection of added esters, other than those of acetic acid and formic acid, is to separate the acids and identify them.

For this purpose 10 c.c. of oil are saponified for one hour with 20 c.c. of 2/N alcoholic potash. 25 c.c. of water are then added and the bulk of the alcohol evaporated off. The solution is then almost neutralised to phenolphthalein and the unsaponified oil removed by shaking out three times with ether.

The aqueous solution is then made acid to methyl orange, and shaken out with ether.

The ethereal solution will now contain acids such as benzoic, cinnamic, oleic, phthalic and lauric, and these will be obtained in a moderately pure condition by evaporating off the ether.

The aqueous solution will contain the readily water soluble acids such as citric, oxalic and tartaric, etc. This solution should therefore be made just alkaline to phenolphthalein, excess of barium chloride solution added, and the whole warmed for about ten minutes.

A crystalline precipitate of barium salt will be obtained, from which the acid can be readily liberated and identified.

THE DETERMINATION OF ALCOHOLS.

The determination of alcohols in essential oils depends on the conversion of these compounds into their acetic esters, and then carrying out an ester determination as described above.

Ten c.c. of the oil (spike, sandalwood and citronella are typical) are boiled under a reflux condenser for two hours with 20 c.c. of acetic anhydride and 2 grams of anhydrous sodium acetate. After the liquid has cooled, it is diluted with water and allowed to stand in the water-bath for fifteen minutes in order to decompose the excess of acetic anhydride. The liquid is then transferred to a separator and repeatedly washed with brine until the wash water is perfectly neutral in reaction. The last washing may be effected with brine containing a little sodium carbonate when the washings should be alkaline. The oil is then separated and the last traces of water removed by digestion with ignited potassium sulphate for an hour. About 2 to 3 grams, depending on the alcohol content of the acetylated (esterified) oil, are then saponified as described under ester determination care being taken to neutralise the oil before saponification, as traces of free acid always remain in the acetylated oil. The amount of ester in the acetylated oil is easily calculated, but to convert this into the percentage of free alcohol in the original oil requires a more tedious calculation. The following formula can be used for this:—

$$x = \frac{N \times M}{10(W - \cdot 042N)},$$

where x is the percentage of the alcohol in the original oil, M is the molecular weight, and N is the number of c.c. of normal alkali used, and W the weight of the acetylated oil. Here the factor ·042N is on account of the increase of the weight due to acetylation. This formula is only true if the original oil contains no esters. In cases where esters and alcohols occur together the best method is to—

1. Estimate the esters in the original oil by a preliminary saponification of a small quantity.
2. Saponify about 20 grams and separate the resulting oil, which now contains all the alcohols in the free state.
3. Estimate the total alcohols in 2 by the acetylation process.

4. Calculate the total alcohols in the original oils from 3, by allowing for the decrease in weight of 1 when saponified.

5. Deduct the alcohols combined as esters from the total alcohols, which gives the amount of free alcohols.

In these estimations it is necessary to calculate all the esters and all the alcohols to one formula, expressing the result, for instance, as menthyl acetate, although as a matter of fact small quantities of the corresponding propionate and butyrate may also be present, which it is impossible to estimate separately.

Cocking[1] has constructed a simple formula by which the amount of free alcohol may be accurately determined in the presence of any ester or mixture of esters, providing that these are unaffected by acetylation.

The formula is as follows :—

$$\text{Percentage of free alcohol} = \frac{(B - A)Y}{0{\cdot}42016(1335{\cdot}5 - B)}.$$

A = Saponification value of the original oil.

B = Saponification value of the original oil after acetylation (not of saponified oil).

Y = Molecular weight of alcohol if monatomic.

In certain cases the results thus obtained are very nearly scientifically accurate, but in certain cases the alcohol breaks down under the influence of the acetic anhydride and the results are considerably lower than the truth, the variation depending entirely on the conditions of the experiment, which should therefore be kept constant as above recommended. Linalol and terpineol are two cases in point. To meet such cases Boulez[2] has recommended diluting 5 grams of the oil with 25 grams of turpentine, and then boiling with 40 c.c. of acetic anhydride and 3 to 4 grams of pure sodium acetate. A blank experiment to allow for the "alcohol value" of the turpentine must be performed, and the proper deduction made. It is claimed by Boulez that this method yields accurate results, but, although in the case of terpineol the results are fairly good, the process does not give scientifically accurate results.

The following tables have been prepared by Schimmel & Co., who gave permission for them to be reproduced in a previous edition, in order to save calculations. Having determined the saponification value of the oil before or after acetylation, the amounts of esters or alcohols respectively can be calculated. It must be borne in mind that the alcohol values are only strictly accurate when there are no esters present in the oil. Table I. gives the values for alcohols of the formula $C_{10}H_{18}O$ and $C_{10}H_{20}O$ (geraniol and citronellol) and their acetic esters. Table II. gives the corresponding values for the alcohols $C_{15}H_{24}O$ and $C_{15}H_{26}O$. Table III. gives the ester values for geranyl tiglinate.

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[1] *P. and E.O.R.*, **1918**, 37.

[2] *Bull. Soc. Chim.*, iv. (**1907**), i. 117.

TABLE I.

$C_{10}H_{18}O$.				$C_{10}H_{20}O$.			
Sap. Figure.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Sap. Figure.
1	0·35	0·28	0·27	0·35	0·28	0·28	1
2	0·70	0·55	0·55	0·71	0·56	0·56	2
3	1·05	0·83	0·83	1·06	0·84	0·84	3
4	1·40	1·10	1·10	1·41	1·11	1·12	4
5	1·75	1·38	1·38	1·77	1·39	1·40	5
6	2·10	1·65	1·66	2·12	1·67	1·68	6
7	2·45	1·93	1·94	2·47	1·95	1·96	7
8	2·80	2·20	2·21	2·83	2·23	2·24	8
9	3·15	2·48	2·49	3·18	2·51	2·52	9
10	3·50	2·75	2·77	3·54	2·79	2·81	10
11	3·85	3·03	3·05	3·89	3·06	3·09	11
12	4·20	3·30	3·33	4·24	3·34	3·37	12
13	4·55	3·58	3·61	4·60	3·62	3·66	13
14	4·90	3·85	3·89	4·95	3·90	3·94	14
15	5·25	4·13	4·17	5·30	4·18	4·23	15
16	5·60	4·40	4·45	5·66	4·46	4·51	16
17	5·95	4·68	4·74	6·01	4·74	4·80	17
18	6·30	4·95	5·02	6·36	5·01	5·08	18
19	6·65	5·23	5·30	6·72	5·29	5·37	19
20	7·00	5·50	5·58	7·07	5·57	5·66	20
21	7·35	5·78	5·87	7·42	5·85	5·94	21
22	7·70	6·05	6·15	7·78	6·13	6·23	22
23	8·05	6·33	6·44	8·13	6·41	6·52	23
24	8·40	6·60	6·72	8·49	6·69	6·81	24
25	8·75	6·88	7·01	8·84	6·96	7·10	25
26	9·10	7·15	7·29	9·19	7·24	7·39	26
27	9·45	7·43	7·58	9·55	7·52	7·68	27
28	9·80	7·70	7·87	9·90	7·80	7·97	28
29	10·15	7·98	8·15	10·25	8·08	8·26	29
30	10·50	8·25	8·44	10·61	8·36	8·55	30
31	10·85	8·53	8·73	10·96	8·64	8·84	31
32	11·20	8·80	9·02	11·31	8·91	9·13	32
33	11·55	9·08	9·31	11·67	9·19	9·43	33
34	11·90	9·35	9·59	12·02	9·47	9·72	34
35	12·25	9·63	9·88	12·37	9·75	10·01	35
36	12·60	9·90	10·17	12·73	10·03	10·31	36
37	12·95	10·18	10·47	13·08	10·31	10·60	37
38	13·30	10·45	10·76	13·44	10·59	10·90	38
39	13·65	10·73	11·05	13·79	10·86	11·19	39
40	14·00	11·00	11·34	14·14	11·14	11·49	40
41	14·35	11·28	11·63	14·50	11·42	11·78	41
42	14·70	11·55	11·93	14·85	11·70	12·08	42
43	15·05	11·83	12·22	15·20	11·98	12·38	43
44	15·40	12·10	12·51	15·56	12·26	12·68	44
45	15·75	12·38	12·81	15·91	12·54	12·97	45
46	16·10	12·65	13·10	16·26	12·81	13·27	46
47	16·45	12·93	13·40	16·62	13·09	13·57	47
48	16·80	13·20	13·69	16·97	13·37	13·87	48
49	17·15	13·48	13·99	17·32	13·65	14·17	49
50	17·50	13·75	14·29	17·68	13·93	14·47	50

TABLE I. (*continued*).

$C_{10}H_{18}O$.				$C_{10}H_{20}O$.			
Sap. Figure.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Sap. Figure.
51	17·85	14·03	14·58	18·03	14·21	14·77	51
52	18·20	14·30	14·88	18·39	14·49	15·07	52
53	18·55	14·58	15·18	18·74	14·76	15·38	53
54	18·90	14·85	15·48	19·09	15·04	15·68	54
55	19·25	15·13	15·77	19·45	15·32	15·98	55
56	19·60	15·40	16·07	19·80	15·60	16·28	56
57	19·95	15·68	16·38	20·15	15·88	16·59	57
58	20·30	15·95	16·68	20·51	16·16	16·89	58
59	20·65	16·23	16·98	20·86	16·44	17·20	59
60	21·00	16·50	17·28	21·21	16·71	17·50	60
61	21·35	16·78	17·58	21·57	16·99	17·81	61
62	21·70	17·05	17·88	21·92	17·27	18·11	62
63	22·05	17·33	18·18	22·27	17·55	18·42	63
64	22·40	17·60	18·49	22·63	17·83	18·73	64
65	22·75	17·88	18·79	22·98	18·11	19·04	65
66	23·10	18·15	19·10	23·34	18·39	19·34	66
67	23·45	18·43	19·40	23·69	18·66	19·65	67
68	23·80	18·70	19·70	24·04	18·94	19·96	68
69	24·15	18·98	20·01	24·40	19·22	20·27	69
70	24·50	19·25	20·32	24·75	19·50	20·58	70
71	24·85	19·53	20·62	25·10	19·78	20·89	71
72	25·20	19·80	20·93	25·46	20·06	21·20	72
73	25·55	20·08	21·24	25·81	20·34	21·51	73
74	25·90	20·35	21·55	26·16	20·61	21·83	74
75	26·25	20·63	21·85	26·52	20·89	22·14	75
76	26·60	20·90	22·16	26·87	21·17	22·45	76
77	26·95	21·18	22·47	27·22	21·45	22·77	77
78	27·30	21·45	22·78	27·58	21·73	23·08	78
79	27·65	21·73	23·09	27·93	22·01	23·39	79
80	28·00	22·00	23·40	28·29	22·29	23·71	80
81	28·35	22·28	23·72	28·64	22·56	24·02	81
82	28·70	22·55	24·03	28·99	22·84	24·34	82
83	29·05	22·83	24·34	29·35	23·12	24·66	83
84	29·40	23·10	24·65	29·70	23·40	24·97	84
85	29·75	23·38	24·97	30·05	23·68	25·29	85
86	30·10	23·65	25·28	30·41	23·96	25·61	86
87	30·45	23·93	25·60	30·76	24·24	25·93	87
88	30·80	24·20	25·91	31·11	24·51	26·25	88
89	31·15	24·48	26·23	31·47	24·79	26·57	89
90	31·50	24·75	26·54	31·82	25·07	26·89	90
91	31·85	25·03	26·86	32·17	25·35	27·21	91
92	32·20	25·30	27·18	32·53	25·63	27·53	92
93	32·55	25·58	27·49	32·88	25·91	27·85	93
94	32·90	25·85	27·81	33·24	26·19	28·17	94
95	33·25	26·13	28·13	33·59	26·46	28·49	95
96	33·60	26·40	28·45	33·94	26·74	28·82	96
97	33·95	26·68	28·77	34·30	27·02	29·14	97
98	34·30	26·95	29·09	34·65	27·30	29·47	98
99	34·65	27·23	29·41	35·00	27·58	29·79	99
100	35·00	27·50	29·73	35·36	27·86	30·11	100

TABLE I. (*continued*).

	$C_{10}H_{18}O$.			$C_{10}H_{20}O$.			
Sap. Figure.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Sap. Figure.
101	35·35	27·78	30·05	35·71	28·14	30·44	101
102	35·70	28·05	30·37	36·06	28·41	30·77	102
103	36·05	28·33	30·70	36·42	28·69	31·09	103
104	36·40	28·60	31·02	36·77	28·97	31·42	104
105	36·75	28·88	31·34	37·12	29·25	31·75	105
106	37·10	29·15	31·67	37·48	29·53	32·08	106
107	37·45	29·43	31·99	37·83	29·81	32·41	107
108	37·80	29·70	32·32	38·19	30·09	32·74	108
109	38·15	29·98	32·64	38·54	30·36	33·07	109
110	38·50	30·25	32·97	38·89	30·64	33·40	110
111	38·85	30·53	33·30	39·25	30·92	33·73	111
112	39·20	30·80	33·62	39·60	31·20	34·06	112
113	39·55	31·08	33·95	39·95	31·48	34·39	113
114	39·90	31·35	34·28	40·31	31·76	34·73	114
115	40·25	31·63	34·61	40·66	32·04	35·06	115
116	40·60	31·90	34·94	41·01	32·31	35·39	116
117	40·95	32·18	35·27	41·37	32·59	35·73	117
118	41·30	32·45	35·60	41·72	32·87	36·06	118
119	41·65	32·73	35·93	42·07	33·15	36·40	119
120	42·00	33·00	36·26	42·43	33·43	36·73	120
121	42·35	33·28	36·60	42·78	33·71	37·07	121
122	42·70	33·55	36·93	43·14	33·99	37·41	122
123	43·05	33·83	37·26	43·39	34·26	37·75	123
124	43·40	34·10	37·60	43·84	34·54	38·08	124
125	43·75	34·38	37·93	44·20	34·82	38·42	125
126	44·10	34·65	38·27	44·55	35·10	38·76	126
127	44·45	34·93	38·60	44·90	35·38	39·10	127
128	44·80	35·20	38·94	45·26	35·66	39·44	128
129	45·15	35·48	39·27	45·61	35·94	39·78	129
130	45·50	35·75	39·61	45·96	36·21	40·13	130
131	45·85	36·03	39·95	46·32	36·49	40·47	131
132	46·20	36·30	40·29	46·67	36·77	40·81	132
133	46·55	36·58	40·63	47·02	37·05	41·16	133
134	46·90	36·85	40·97	47·38	37·33	41·50	134
135	47·25	37·13	41·31	47·73	37·61	41·84	135
136	47·60	37·40	41·65	48·09	37·89	42·19	136
137	47·95	37·68	41·99	48·44	38·16	42·53	137
138	48·30	37·95	42·33	48·79	38·44	42·88	138
139	48·65	38·23	42·67	49·15	38·72	43·23	139
140	49·00	38·50	43·02	49·50	39·00	43·58	140
141	49·35	38·78	43·36	49·85	39·28	43·92	141
142	49·70	39·05	43·71	50·21	39·56	44·27	142
143	50·05	39·33	44·05	50·56	39·84	44·62	143
144	50·40	39·60	44·39	50·91	40·11	44·97	144
145	50·75	39·88	44·74	51·27	40·39	45·32	145
146	51·10	40·15	45·09	51·62	40·67	45·67	146
147	51·45	40·43	45·44	51·97	40·95	46·02	147
148	51·80	40·70	45·78	52·33	41·23	46·38	148
149	52·15	40·98	46·13	52·68	41·51	46·73	149
150	52·50	41·25	46·48	53·04	41·79	47·08	150

TABLE I. (*continued*).

$C_{10}H_{18}O$.				$C_{10}H_{20}O$.			
Sap. Figure.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Sap. Figure.
151	52·85	41·53	46·83	53·39	42·06	47·44	151
152	53·20	41·80	47·18	53·74	42·34	47·79	152
153	53·55	42·08	47·53	54·10	42·62	48·15	153
154	53·90	42·35	47·88	54·45	42·90	48·50	154
155	54·25	42·63	48·23	54·80	43·18	48·86	155
156	54·60	42·90	48·58	55·16	43·46	49·21	156
157	54·95	43·18	48·94	55·51	43·74	49·57	157
158	55·30	43·45	49·29	55·86	44·01	49·93	158
159	55·65	43·73	49·65	56·22	44·29	50·29	159
160	56·00	44·00	50·00	56·57	44·57	50·65	160
161	56·35	44·28	50·36	56·92	44·85	51·01	161
162	56·70	44·55	50·71	57·28	45·13	51·37	162
163	57·05	44·83	51·07	57·63	45·41	51·73	163
164	57·40	45·10	51·42	57·99	45·69	52·09	164
165	57·75	45·38	51·78	58·34	45·96	52·46	165
166	58·10	45·65	52·14	58·69	46·24	52·82	166
167	58·45	45·93	52·50	59·05	46·52	53·18	167
168	58·80	46·20	52·86	59·40	46·80	53·55	168
169	59·15	46·48	53·22	59·75	47·08	53·91	169
170	59·50	46·75	53·58	60·11	47·36	54·28	170
171	59·85	47·03	53·94	60·46	47·64	54·64	171
172	60·20	47·30	54·31	60·81	47·91	55·01	172
173	60·55	47·58	54·67	61·17	48·19	55·38	173
174	60·90	47·85	55·03	61·52	48·47	55·75	174
175	61·25	48·13	55·40	61·87	48·75	56·12	175
176	61·60	48·40	55·76	62·23	49·03	56·48	176
177	61·95	48·68	56·13	62·58	49·31	56·85	177
178	62·30	48·95	56·49	62·94	49·59	57·23	178
179	62·65	49·23	56·86	63·29	49·86	57·60	179
180	63·00	49·50	57·22	63·64	50·14	57·97	180
181	63·35	49·78	57·59	64·00	50·42	58·34	181
182	63·70	50·05	57·96	64·35	50·70	58·71	182
183	64·05	50·33	58·33	64·70	50·98	59·09	183
184	64·40	50·60	58·70	65·06	51·26	59·46	184
185	64·75	50·88	59·07	65·41	51·54	59·84	185
186	65·10	51·15	59·44	65·76	51·81	60·21	186
187	65·45	51·43	59·81	66·12	52·09	60·59	187
188	65·80	51·70	60·19	66·47	52·37	60·97	188
189	66·15	51·98	60·56	66·82	52·65	61·35	189
190	66·50	52·25	60·93	67·18	52·93	61·72	190
191	66·85	52·53	61·31	67·53	53·21	62·10	191
192	67·20	52·80	61·68	67·89	53·49	62·48	192
193	67·55	53·08	62·06	68·24	53·76	62·86	193
194	67·90	53·35	62·43	68·59	54·04	63·24	194
195	68·25	53·63	62·81	68·95	54·32	63·63	195
196	68·60	53·90	63·19	69·30	54·60	64·01	196
197	68·95	54·18	63·57	69·65	54·88	64·39	197
198	69·30	54·45	63·95	70·01	55·16	64·78	198
199	69·65	54·73	64·33	70·36	55·44	65·16	199
200	70·00	55·00	64·71	70·71	55·71	65·55	200

TABLE I. (*continued*).

$C_{10}H_{18}O$.				$C_{10}H_{20}O$.			
Sap. Figure.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Sap. Figure.
201	70·35	55·28	65·09	71·07	55·99	65·93	201
202	70·70	55·55	65·47	71·42	56·27	66·32	202
203	71·05	55·83	65·85	71·77	56·55	66·71	203
204	71·40	56·10	66·23	72·13	56·83	67·09	204
205	71·75	56·38	66·62	72·48	57·11	67·48	205
206	72·10	56·65	67·00	72·84	57·39	67·87	206
207	72·45	56·93	67·39	73·19	57·66	68·26	207
208	72·80	57·20	67·77	73·54	57·94	68·65	208
209	73·15	57·48	68·16	73·90	58·22	69·04	209
210	73·50	57·75	68·55	74·25	58 50	69·44	210
211	73·85	58·03	68·93	74·60	58·78	69·83	211
212	74·20	58·30	69·32	74·96	59·06	70·22	212
213	74·55	58·58	69·71	75·31	59·34	70·62	213
214	74·90	58·85	70·10	75·66	59·61	71·01	214
215	75·25	59·13	70·49	76·02	59·89	71·41	215
216	75·60	59·40	70·88	76·37	60·17	71·80	216
217	75·95	59·68	71·28	76·72	60·45	72·20	217
218	76·30	59·95	71·67	77·08	60·73	72·60	218
219	76·65	60·23	72·06	77·43	61·01	73·00	219
220	77·00	60·50	72·45	77·79	61·29	73·40	220
221	77·35	60 78	72·85	78·14	61·56	73·80	221
222	77·70	61·05	73·25	78·49	61·84	74·20	222
223	78·05	61·33	73·64	78·85	62·12	74·60	223
224	78·40	61·60	74·04	79·20	62·40	75·00	224
225	78·75	61·88	74·44	79·55	62·68	75·40	225
226	79·10	62·15	74·84	79·91	62·96	75·81	226
227	79·45	62·43	75·23	80·26	63·24	76·21	227
228	79·80	62·70	75·63	80·61	63·51	76·62	228
229	80·15	62·98	76·03	80·97	63·79	77·02	229
230	80·50	63·25	76·44	81·32	64·07	77·43	230
231	80·85	63·53	76·84	81·67	64·35	77·83	231
232	81·20	63·80	77·24	82·03	64·63	78·24	232
233	81·55	64·08	77·64	82·38	64·91	78·65	233
234	81·90	64·35	78·05	82·74	65·19	79·06	234
235	82·25	64·63	78·45	83·09	65·46	79·47	235
236	82·60	64 90	78·86	83·44	65·74	79·88	236
237	82·95	65·18	79·27	83·80	66·02	80·29	237
238	83·30	65·45	79·67	84·15	66·30	80·71	238
239	83·65	65·73	80·08	84·50	66·58	81·12	239
240	84·00	66·00	80·49	84·86	66·86	81·53	240
241	34·35	66·28	80·90	85·21	67·14	81·95	241
242	84·70	66·55	81·31	85·56	67·41	82·36	242
243	85·05	66·83	81·72	85·92	67·69	82·78	243
244	85·40	67·10	82·13	86·27	67·97	83·20	244
245	85·75	67·38	82·54	86·62	68·25	83·61	245
246	86·10	67·65	82·96	86 98	68·53	84·03	246
247	86·45	67·93	83·37	87·33	68·81	84·45	247
248	86·80	68·20	83·78	87·69	69·09	84·87	248
249	87·15	68 48	84·20	88·04	69·36	85·29	249
250	87·50	68·75	84·62	88·39	69·64	85·71	250

TABLE I. (*continued*).

$C_{10}H_{18}O$.				$C_{10}H_{20}O$.			
Sap. Figure.	Acetate	Alcohol.	Alcohol in the Orig. Oil.	Acetate.	Alcohol.	Alcohol in the Orig. Oil.	Sap. Figure.
251	87·85	69·03	85·03	88·75	69·92	86·14	251
252	88·20	69·30	85·45	89·10	70·20	86·56	252
253	88·55	69·58	85·87	89·45	70·48	86·98	253
254	88·90	69·85	86·29	89·81	70·76	87·41	254
255	89·25	70·13	86·71	90·16	71·04	87·83	255
256	89·60	70·40	87·13	90·51	71·31	88·26	256
257	89·95	70·68	87·55	90·87	71·59	88·69	257
258	90·30	70 95	87·97	91·22	71·87	89·11	258
259	90·65	71·23	88·40	91·57	72·15	89·54	259
260	91·00	71·50	88·82	91·93	72·43	89·97	260
261	91·35	71·78	89·25	92·28	72·71	90·40	261
262	91·70	72·05	89·67	92·64	72·99	90·83	262
263	92·05	72·33	90·10	92·99	73·26	91·27	263
264	92·40	72·60	90·52	93·34	73·54	91·70	264
265	92·75	72·88	90·95	93·70	73·82	92·13	265
266	93·10	73·15	91·38	94·05	74·10	92·57	266
267	93·45	73·43	91·81	94·40	74·38	93·00	267
268	93·80	73·70	92·24	94 76	74·66	93·44	268
269	94·15	73·98	92·67	95·11	74·94	93·87	269
270	94·50	74·25	93·10	95·46	75·21	94·31	270
271	94·85	74·53	93·54	95·82	75·49	94·75	271
272	95·20	74·80	93·97	96·17	75·77	95·19	272
273	95·55	75·08	94·40	96·52	76·05	95·63	273
274	95·90	75·35	94·84	96·88	76·33	96·07	274
275	96·25	75·63	95·28	97·23	76·61	96·51	275
276	96·60	75·90	95·71	97·59	76·89	96·96	276
277	96·95	76·18	96·15	97·94	77·16	97·40	277
278	97·30	76·45	96·59	98·29	77·44	97·84	278
279	97·65	76·73	97·03	98·65	77·72	98·29	279
280	98·00	77·00	97·47	99·00	78·00	98·73	280
281	98·35	77·28	97·91	99·35	78·28	99·18	281
282	98·70	77·55	98·35	99·71	78·56	99·63	282
283	99·05	77·83	98·80	100·06	78·84	100·08	283
284	99·40	78·10	99·24				
285	99·75	78·38	99·68				
286	100·10	78·65	100·13				

TABLE II.

$C_{15}H_{24}O$.				$C_{15}H_{26}O$.			
Ester Number.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent. Alcohol in the Original Oil.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent. Alcohol in the Original Oil.	Ester Number.
1	0·47	0·39	0·39	0·47	0·40	0·40	1
2	0·94	0·79	0·79	0·94	0·79	0·79	2
3	1·40	1·18	1·18	1·41	1·19	1·19	3
4	1·87	1·57	1·58	1·89	1·59	1·59	4
5	2·34	1·96	1·97	2·36	1·98	1·99	5
6	2·81	2·36	2·37	2·83	2·38	2·39	6
7	3·28	2·75	2·76	3·30	2·78	2·79	7
8	3·74	3·14	3·16	3·77	3·17	3·19	8
9	4·21	3·53	3·56	4·24	3·57	3·59	9
10	4·68	3·93	3·96	4·71	3·96	3·99	10
11	5·15	4·32	4·36	5·19	4·36	4·40	11
12	5·61	4·71	4·76	5·66	4·76	4·80	12
13	6·08	5·11	5·16	6·13	5·15	5·20	13
14	6·55	5·50	5·56	6·60	5·55	5·61	14
15	7·02	5·89	5·96	7·07	5·95	6·01	15
16	7·49	6·29	6·36	7·54	6·34	6·42	16
17	7·95	6·68	6·77	8·01	6·74	6·83	17
18	8·42	7·07	7·17	8·49	7·14	7·23	18
19	8·89	7·46	7·57	8·96	7·53	7·64	19
20	9·36	7·86	7·98	9·43	7·93	8·05	20
21	9·83	8·25	8·38	9·90	8·33	8·46	21
22	10·29	8·64	8·79	10·37	8·72	8·87	22
23	10·76	9·03	9·19	10·84	9·12	9·28	23
24	11·23	9·42	9·60	11·31	9·51	9·69	24
25	11·70	9·82	10·01	11·79	9·91	10·10	25
26	12·16	10·21	10·42	12·26	10·30	10·51	26
27	12·63	10·60	10·83	12·73	10·70	10·92	27
28	13·10	11·00	11·24	13·20	11·10	11·34	28
29	13·57	11·39	11·65	13·67	11·49	11·75	29
30	14·04	11·79	12·06	14·14	11·89	12·17	30
31	14·51	12·18	12·47	14·61	12·28	12·58	31
32	14·98	12·57	12·88	15·08	12·68	13·00	32
33	15·45	12·96	13·29	15·55	13·08	13·41	33
34	15·91	13·35	13·71	16·02	13·48	13·83	34
35	16·38	13·75	14·12	16·50	13·88	14·25	35
36	16·85	14·14	14·54	16·97	14·27	14·67	36
37	17·32	14·54	14·95	17·44	14·76	15·09	37
38	17·79	14·93	15·37	17·91	15·06	15·51	38
39	18·25	15·32	15·78	18·38	15·46	15·93	39
40	18·71	15·71	16·20	18·86	15·86	16·35	40
41	19·18	16·10	16·62	19·33	16·25	16·77	41
42	19·65	16·50	17·04	19·80	16·65	17·19	42
43	20·12	16·89	17·46	20·27	17·05	17·61	43
44	20·59	17·28	17·88	20·74	17·44	18·04	44
45	21·05	17·68	18·30	21·21	17·84	18·46	45
46	21·52	18·07	18·72	21·69	18·24	18·89	46
47	21·99	18·46	19·14	22·16	18·63	19·32	47
48	22·46	18·85	19·56	22·63	19·03	19·74	48
49	22·93	19·25	19·98	23·10	19·82	20·17	49
50	23·39	19·64	20·41	23·57	19·43	20·59	50

TABLE II. (*continued*).

$C_{15}H_{24}O$.				$C_{15}H_{26}O$.			
Ester Number.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent. Alcohol in the Original Oil.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent. Alcohol in the Original Oil.	Ester Number.
51	23·86	20·03	20·83	24·04	20·22	21·02	51
52	24·33	20·42	21·26	24·51	20·62	21·45	52
53	24·80	20·82	21·68	24·99	21·01	21·88	53
54	25·26	21·21	22·11	25·46	21·41	22·31	54
55	25·73	21·60	22·54	25·93	21·81	22·74	55
56	26·20	22·00	22·96	26·40	22·20	23·17	56
57	26·67	22·39	23·39	26·87	22·60	23·61	57
58	27·14	22·78	23·82	27·34	23·00	24·04	58
59	27·61	23·17	24·25	27·81	23·39	24·47	59
60	28·07	23·57	24·68	28·29	23·79	24·91	60
61	28·54	23·96	25·11	28·76	24·19	25·34	61
62	29·01	24·35	25·54	29·23	24·58	25·77	62
63	29·48	24·75	25·97	29·70	24·98	26·21	63
64	29·95	25·14	26·41	30·17	25·38	26·65	64
65	30·41	25·53	26·84	30·64	25·77	27·09	65
66	30·88	25·93	27·27	31·11	26·17	27·53	66
67	31·35	26·32	27·71	31·59	26·57	27·97	67
68	31·81	26·71	28·14	32·06	26·96	28·41	68
69	32·28	27·10	28·58	32·53	27·35	28·85	69
70	32·75	27·50	29·02	33·00	27·75	29·29	70
71	33·22	27·89	29·46	33·47	28·15	29·73	71
72	33·69	28 28	29·90	33·94	28·54	30·17	72
73	34·15	28·67	30·34	34·41	28·94	30·61	73
74	34·62	29·07	30·78	34·89	29·34	31·06	74
75	35·09	29·46	31·22	35·36	29·73	31·50	75
76	35·56	29·85	31·66	35·83	30·13	31·95	76
77	36·03	30·25	32·10	36·30	30·53	32·40	77
78	36·49	30·64	32·54	36·77	30·92	32·84	78
79	36·96	31·03	32·98	37·24	31·31	33·29	79
80	37·43	31·43	33·43	37·71	31·71	33·74	80
81	37 90	31·82	33·87	38·19	32·11	34·19	81
82	38·37	32·21	34·32	38·66	32·50	34·64	82
83	38·84	32·60	34·77	39·13	32·90	35·09	83
84	39·30	33·00	35·22	39·60	33·30	35·54	84
85	39·77	33·39	35·66	40·07	33·69	35·99	85
86	40·24	33·78	36·11	40·54	34·09	36·44	86
87	40·70	34·18	36·56	41·01	34·49	36·90	87
88	41·17	34·57	37·01	41·49	34·88	37·35	88
89	41·64	34·96	37·46	41·96	35·28	37·80	89
90	42·11	35·36	37·92	42·43	35·68	38·26	90
91	42·57	35·75	38·37	42 90	36·08	38·71	91
92	43·04	36·14	38·82	43·37	36·47	39·17	92
93	43·51	36·53	39·27	43·84	36·87	39·63	93
94	43·98	36·92	39·73	44·31	37·26	40·09	94
95	44·45	37·32	40·18	44·79	37·66	40·55	95
96	44·92	37·71	40·64	45·26	38·05	41·01	96
97	45·39	38·10	41·10	45·73	38·45	41·47	97
98	45·85	38·50	41·55	46·20	38·85	41·93	98
99	46·32	38·89	42·01	46·67	39·24	42·39	99
100	46·79	39·29	42·47	47·14	39·64	42·86	100

TABLE II. (*continued*).

	$C_{15}H_{24}O$.			$C_{15}H_{26}O$.			
Ester Number.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent Alcohol in the Original Oil.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent. Alcohol in the Original Oil.	Ester Number.
101	47·26	39·68	42·93	47·61	40·04	43·32	101
102	47·72	40·07	43·39	48·09	40·43	43·78	102
103	48·19	40·46	43·85	48·56	40·83	44·24	103
104	48·66	40·85	44·32	49·03	41·23	44·71	104
105	49·13	41·25	44·78	49·50	41·63	45·18	105
106	49·59	41·64	45·24	49·97	42·02	45·65	106
107	50·06	42·04	45·70	50·44	42·42	46·12	107
108	50·53	42·43	46·16	50·91	42·81	46·59	108
109	51·00	42·82	46·63	51·39	43·21	47·06	109
110	51·46	43·21	47·10	51·86	43·61	47·53	110
111	51·93	43·60	47·57	52·33	44·00	48·00	111
112	52·40	44·00	48·04	52·80	44·40	48·47	112
113	52·87	44·39	48·50	53·27	44·80	48·94	113
114	53·34	44·78	48·97	53·74	45·19	49·42	114
115	53·81	45·17	49·44	54·21	45·59	49·89	115
116	54·28	45·57	49·91	54·69	45·99	50·36	116
117	54·74	45·96	50·39	55·16	46·38	50·84	117
118	55·21	46·35	50·86	55·63	46·78	51·32	118
119	55·68	46·74	51·33	56·10	47·18	51·80	119
120	56·14	47·14	51·81	56·57	47·57	52·28	120
121	56·61	47·53	52·28	57·04	47·97	52·76	121
122	57·08	47·92	52·76	57·51	48·36	53·24	122
123	57·55	48·32	53·23	57·99	48·76	53·72	123
124	58·01	48·71	53·71	58·46	49·16	54·20	124
125	58·48	49·10	54·18	58·93	49·55	54·68	125
126	58·95	49·50	54·66	59·40	49·95	55·17	126
127	59·42	49·89	55·14	59·87	50·35	55·65	127
128	59·89	50·28	55·62	60·34	50·74	56·13	128
129	60·36	50·67	56·11	60·81	51·14	56·62	129
130	60·82	51·07	56·59	61·28	51·54	57·10	130
131	61·29	51·46	57·07	61·75	51·93	57·59	131
132	61·76	51·85	57·55	62·22	52·33	58·08	132
133	62·23	52·25	58·03	62·70	52·73	58·57	133
134	62·70	52·64	58·52	63·17	53·12	59·06	134
135	63·16	53·03	59·00	63·64	53·52	59·55	135
136	63·63	53·42	59·49	64·11	53·92	60·04	136
137	64·10	53·82	59·98	64·59	54·31	60·53	137
138	64·57	54·21	60·47	65·06	54·71	61·02	138
139	65·04	54·60	60·96	65·53	55·11	61·51	139
140	65·50	55·00	61·45	66·00	55·50	62·01	140
141	65·97	55·39	61·94	66·47	55·90	62·50	141
142	66·44	55·78	62·43	66·94	56·30	63·00	142
143	66·90	56·18	62·93	67·41	56·69	63·50	143
144	67·37	56·57	63·42	67·89	57·09	64·00	144
145	67·84	56·96	63·92	68·36	57·49	64·50	145
146	68·31	57·35	64·41	68·83	57·88	65·00	146
147	68·78	57·75	64·91	69·30	58·28	65·50	147
148	69·25	58·14	65·40	69·77	58·68	66·00	148
149	69·72	58·53	65·90	70·24	59·07	66·50	149
150	70·18	58·93	66·40	70·71	59·46	67·00	150

TABLE II. (*continued*).

	$C_{15}H_{24}O$.			$C_{15}H_{26}O$			
Ester Number.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent. Alcohol in the Original Oil.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent. Alcohol in the Original Oil.	Ester Number.
151	70·65	59·32	66·90	71·19	59·86	67·51	151
152	71·12	59·71	67·40	71·66	60·26	68·01	152
153	71·58	60·10	67·90	72·13	60·65	68·52	153
154	72·05	60·50	68·40	72·60	61·05	69·02	154
155	72·52	60·89	68·90	73·07	61·45	69·53	155
156	72·99	61·28	69·41	73·54	61·84	70·04	156
157	73·46	61·68	69·91	74·01	62·24	70·55	157
158	73·92	62·07	70·42	74·49	62·64	71·06	158
159	74·39	62·46	70·29	74·96	63·03	71·57	159
160	74·86	62·86	71·43	75·43	63·43	72·08	160
161	75·33	63·25	71·93	75·90	63·83	72·59	161
162	75·80	63·64	72·44	76·37	64·22	73·10	162
163	76·26	64·03	72·95	76·84	64·62	73·62	163
164	76·73	64·42	73·46	77·31	65·02	74·13	164
165	77·20	64·82	73·97	77·78	65·41	74·65	165
166	77·67	65·21	74·49	78·26	65·81	75·16	166
167	78·14	65·60	75·00	78·73	66·21	75·68	167
168	78·60	66·00	75·52	79·20	66·60	76·20	168
169	79·07	66·39	76·03	79·67	67·00	76·72	169
170	79·54	66·79	76·55	80·14	67·39	77·24	170
171	80·01	67·18	77·06	80·61	67·79	77·76	171
172	80·48	67·57	77·58	81·03	68·19	78·28	172
173	80·94	67·96	78·10	81·56	68·58	78·81	173
174	81·41	68·35	78·62	82·03	68·98	79·33	174
175	81·88	68·75	79·14	82·50	69·38	79·85	175
176	82·35	69·14	79·66	82·97	69·77	80·38	176
177	82·81	69·54	80·18	83·44	70·17	80·91	177
178	83·28	69·93	80·70	83·91	70·57	81·43	178
179	83·75	70·32	81·23	84·38	70·96	81·96	179
180	84·21	70·71	81·75	84·86	71·36	82·49	180
181	84·68	71·10	82·28	85·33	71·76	83·02	181
182	85·15	71·50	82·80	85·80	72·15	83·55	182
183	85·62	71·89	83·33	86·27	72·55	84·09	183
184	86·09	72·28	83·86	86·74	72·95	84·62	184
185	86·56	72·68	84·39	87·21	73·34	85·15	185
186	87·03	73·07	84·92	87·68	73·74	85·69	186
187	87·49	73·46	85·45	88·16	74·14	86·22	187
188	87·96	73·86	85·98	88·63	74·53	86·76	188
189	88·43	74·25	86·51	89·10	74·93	87·30	189
190	88·89	74·64	87·05	89·57	75·32	87·84	190
191	89·36	75·03	87·58	90·04	75·72	88·38	191
192	89·83	75·42	88·12	90·51	76·12	88·92	192
193	90·30	75·82	88 65	90·98	76·51	89·46	193
194	90·77	76·21	89·19	91·46	76·91	90·09	194
195	91·24	76·60	89·73	91·93	77·31	90·54	195
196	91·70	77·00	90·27	92·40	77·70	91·09	196
197	92·17	77·39	90·81	92·87	78·10	91·64	197
198	92·64	77·78	91·35	93·34	78·50	92·18	198
199	93·11	78·17	91·89	93·81	78·89	92·73	199
200	93·57	78·57	92·44	94·28	79·29	93·28	200

TABLE II. (*continued*).

$C_{15}H_{24}O$				$C_{15}H_{26}O$.			
Ester Number.	Per Cent. Acetate.	Per Cent. Alcohol.	Per Cent. Alcohol in the Original Oil	Per Cent. Acetate.	Per Cent. Alcohol	Per Cent. Alcohol in the Original Oil.	Ester Number.
201	94·04	78·96	92·98	94·76	79·68	93·83	201
202	94·51	79·35	93·53	95·23	80·08	94·38	202
203	94·98	79·75	94·07	95·70	80·48	94·93	203
204	95·44	80·14	94·62	96·17	80·87	95·48	204
205	95·91	80·53	95·17	96·64	81·26	96·03	205
206	96·38	80·92	95·72	97·11	81·66	96·59	206
207	96·85	81·32	96·27	97·58	82·06	97·14	207
208	97·32	81·71	96·82	98·05	82·45	97·70	208
209	97·79	82·10	97·37	98·52	82·85	98·25	209
210	98·25	82·50	97·92	99·00	83·25	98·81	210
211	98·72	82·89	98·48	99·47	83·64	99·37	211
212	99·19	83·28	99·03	99·94	84·04	99·93	212
213	99·66	83·67	99·59	100·41	84·44	100·49	213
214	100·12	84·07	100·14				214

TABLE III.—GERANYL TIGLINATE: $C_4H_7CO_2C_{10}H_{17}$.

Ester Number	Per Cent. Ester	Ester Number	Per Cent Ester.	Ester Number.	Per Cent. Ester.	Ester Number.	Per Cent. Ester	Ester Number.	Per Cent Ester.
1	0·42	21	8·85	41	17·28	61	25·71	81	34·13
2	0·84	22	9·27	42	17·70	62	26·13	82	34·55
3	1·26	23	9·69	43	18·12	63	26·55	83	34·98
4	1·69	24	10·11	44	18·54	64	26·97	84	35·40
5	2·11	25	10·54	45	18·96	65	27·39	85	35·82
6	2·53	26	10·96	46	19·38	66	27·81	86	36·24
7	2·95	27	11·38	47	19·80	67	28·23	87	36·66
8	3·37	28	11·80	48	20·23	68	28·65	88	37·09
9	3·79	29	12·22	49	20·65	69	29·08	89	37·51
10	4·21	30	12·64	50	21·07	70	29·50	90	37·93
11	4·63	31	13·06	51	21·49	71	29·92	91	38·35
12	5·05	32	13·49	52	21·91	72	30·34	92	38·77
13	5·47	33	13·91	53	22·33	73	30·76	93	39·19
14	5·90	34	14·33	54	22·75	74	31·18	94	39·62
15	6·32	35	14·75	55	23·18	75	31·61	95	40·04
16	6·74	36	15·17	56	23·60	76	32·03	96	40·46
17	7·16	37	15·59	57	24·02	77	32·45	97	40·88
18	7·58	38	16·01	58	24·44	78	32·87	98	41·30
19	8·01	39	16·44	59	24·87	79	33·29	99	41·72
20	8·43	40	16·86	60	25·29	80	33·71	100	42·14

The importance of strictly adhering to the conditions above set out in the acetylation process has been emphasised by several analysts. According to Durrans[1] the anhydrous sodium acetate acts rather as a

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[1] *P. and E.O.R.*, **1912**, 123.

dehydrating agent than a catalytic agent, since increasing the proportion results in higher values for the alcohol percentage. This was confirmed by Umney and Bennett,[1] who showed that with pure geraniol 109 per cent. was indicated when the propoition of anhydrous sodium acetate was increased to 5 grams, whilst with 2 grams the theoretical percentage was obtained.

SEPARATE DETERMINATION OF CITRONELLOL IN PRESENCE OF GERANIOL.

Several methods have been proposed for the separation of geraniol and citronellol which occur together in otto of rose and in rose-geranium oils. On treating the mixture with phosphorus trichloride in ethereal solution, geraniol is partly converted into hydrocarbons and partly into geranyl chloride, whilst citronellol is converted into a chlorinated acid ester of phosphorous acid which is soluble in alkalis and can thus be separated. By heating a mixture of geraniol and citronellol with phthalic anhydride to 200° the geraniol is destroyed and the citronellol converted into a phthalic acid ester, the sodium salt of which is soluble in water and can be saponified by alcoholic potash. Geraniol can also be destroyed by heating with benzoyl chloride to 140° to 160°.

The only practical method which appears to give good results depends on the fact that when a mixture of geraniol and citronellol are heated with strong formic acid (100 per cent.) the geraniol is decomposed and the citronellol is converted into citronellyl formate. The estimation is best carried out as follows:—

To 10 c.c. of the oil (otto of rose or rose-geranium oil) 10 c.c. of formic acid 100 per cent. (specific gravity 1·22) is added, and the mixture gently boiled under a reflux condenser for one hour. The mixture is cooled, 100 c.c. of water added, and the whole transferred to a separator. The aqueous layer is rejected, and the oil washed with successive quantities of water as in the acetylation process. The formylated oil is dried with anhydrous sodium sulphate, and about 2 grams neutralised and saponified with alcoholic potash in the usual manner. The percentage of citronellol is then calculated from the following formula:—

$$\text{citronellol percentage} = \frac{x \times 15{\cdot}6}{w - x(0{\cdot}028)},$$

where x = the number of c.cs. of normal potash absorbed and W = the weight of formylated oil taken.

Citronellal and geraniol occur together in citronella oils, and several methods have been proposed for the estimation of these two constituents. The results are only approximate in each case. These are as follows:—

1. Phenylhydrazine method of Kleber.
2. Oximation method of Dupont and Labaune.
3. Sulphite—Bisulphite method of Boulez.

The Phenylhydrazine method is carried out as follows:—

One gram of Ceylon citronella oil or 0·5 grams of Java citronella oil is mixed with 10 c.c. of a freshly prepared 2 per cent. alcoholic solution of redistilled phenylhydrazine and allowed to stand for one to one and a half hours in a flask of about 50 c.c. capacity closed with a glass stopper. Twenty c.c. of decinormal hydrochloric acid is then added, thoroughly

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[1] *P. and E.O.R.*, **1912**, 250.

mixed, 10 c.c. of benzene is then added, and the mixture allowed to stand in a separator after being well shaken. The acid layer which measures 30 c.c. is filtered through a small filter and 20 c.c. of the filtrate is titrated with decinormal alcoholic potash, using ethyl orange as indicator. The amount required for the whole 30 c.c. of filtrate is then calculated, and the quantity deducted from the amount required in a blank experiment without the oil. Each c.c. of decinormal potash shown by the difference in titration represents 0·0154 grams citronellal. The results obtained vary somewhat according to the excess of phenylhydrazine absorbed and according to the time allowed for the reaction.

The Oximation process depends on the fact that citronellal oxime, produced by shaking in the cold with a solution of hydroxylamine, is converted on heating with acetic anhydride into a nitrile which is not affected by saponification with alcoholic potash. The difference between the molecular weight of the nitrile formed and that of citronellal is so small as to be negligible, and the calculation of the percentage of geraniol from the saponification value is made by the usual formula. The method of procedure is as follows:—

Ten grams of hydroxylamine hydrochloride are dissolved in 25 c.c. of water; 10 grams of carbonate of potash, separately dissolved in 25 c.c. of water, are then added and the mixture filtered. With this solution 10 grams of the oil are thoroughly shaken for two hours at 15° to 18° C. The oil is then separated, dried with anhydrous sodium sulphate, and acetylated with twice its volume of acetic anhydride and one-fifth of its weight of anhydrous sodium acetate for two hours under a reflux condenser. The oil is washed, dried, and neutralised, and a weighed quantity (about 2 grams) saponified with alcoholic potash in the usual manner.

A Java oil which showed 83 per cent. of total acetylisable constituents gave 43 per cent. of geraniol and 40 per cent. of citronellal, whilst a Ceylon oil containing 60·2 per cent. of total acetylisable constituents was found to contain 43 per cent. of geraniol.

The Sulphite-Bisulphite method devised by Boulez is conducted as follows:—

25 or 50 grams of the oil are shaken in an Erlenmeyer flask with 100 or 200 grams of solution of bisulphite of soda, saturated with neutral sodium sulphite, and allowed to stand for two to three hours with occasional agitation. 100 to 200 grams of water are then added and the mixture heated for several hours under a reflux condenser, with frequent shaking until a clear oily layer is obtained on standing. The mixture is transferred to a separator and the oil separated and measured. The loss is taken to represent the amount of aldehyde, but the separated bisulphite solution retains a small quantity of oil which can be extracted with ether.[1] The geraniol content is determined in the residual oil by acetylation. The results obtained by this method compare favourably with those obtained by the oximation process.

DETERMINATION OF ALDEHYDES AND KETONES.

These two classes of bodies are somewhat closely related in chemical constitution, and similar processes are therefore available for their estimation. Both contain the carbonyl group, $>\mathrm{CO}$, owing to the presence of

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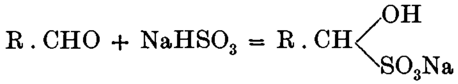
[1] *P. and E.O.R.*, **1912**, 334.

which they are capable of forming various addition and condensation products with certain inorganic and organic reagents, as, for example, sodium bisulphite or sulphite, hydroxylamine, phenylhydrazine, and its nitro-derivative, *p*-nitrophenylhydrazine, cyanacetic acid, hydrocyanic acid, and semioxamazide. Some of these compounds are soluble in water, and thus allow of the separation of the aldehydes or ketones from the other insoluble constituents of the essential oils; others, on the other hand, are crystalline, and can be separated by filtration from the rest of the oil; while in the remaining cases, the reagent is added in excess, and the quantity absorbed by the aldehyde or ketone determined.

The processes depending on the use of sodium bisulphite or sulphite, and in which the aldehyde or ketone compounds dissolve in the solution of the reagent, are known as *absorption* processes, and are those most commonly employed for oils containing a high proportion of aldehydes and ketones, the use of sodium bisulphite being probably still the method most usually adopted for aldehydes, though the use of neutral sodium sulphite is the official process in the *British Pharmacopœia* of 1914, and is also that most suitable for the estimation of ketones.

Bisulphite Method.—This is based on the general reaction



$$R.CHO + NaHSO_3 = R.CH\begin{cases} OH \\ SO_3Na \end{cases}$$

and many variations have been proposed for carrying it out, some favouring the addition of acid, such as acetic, others the use of alkali, such as sodium carbonate. The process, as now ordinarily employed, is carried out as follows:—

From 5 to 10 c.c. of the oil are measured carefully into a flask capable of holding about 150 to 200 c.c., having a long narrow neck graduated into 1/10 c.c. About an equal volume of a hot nearly saturated solution (35 per cent.) of sodium bisulphite is added, the whole well shaken for a few minutes, and then introduced into a boiling water-bath. Successive small quantities of the bisulphite solution are gradually added with vigorous shaking, until the flask is nearly full, and the flask kept in the boiling water-bath until the solid compound at first produced is completely dissolved, and the oily layer of unabsorbed residue rises to the surface. More bisulphite salution is then run in until the unabsorbed oil rises in the graduated neck of the flask, when its volume is read, after cooling. Two precautions must here be taken. Firstly, the temperature at which the oil is measured originally, and that at which the unabsorbed residue is measured, must be identical. Secondly, it must be remembered that the measurements only give the volume percentages, hence to determine the percentage by weight it is necessary to know the specific gravity of the oil and of the non-absorbable residue. Of course the latter can be separated and weighed, but the advantages of this are more than counterbalanced by the loss in weight experienced whilst removing the last traces of water.

It is advisable, generally speaking, to take about an hour over the addition of the bisulphite solution, and heating in a water-bath, but in the case of cassia oils containing much resinous matter it is sometimes necessary to prolong the heating in boiling water for three or four hours before the unabsorbed oil separates as a clear oil on the top of the solution.

This method gives good results for the estimation of cinnamic aldehyde in cassia and cinnamon bark oils, citral in lemon-grass oil, benzaldehyde in bitter almond oil, citronellal in eucalyptus citriodora oil, and anisic aldehyde in aubepine or crategine. It has, however, the disadvantages that it takes not less than one hour, and there is no definite indication when all the aldehyde has been completely absorbed, as there is with the *Neutral Sulphite process.*

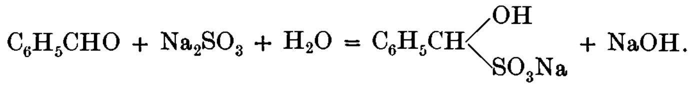
This is based on an observation of Tiemann's that when citral is shaken with a neutral solution of sodium sulphite, a compound with the citral is produced, with simultaneous liberation of sodium hydroxide. The reaction which takes place has not been absolutely established. Tiemann considered that it proceeded according to the equation—

$$C_9H_{15}CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}(NaSO_3)_2 . CHO + 2NaOH$$

in which case reaction would only occur with unsaturated aldehydes or ketones, but Sadtler,[1] as the result of an investigation of a large number of aldehydes and ketones was at first led to conclude that the reaction was a general one for saturated and unsaturated aldehydes of both the aliphatic and aromatic series, and that it should be represented by the following equations for aldehydes and ketones respectively :—

$$R . CHO + 2Na_2SO_3 + 2H_2O = R . CH : (NaSO_3) + 2NaOH + H_2O.$$
$$R . CO . R' . + 2Na_2SO_3 + 2H_2O = RR' . C : (NaSO_3) + 2NaOH + H_2O,$$

though with ketones the reaction was not so general, carvone and pulegone readily entering into combination with the sodium sulphite, whereas thujone did not do so. Based on the above equations, the amount of alkali liberated is proportional to the quantity of aldehyde or ketone entering into reaction, and Sadtler[2] proposed this as a method for determining the percentage of these substances in an essential oil, titrating the liberated alkali with semi-normal hydrochloric acid, and using rosolic acid as indicator. Unfortunately the end point of this reaction is not very definite, and Sadtler, moreover, as the result of fuller investigation of the subject,[3] found the reaction was neither so general nor so definite for aldehydes and ketones as was at first supposed. Whilst citral, cinnamic aldehyde, carvone, and pulegone combine with two molecules of sodium sulphite, benzaldehyde and vanillin are found to react with only one molecule, the reaction with benzaldehyde being represented by the equation—



$$C_6H_5CHO + Na_2SO_3 + H_2O = C_6H_5CH\left\langle\begin{matrix}OH\\SO_3Na\end{matrix}\right. + NaOH.$$

Besides thujone, citronellal, camphor, menthone, and fenchone did not react with the sodium sulphite at all.

Sadtler concluded finally that double bonds seem to aid in bringing about reaction when close to the . CHO group, *e.g.*, citral, cinnamic aldehyde, and that proximity of the benzene nucleus to the . CHO group, as in the case of benzaldehyde and vanillin, was also probably a factor, while the only active ketones were those containing double bonds near to the . CO group.

The aldehyde and ketone compounds formed with the sodium sulphite are readily soluble in water, and H. E. Burgess[4] makes use of this fact

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[1] *Amer. J. Pharm.*, **1904**, 84, and *Jour. Soc. Chem. Ind.*, **1904**, 303.

[2] *Loc. cit.*

[3] *J. Amer. Chem. Soc.*, **1905**, 1325.

[4] *Analyst*, **1904**, 78.

to employ the reaction as the basis for an absorption process, a measured quantity of the oil being heated with a neutral solution of sodium sulphite, and the reduction in volume due to the solution of the aldehyde or ketone compound, indicating the proportion of aldehyde or ketone present in the oil. The alkali liberated as the result of the reaction must be neutralised as fast as produced, and the absence of any further production of alkali serves to denote the completion of the process. The estimation as devised by Burgess is carried out as follows:—

Five c.c. of the oil are introduced into a 200 c.c. flask having a neck graduated to 5 c.c. in 1/10 of a c.c., with a side tubulus reaching to the bottom of the flask for introducing the oil, reagents, and water. To the measured oil is added a saturated solution of neutral sulphite of soda and two drops of ordinary phenolphthalein solution; it is then placed in a water-bath and thoroughly shaken, when a red colour is quickly produced. It is carefully neutralised with 1 to 10 solution of acetic acid until, after the addition of a few drops of acid, no further colour is produced. The oil is then run up into the graduated neck, and when cold carefully read. The difference between 5 c.c. and the reading will give the amount of oil absorbed, and this multiplied by 20 the percentage of aldehyde or ketone. It will be noticed that Burgess recommends a special and rather more complicated absorption flask than that used in the bisulphite process, but this is not necessary, and offers no advantage over the ordinary absorption flask already described (p. 336).

Burgess has applied this process to many aldehydes and ketones, and finds it to give good results with anisic aldehyde, benzaldehyde, cinnamic aldehyde, citral, carvone, pulegone, and the oils of bitter almonds, caraway, cassia, cinnamon, cumin, dill, lemon-grass, pennyroyal, and spearmint. Contrary to Sadtler, citronellal is found to react, but it forms a milky solution, and at first is very frothy, so that care is necessary to prevent loss. The reaction takes considerable time and heating for completion, but good results were obtained. Cumic aldehyde at first forms a solid compound, but this goes into solution on heating with addition of acetic acid. Litmus is a better indicator than phenolphthalein in the case of this aldehyde, and should also be used for the oils of cumin and pennyroyal. Considerable time and heating are required to complete the reaction with nonyl and decyl aldehydes, but satisfactory results may be obtained.

Mention has already been made of the fact that thujone and fenchone do not react with sodium sulphite; consequently the method is useless for tansy, thuja, wormseed, and fennel oils.

The determination of citral in lemon-grass oil by the neutral sulphite absorption process gives results some 4 per cent. lower than those obtained by the bisulphite method, but the latter is that usually adopted in commerce, though, as alreadv stated, the former is official in the new *British Pharmacopœia*.

Labbé[1] recommends a slight modification of the above process, by which he claims that the separation of crystals at the junction between the unabsorbed oil and the sulphite liquor is prevented, and greater accuracy in reading off the percentage therefore attained. He employs a stoppered bulb, prolonged at the bottom into a graduated cylindrical closed tube, and into this are introduced 5 c.c. of the oil, together with

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[1] *Journ. de la Parf. Francaise*, **1913**, 37.

about 60 c.c. of a cold saturated solution of sodium bicarbonate and neutral sodium sulphite. After shaking vigorously for half a minute, the apparatus is almost filled with the sulphite solution, the whole again shaken for a few minutes, and the apparatus inverted when the unabsorbed oil rises cleanly into the graduated tube, and its volume may be read off.

In all the foregoing cases, the percentage of aldehyde or ketone is so high that the estimation by the above processes can be sufficiently accurately carried out on the original oil. With such oils as lemon, orange, hand-pressed lime, and citron or cedrat, however, the proportion of aldehydes is so small that it is not possible to satisfactorily determine it directly on the oil itself by absorption processes, and a preliminary concentration of the aldehydes in the oils by carefully fractionating out the hydrocarbons *in vacuo* has therefore been proposed by Burgess and Child who recommend the operation to be carried out as follows:—

One hundred c.c. of the oil to be examined are put into a distilling flask having three bulbs blown in the neck, and fitted with cork and thermometer. This is connected to a condenser with a suitable receiver, having two vessels graduated at 10 c.c. and 80 c.c. respectively. A Bruhl's apparatus answers the purpose very well. The whole is exhausted, and a pressure of not more than 15 mm. should be obtained. The flask is now gently heated by means of an oil-bath, and 10 c.c. distilled into the first tube. The next vessel is then put into position and the distillation continued until 80 c.c. have distilled over. The pressure is now relieved, and the residual oil in the flask distilled over with steam, when the terpeneless oil, or aldehydes and other oxygenated constituents are obtained. The volume of this fraction is carefully noted, and the optical rotations and refractive indices of all three fractions determined, after which the proportion of aldehyde is estimated on a known volume of the third fraction by either the bisulphite or the neutral sulphite method described above. For example, supposing 7 c.c. of oil were obtained for the third fraction of a sample of lemon oil, and that of the 5 c.c., 2·1 c.c. were absorbed in the aldehyde determination, the percentage of citral in the original lemon oil would be $\frac{2{\cdot}1 \times 20 \times 7}{100} = 2{\cdot}9$ per cent. By this process lemon oils are found to contain some 2·5 to 3 per cent. aldehydes, hand-pressed lime oil 8 per cent., citron or cedrat oil 4 per cent., and orange oil 0·75 to 1 per cent. but more recent work has shown that these results are somewhat too low, due probably in part to some of the aldehydes distilling over with the terpenes, and for oils containing only a small percentage of aldehydes, a volumetric method, such as the *hydroxylamine process*, as modified by A. H. Bennet[1] is much to be preferred, as being both simpler and more rapid to carry out, and also more accurate.

For the estimation of benzaldehyde, Ripper[2] proposed a volumetric modification of the bisulphite process, the aldehyde being shaken with a measured volume of a standard solution of bisulphite, and the excess of bisulphite titrated back with iodine solution at a low temperature. Dodge[3] found this give fairly accurate results, and recommends the following method of carrying out the determination. About 0·15 gram

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[1] *Analyst*, **1909**, 14.

[2] *Monats. f. Chem.*, **1900**, 1079.

[3] *Int. Congress of Applied Chem.*, **1912**, xvii. 15.

bitter almond oil is weighed into a flask containing exactly 25 c.c. N/5 bisulphite solution, and the mixture gently shaken. The flask is then closed, immersed in an ice-bath for one and a half to two hours, and the cold solution titrated with N/10 iodine solution, using starch as indicator. A blank test is made in a similar manner, and from the bisulphite used up, the benzaldehyde may be calculated, 1 c.c. N/10 iodine solution being equivalent to 0·0053 gram benzaldehyde. Feinberg[1] also finds this method very suitable for the estimation of benzaldehyde.

Hydroxylamine Method.—The use of hydroxylamine for the estimation of citral in lemon oil was first proposed by J. Walther[2] who dissolved the oil in alcohol, and boiled the solution under a reflux condenser, with excess of a 5 per cent. solution of hydroxylamine hydrochloride, the hydroxylamine being liberated from the hydrochloride by addition of 0·5 to 1 gram of sodium bicarbonate. The resulting evolution of carbon dioxide has been found, however, to carry off hydroxylamine with it, the error thus produced varying with the time and rate of boiling and other conditions, while a further objection to the process is that oils containing different percentages of aldehydes and ketones require different treatment with regard to the quantity of hydroxylamine and bicarbonate of soda necessary, and no definite instructions for its use, which will apply to all oils, can therefore be given.

The reaction is a general one for aldehydes and ketones, aldoximes and ketoximes respectively being produced, according to the equations:—

$$R.CHO + H_2NOH = RCH.NOH + H_2O$$
$$RR'.CO + H_2NOH = RR'C.NOH + H_2O$$

and the following are some results which have been obtained with various aldehydes and carvone under different conditions as to quantities of hydroxylamine and sodium bicarbonate, and as to time of boiling:—

Substance.	Weight taken.	Bicarbonate Soda.	Mol. Bicarbonate.	Hydroxylamine taken = c.c. $\frac{N}{10}$ NaOH.	Hydroxylamine used.	Time of Heating (minutes).	Percentage.
Benzaldehyde .	1·034	0·4	0·5	124	91	30	93·3
,, . .	1·039	0·8	1·0	124	94	30	95·9
,, . .	1·037	0·8	1·0	378	85	60	86·9
,, . .	0·935	1·1	1·5	378	79	30	89·6
,, . .	0·900	1·0	1·5	150	75	60	88·3
Carvone . . .	1·411	0·8	1·0	378	90	30	95·7
,, . . .	1·410	0·8	1 0	378	83	60	88·9
,, . . .	1·408	1·1	1·3	378	89	30	94·8
,, . . .	1·346	1·0	1·3	150	80	60	89·2
Caraway oil . .	2·135	1·0	—	150	78	60	54·8
Citronellal . .	1·276	0 35	0·5	124	40	30	48·3
,, . .	1·308	0·7	1·0	124	61	30	71·8
,, . .	1·320	1·1	1·5	378	50	30	58·3
Cuminic aldehyde .	1·442	0·4	0·5	124	91	30	93 4
,, .	1·459	0·8	1·0	124	93	30	94·3

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[1] *Int. Congress of Applied Chem.*, i. 187.

[2] *Pharm. Centralb.*, **40**, 1899, 621.

As regards the use of hydroxylamine for the estimation of ketones, it was recommended by Kremers in 1901[1] for the estimation of carvone in spearmint oil, the ketoxime being formed by treating the oil with hydroxylamine, and the remainder of the oil removed by steam distillation, the crystalline ketoxime which is left being separated, dried, and weighed.

E. K. Nelson[2] has applied a slight modification of Walther's process, especially to the determination of ketones. He heats from 1 to 2 grams in a water-bath under a reflux condenser, with 35 c.c. of a hydroxylamine solution, prepared by dissolving 20 grams hydroxylamine hydrochloride in 30 c.c. water and adding 125 c.c. alcohol free from aldehyde, and 2 grams sodium bicarbonate. The mixture is cooled, rendered acid by addition of 6 c.c. concentrated hydrochloric acid through the condenser, and the whole diluted to 500 c.c. with water. The solution is then filtered and an aliquot part neutralised with N/2 NaOH solution to methyl orange, and finally the excess of hydroxylamine titrated with N/10 NaOH to phenolphthalein. This method is found to give fairly accurate results for the estimation of carvone in spearmint, thujone in tansy and wormwood oils, pulegone in pennyroyal oil, and camphor in rosemary oil, but proved less satisfactory for the estimation of fenchone.

The process has been much improved by A. H. Bennett[3] who substitutes N/2 alcoholic potash for sodium bicarbonate in order to liberate the hydroxylamine, and this modification is now adopted in the *British Pharmacopœia* as the official method for the estimation of citral in lemon oil, and is also the process in general use in this country for the purpose. It is carried out by taking 20 c.c. of oil, adding 20 c.c. of N/2 alcoholic hydroxylamine hydrochloride solution (in 80 per cent. alcohol), and 8 c.c. of N/1 alcoholic potash, together with 20 c.c. strong alcohol, and gently boiling the mixture, under a reflux condenser for half an hour, after which it is cooled, the condenser carefully washed down with distilled water, and the whole diluted with distilled water to about 250 c.c., the undecomposed hydroxylamine hydrochloride being then neutralised to phenolphthalein with N/2 alcoholic potash, and the hydroxylamine remaining unabsorbed by the aldehyde then titrated with N/2 sulphuric acid, using methyl orange as indicator. A blank test is made in exactly the same manner, omitting only the oil, and the difference between the number of c.c. of N/2 acid required in the two cases in the final titration represents the number of c.cs. of N/2 acid which will neutralise the hydroxylamine absorbed by the aldehyde or ketone, and this, in the case of lemon oil, multiplied by 0·076 gives the grams of citral in 20 c.c. of the oil, and from a knowledge of the specific gravity of the oil, the percentage of citral by weight can thence be readily calculated. The process gives slightly too low results, some 5 to 10 per cent. below the true aldehyde content, but in the case of oils containing only a comparatively small quantity of aldehyde or ketone, as with lemon or lime oil, this is unimportant, and concordant results by different observers are readily obtained.[4] In the case of oils containing a large proportion of aldehyde or ketone, however, the error would be of considerable importance, and the process is therefore not suitable in such cases.

Phenylhydrazine Methods.—In addition to the general reaction between almost all aldehydes and ketones and hydroxylamine, there is another

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[1] *Journ. Soc. Chem. Ind.*, **1901**, 16.

[2] *J. Ind. Eng. Chem.*, **1911**, 588.

[3] *Loc. cit.*

[4] *P. and E.O.R.*, **1913**, 269.

equally characteristic reaction between both these classes of compounds and phenylhydrazine, the condensation products formed being usually crystalline, and sparingly soluble compounds, termed phenylhydrazones, or simply hydrazones. The reactions taking place may be represented by the following equations:—

$$\underset{\text{Benzaldehyde.}}{C_6H_5CHO} + \underset{\text{Phenylhydrazine.}}{C_6H_5NH \,.\, NH_2} = C_6H_5CH : N \,.\, NH \,.\, C_6H_5.$$

$$\underset{\text{Methyl nonyl ketone.}}{CH_3 \,.\, C_9H_{19} \,.\, CO} + \underset{\text{Phenylhydrazine.}}{C_6H_5NH \,.\, NH_2} = CH_3 \,.\, C_9H_{19} \,.\, C : N \,.\, NH \,.\, C_6H_5.$$

Several processes for the estimation of aldehydes and ketones have been based on these reactions, some depending on the separation and weighing of the insoluble hydrazone, others on treatment of the substance with an excess of phenylhydrazine, and estimation of the unused reagent.

Among the earliest to suggest this method for the estimation of aldehydes and ketones were Benedikt and Strache,[1] who treated the aldehyde or ketone with an excess of phenylhydrazine, filtered off the hydrazone produced, and oxidised the uncombined phenylhydrazine with Fehling's solution, measuring the nitrogen thereby evolved. The process, which really measures the —CO contained by the bodies, has been slightly modified by Watson Smith, junior,[2] who uses a current of carbon dioxide instead of steam for driving off the nitrogen. Each c.c. of nitrogen corresponds to 1·252 mgs.—CO, and the process gives good results with benzaldehyde, cuminic aldehyde, and methyl nonyl ketone (rue oil), but with other aldehydes is unsatisfactory.

P. B. Rother has proposed to estimate the excess of phenylhydrazine by adding to it an excess of standard N/10 iodine solution and titrating back with N/10 thiosulphate solution, 0·1 gram phenylhydrazine corresponding to 37 c.c. N/10 iodine solution. From 0·5 to 1 gram of oil (or in the case of lemon oil, 10 grams) is dissolved in a 250 c.c. flask in about 30 c.c. alcohol, and enough of a 1 per cent. phenylhydrazine solution added to give 1 molecule for each molecule of aldehyde. The mixture is well shaken, and allowed to stand for fifteen hours in the dark with occasional shaking. It is then diluted with water and filtered through a plaited paper into a litre flask containing about 500 c.c. water and 10 to 20 c.c. N/10 iodine solution. The filter is well washed with water, and the filtrate titrated back with N/10 thiosulphate solution, using starch as indicator. The method gives good results with oils rich in aldehydes, but for lemon oil is not nearly so accurate as the Kleber modification described below.

The gravimetric method which is specially suitable for the determination of small quantities of benzaldehyde is recommended both by Hérissey,[3] Denis, and Dunbar.[4] The former adds 1 c.c freshly-distilled phenylhydrazine and 0·5 c.c. glacial acetic acid to so much of the benzaldehyde as will yield 0·1 to 0·2 gram hydrazone, heats for twenty to thirty minutes in a boiling-water bath, and after twelve hours, filters on a Gooch crucible, washes with 20 c.c. water, and dries in the vacuum desiccator. Denis and Dunbar, whose process is suggested for the examination of extracts of almonds, mix 10 c.c. of the extract with 10 to 15 c.c. of a freshly prepared 10 per cent. phenylhydrazine solution, shake thoroughly, and allow to

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[1] *Monats. f. Chem.*, **1893**, 273.

[2] *Chem. News*, **1906**, 83.

[3] *Journ. de Pharm. et Chem.*, **1906**, 60.

[4] *Journ. Ind. and Eng. Chem.*, **1909**, 256.

stand in dark for twelve hours, at the end of which 200 c.c. cold water are added, and the mixture filtered through a Gooch crucible. The precipitate is washed first with cold water and afterwards with 10 c.c. of 10 per cent. alcohol, dried for three hours *in vacuo* at 70° to 80° C., and weighed. The weight obtained multiplied by 5·408 gives grams benzaldehyde in 100 c.c. of the solution.

The most important application of the phenylhydrazine reaction to essential oil analysis is the process devised by Kleber for the determination of citral in lemon oil[1] in which the excess of phenylhydrazine is titrated with standard acid to diethyl orange as indicator. Kleber recommends the process to be carried out as follows: About 10 grams lemon oil are accurately weighed into a flask, 20 c.c. of freshly prepared 5 per cent. alcoholic phenylhydrazine solution added, the flask closed, and allowed to stand about thirty minutes, after which sufficient N/2 hydrochloric acid is added to exactly neutralise the phenylhydrazine solution, this quantity being previously determined by a blank test with the phenylhydrazine only. The neutralised mixture is transferred to a separator, the flask being rinsed with 20 c.c. water, and the whole vigorously shaken, when on standing two layers separate, the lower one of which is drawn off into a flask, the residue in the separator washed with 5 c.c. water, and the washing added to the liquor previously withdrawn, this being then titrated with N/2 soda, using diethyl orange as indicator, and titrating to a brownish tint which precedes the pink coloration. Each c.c. of N/2 soda required corresponds to 0·076 gram citral. Kleber found this process satisfactory for the estimation of citral in lemon oil and citronellal in citronella oils, and considered it capable of general application for the estimation of aldehydes and ketones. The accuracy of the method for the examination of lemon oil has been confirmed by several American chemists, and also by Schimmel,[2] who recommend the following modification: About 2 c.c. of lemon oil are accurately weighed into a 50 c.c. glass-stoppered bottle, mixed with 10 c.c. of a freshly prepared 2 per cent. phenylhydrazine solution, and allowed to stand for one hour; 20 c.c. N/10 HCl are then added, together with 10 c.c. benzene, the mixture thoroughly shaken, and transferred to a separating funnel. After standing, an acid layer amounting to about 30 c.c. separates to the bottom. This is filtered off, and 20 c.c. of the filtrate titrated with N/10 KOH, using 10 drops of a 1 in 2000 diethyl orange solution, as indicator, and adding potash until a distinct yellow colour appears. A blank test without oil is made in a similar manner, and from the difference in the amount of potash required by the two tests, the quantity of citral in the oil can be calculated. The phenylhydrazine solution rapidly deteriorates and should be prepared fresh each time; it should never be used more than twenty-four hours old. Schimmel has also proved the value of this process in the estimation of cuminic aldehyde, benzaldehyde, and methyl nonyl ketone, but find it useless for fenchone, thujone, camphor, and menthone.

Phenylhydrazine Derivatives.—The use of *m*-nitrophenylhydrazine and *p*-bromphenylhydrazine has been proposed by Hanus for the determination of vanillin, and Van Ekenstein and J. J. Blanksma in 1905 suggested the use of *p*-nitrophenylhydrazine as a reagent for aldehydes and ketones generally, in all three cases the precipitated hydrazone being

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[1] *Amer. Perfumer*, 1912, 284.

[2] *Semi-annual Report*, April, 1912, 77.

filtered off, washed, dried, and weighed. Feinberg,[1] experimenting with the two latter reagents, finds both to give good results with vanillin and anisic aldehyde. The last-named is also satisfactory for the estimation of benzaldehyde, but *p*-bromphenylhydrazine gives too low results.

Colorimetric Processes.—Various colorimetric methods have been proposed for the estimation of aldehydes, one of the most important being that of E. McK. Chace,[2] which is based on the well-known reaction of aldehydes with a fuchsine solution decolorised by means of sulphur dioxide, the colour produced when this reagent is added to a known quantity of the oil being matched by a standard solution of the pure aldehyde. The fuchsine reagent is prepared by dissolving 0·5 gram. fuchsine in 100 c.c. of water, adding a solution containing 16 grams sulphur dioxide, and allowing it to stand until colourless, when the solution is made up to 1 litre. In carrying out the estimation, 2 grams of the lemon oil are diluted to 100 c.c. with aldehyde free alcohol, prepared by allowing to stand over alkali for several days, distilling, boiling, the distillate for several hours under a reflux condenser with 25 grams per litre of *m*-phenylenediamine hydrochloride, and redistilling. Four c.c. of this solution are then diluted with 20 c.c. aldehyde free alcohol, 20 c.c. of the fuchsine solution added, and the total volume made up to 50 c.c. with the alcohol. The colour thus produced is compared with standards prepared in the same way, but with known quantities of a 2 per cent. alcoholic solution of pure citral in place of the solution of oil, all the solutions being left for ten minutes in a water-bath at a temperature not exceeding 15° C., and the colours compared either directly or by means of a colorimeter. The method gives good results with lemon extracts or mixtures of citral with limonene, but with lemon oil itself a satisfactory degree of accuracy is not attainable owing to slight turbidity of the solution due to certain wax-like constituents of the oil, and results differing by as much as 1·25 per cent. citral on the oil may be easily obtained, so that this process, though useful for lemon essences, cannot be regarded as suitable for the analysis of lemon oil.

Woodman and Lyford[3] recommend a very slight modification of the above process for the determination of benzaldehyde in extracts of bitter almonds, the aldehyde free alcohol being prepared by treating it first with silver oxide, then with *m*-phenylenediamine hydrochloride, passing a strong current of air through it for three hours, and then distilling, rejecting the first 100 c.c. of distillate.

Another colorimetric method for the estimation of citral is that due to R. S. Hiltner,[4] who substitutes a 1 per cent. solution of *m*-phenylenediamine hydrochloride in 50 per cent. alcohol for the fuchsine solution employed by Chace, but otherwise the process is similar, the yellow colour produced by the *m*-phenylenediamine and the oil being matched by means of a standard alcoholic solution of citral. The reaction is more distinct than in Chace's process, and the results are claimed to be more accurate, as acetaldehyde and citronellal give no coloration under the experimental conditions, with *m*-phenylenediamine. Old lemon oils which have become oxidised give a yellow-green to blue-green coloration, according to the degree of oxidation, and this renders the process useless for old oils. The estimation is carried out by weighing out 1·5 to 2 grams

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[1] *Eighth Inter. Congress Applied Chem.*, **1912**, 1, 187.

[2] *J. Amer. Chem. Soc.*, **1906**, 1472.

[3] *Ibid.*, **1908**, 1607.

[4] *J. Ind. Eng. Chem.*, **1909**, 798.

lemon oil, diluting to 50 c.c. with 90 to 95 per cent. alcohol and to 2 c.c. of this solution, adding 10 c.c. of the *m*-phenylenediamine solution. The mixture is diluted to a given volume, and the colour produced matched by means of a 0·1 per cent. solution of citral in 50 per cent. alcohol.

A modification of the Hiltner method of estimating citral is described in the *Journal of Industrial and Engineering Chemistry*[1] by C. E. Parker and R. S. Hiltner. In the determination of citral by the metaphenylene-diamine method it not infrequently occurs that lemon and orange oils and extracts produce blue or green colours instead of yellow. This abnormal behaviour has somewhat restricted the applicability of the method. Experiments have shown that substances such as Fuller's earth, animal charcoal, talcum, pumice, zinc powder, platinised asbestos, eponite, and kaolin, employed for decolorising the reagent affect the metaphenylene-diamine in some obscure way, rendering it more responsive to the action of a citrus oil which has the property of producing the blue colour. Further experiments favour the presumption that oxidation of the terpene is in part responsible for the production of the blue colour. Stannous chloride was found to prevent the formation of the blue colour, whether added in solid form or in aqueous or alcoholic solution. The addition of a proper amount of oxalic acid to the original Hiltner reagent was found to accomplish the desired object in the most simple and convenient way, and was finally adopted for the proposed method. If the various samples are mixed with the reagent at the same time, as many as a dozen can be compared with a single standard within an hour without any substantial error, but in order to do this it is desirable to employ always a fixed amount of citral in solution. The details of the improved method are as follows: *Reagents.*—Alcohol of 94 to 95 per cent. strength, practically colourless, may be employed. *Citral Standard Solutions.*—0·5 gram of citral is dissolved in alcohol (94 per cent.) and made up to 50 c.c. Of this 1 per cent. solution, 10 c.c. are diluted to 100 c.c. Each c.c. of this contains 0·001 gram citral. These solutions may be kept in a refrigerator, but should be measured at room temperature. *Metaphenylene diamine Hydrochloride : Oxalic Acid Solution.*—Dissolve 1 gram metaphenylene-diamine hydrochloride and 1 gram of crystallised oxalic acid, each in about 45 c.c. of 80 per cent. alcohol. Mix in a stoppered 100 c.c. graduated flask or cylinder, and make up to the mark with 80 per cent. alcohol. Add 2 or 3 grams Fuller's earth, shake well, allow to settle, and decant through a double filter. When most of the liquid has run through, add the turbid residue to the liquid in the filter. *Colorimeter.*—Any form of colorimeter may be used. *Manipulation.*—Weigh into a 50 c.c. graduated flask about 0·5 gram lemon oil, or about 4 grams orange oil, or 10 grams lemon extract, or 50 c.c. orange extract respectively; make up to the mark with 94 per cent. alcohol, stopper and mix the contents. Pipette 5 c.c. of these first dilutions into 50 c.c. graduated flasks. Pipette also 4 c.c. of the standard 0·1 per cent. citral solution into a 100 c.c. flask. As nearly as possible at the same time add from a small graduated cylinder to the 50 c.c. flasks 10 c.c., and to the 100 c.c. flask 20 c.c. of the metaphenylene-diamine reagent; make all up to the mark with 95 per cent. alcohol, stopper the flask and mix well. Empty the 100 c.c. flask of citral dilution into the plunger tube of the colorimeter, and a 50 c.c. flask of the

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[1] August, 1918, p. 608 (through *P. and E.O.R.* (1918), 256).

unknown dilution into a comparison tube. Both comparison tubes should be graduated in millimetres. Adjust the plunger until both halves of the field have the same intensity of colour, and note the heights of the columns compared. Calculate the average of five or more observations. From these preliminary results compute the amount of the first dilution of the unknown, which should be used in making the second dilution to produce the same colour as the standard in the same height of column of liquid. Repeat the determination, preparing at the same time fresh dilutions of the standard and unknown until columns of liquid of equal intensity of colour differ in length not more than 5 or 10 per cent.

Calculation—

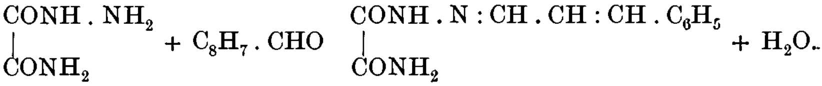
(*a*) = gram of citral (0·002) in 50 c.c. of diluted standard used for comparison.
(*b*) = grams of oil or extract weighed.
(*c*) = volume in c.c. (50) of first dilution of unknown.
(*d*) = volume in c.c. of same used for second dilution.
(*e*) = height of column (mm.) of standard used for comparison.
(*f*) = height of column (mm.) of unknown used for comparison.

$$\text{Then } \frac{a \times c \times e \times 100}{b \times d \times f} = \text{per cent. citral in oil or extract.}$$

For the estimation of vanillin, T. von Fallenburg[1] proposes to make use of the colour produced by treating a dilute aqueous solution with isobutyl alcohol and concentrated sulphuric acid. Five c.c. of the solution are mixed with 5 c.c. of a 1 per cent. isobutyl alcohol solution in 95 per cent. alcohol, and 25 c.c. concentrated sulphuric acid, the colour produced being compared after forty-five minutes with that given by known amounts of vanillin.

The following processes have been recommended for the determination of aldehydes and ketones :—

Semioxamazide.—A gravimetric method for the estimation of cinnamic aldehyde in cassia and cinnamon oils, but which appears to apply only to this aldehyde, has been devised by Hanus[2] based on the formation of a crystalline semioxamazone when cinnamic aldehyde is treated with semioxamazide, the reaction being—



$$\begin{array}{l} CONH.NH_2 \\ | \\ CONH_2 \end{array} + C_8H_7.CHO \quad \begin{array}{l} CONH.N:CH.CH:CH.C_6H_5 \\ | \\ CONH_2 \end{array} + H_2O.$$

The process is carried out by accurately weighing 0·15 to 0·2 gram cinnamon or cassia oil in a 250 c.c. conical flask, adding 85 c.c. water, and shaking thoroughly, after which about 1½ times the quantity of semioxamazide, dissolved in hot water, is added, the mixture well shaken for five minutes, and then allowed to stand for twenty-four hours with occasional shaking, especially during the first three hours. The semioxamazone separates in the form of small flakes, which are filtered through a Gooch tile, washed with cold water, dried at 105° C. till constant, and weighed. The process gives accurate results for the estimation of cinnamic aldehyde not only in cassia and cinnamon oils but also in cinnamon bark, and is for this latter purpose particularly suitable, the oil from 5 to

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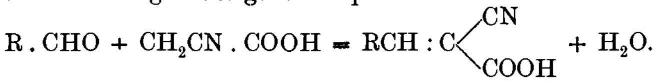
[1] *Chem. Zentr.*, **1916**, 391.

[2] *Zeits. Unters. Nahr. Gen. Mittel*, **1903**, 817.

8 grams bark being steam distilled, the distillate extracted with ether, the ether evaporated off, and the aldehyde estimated as above described.

Cyanacetic Acid, Hydrocyanic Acid.—When an aldehyde is treated with cyanacetic acid in the presence of potassium hydroxide, condensation takes place according to the general equation—



$$R.CHO + CH_2CN.COOH = RCH:C\begin{matrix}\diagup CN \\ \diagdown COOH\end{matrix} + H_2O.$$

The condensation product is soluble, and it has been proposed to make use of this reaction as an absorption process for the determination of citral in lemon oil, but owing to a very indistinct separation between the unabsorbed oil and the absorbing solution, it has been found practically impossible to get satisfactory results and the process has been abandoned in practice.

A general property of aldehydes and ketones is that when heated with hydrocyanic acid, additive compounds, termed nitriles or cyanohydrins, are produced, according to the general equations—

$$R.CHO + HCN = R.CH(OH)CN$$
$$RR'.CO + HCN = RR'.C(OH)CN$$

On this reaction F. de Myttenaere has endeavoured to base a process for the estimation of aldehydes and ketones, adding sufficient of a dilute (0·4 per cent.) aqueous or faintly alkaline solution of hydrocyanic acid to give about 4 molecules hydrocyanic acid per molecule of aldehyde or ketone, and measuring the total and free hydrocyanic acid after first heating the mixture for seventy-five minutes in the water-bath in a sealed flask, and then allowing to stand for twelve hours at room temperature. The total hydrocyanic acid is estimated by adding exactly 6 c.c. of the solution to be tested to 75 c.c. water, followed by 10 drops of 40 per cent. soda solution, 10 c.c. 17 per cent. ammonia solution, and a few drops of 10 per cent. potassium iodide solution, and then titrating with N/100 silver nitrate. The free hydrocyanic acid the author determines by adding 3 c.c. of the solution to be tested to 50 c.c. N/100 silver nitrate in a 100 c.c. flask, diluting to 100 c.c. with water, filtering, and titrating the excess of silver nitrate in 50 c.c. filtrate by means of N/100 ammonium thiocyanate, using iron alum as indicator. The author has obtained good results with this process in the estimation of benzaldehyde, but it failed with citral and vanillin, and also with ketones.

Sodium Salicylate.—When an aldehyde is shaken with a saturated solution of sodium salicylate, there seems to be evidence of the formation of a weak molecular compound, and with cinnamic aldehyde well-defined crystals have been obtained which give on analysis :—

	Found.	Theoretical.
Sodium	7·3 per cent.	7·9 per cent.
,, salicylate	53·5 ,,	54·8 ,,

This process, though referred to by Burgess,[1] never seems to have been very seriously investigated.

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[1] *Analyst*, 1904, p. 79.

Acetylation.—Citronellal may be quantitatively estimated by the ordinary acetylation process[1] when the aldehyde is quantitatively converted into isopulegyl acetate, which is then determined by saponification with potash in the ordinary way. Dupont and Labaume[2] have attempted to base a method for the separation of geraniol from citronellal in citronella oils on the fact that the citronellal oxime formed by shaking with hydroxylamine solution at the ordinary temperature is not converted into an ester by subsequent acetylation, but into the nitrile of citronellic acid which is stable towards alkali during the saponification process.

Cannizzaro's Reaction.—On this reaction, which may be represented thus—

$$2C_6H_5CHO + KOH = C_6H_5COOK + C_6H_5CH_2OH,$$

Dodge[3] has based a process for the determination of benzaldehyde. A strong (2·5 N) alcoholic potash solution is required for the estimation, which is performed by allowing a mixture of 10 c.c. of this solution with 1 to 2 grams benzaldehyde to stand at the ordinary temperature for twenty-four hours, after which the unabsorbed potash is titrated back with N/2 hydrochloric acid. A blank test is also made, and from the amount of potash entering into reaction, the percentage of aldehyde can be calculated. The process breaks down in the assay of natural oil of bitter almonds, probably due to the presence of benzaldehyde cyanhydrin.

THE DETERMINATION OF PHENOLS.

The usual method for the determination of phenols is based on the solubility of these compounds in solutions of caustic alkali. Such absorption methods are not strictly accurate, since a small portion of constituents other than phenols are dissolved by the alkali. So long, however, as the conditions are kept constant, useful comparative results are obtained. The process is best carried out as follows:—

Five to 10 c.c. of the oil are shaken in a Hirschsohn flask, as used for cassia oil analysis, with a 5 per cent. solution of caustic soda, until absorption is complete, and the unabsorbed oil driven into the neck of the flask by more of the solution and its volume read off. The difference between the original amount of oil used and the unabsorbed portion may be taken as phenols. Strictly speaking, this method gives a volume percentage, which can be converted into a weight percentage if the specific gravities of the two portions of the oil be known.

Schryver[4] has recommended the use of sodamide for the determination of phenols; the hydrogen of the phenolic hydroxyl replaces the sodium with the formation of an equivalent quantity of ammonia,

$$NaNH_2 + HO.R' = NaOR' + NH_3.$$

About 1 gram of sodamide in fine powder is washed several times with benzene and placed in a 200 c.c. flask. About 50 c.c. of benzene, free from thiophene, is added, and the flask, attached to a condenser, warmed on the water-bath, and traces of ammonia are removed by a stream of carbon dioxide. From 1 to 2 grams of the phenol-containing oil is then admitted to the flask through a stoppered funnel inserted through the

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[1] *Determination of Alcohols*, p. 297.

[2] Roure-Bertrand's *Report*, April, 1912, 3.

[3] *Eighth Inter. Congress of Applied Chem.*, 1912, xvii. 15.

[4] *Jour. Soc. Chem. Ind.*, 18 (1899), 553.

cork, the last traces being washed through with benzene. The contents of the flask are again heated and a current of air driven through until all the ammonia generated is carried over and absorbed in a given volume (about 20 c.c.) of normal sulphuric acid in a suitable collecting vessel. The amount of phenol is calculated on the basis of the equation given above.

Kremers recommends the following method of estimating thymol:—

Five c.c. of the oil to be examined are weighed and brought into a glass-stoppered burette graduated to $\frac{1}{10}$ c.c., and is diluted with about an equal volume of petroleum ether; a 5 per cent. potassium hydroxide solution is added, and the mixture shaken for a short time, then the liquid is left standing until separation is complete. Then the alkaline solution is allowed to run into a 100 c.c. graduated flask. This operation is repeated until no further decrease in the volume of the oil takes place.

The alkaline solution of thymol is made up to 100 or 200 c.c. as the case may require, using a 5 per cent. soda solution. To 10 c.c. of this solution in a graduated 500 c.c. flask is added a $\frac{1}{10}$ normal iodine solution in slight excess, whereupon the thymol is precipitated as a dark reddish-brown iodine compound. In order to ascertain whether a sufficient quantity of iodine has been added, a few drops are transferred into a test tube and a few drops of dilute hydrochloric acid are added. When enough iodine is present, the brown colour of the solution indicates the presence of iodine, otherwise the liquid appears milky by the separation of thymol. If an excess of iodine is present, the solution is slightly acidified with dilute hydrochloric acid and diluted to 500 c.c. From this 100 c.c. are filtered off, and the excess of iodine determined by titration with $\frac{1}{10}$ normal solution of sodium thiosulphate. For calculation, the number of cubic centimetres required is deducted from the number of cubic centimetres of $\frac{1}{10}$ normal iodine solution added and the resultant figure multiplied by 5, which gives the number of cubic centimetres of iodine required by the thymol.

Every cubic centimetre of $\frac{1}{10}$ normal iodine solution equals 0·003753 gram of thymol. Knowing the quantity of thymol in the alkaline solution, the percentage in the original oil is readily found.

The reaction taking place is represented by the equation—

$$C_{10}H_{14}O + 41 + 2NaOH = C_{10}H_{12}I_2O + 2NaI + 2H_2O$$

In the estimation of carvacrol a slight modification of this method must be made, because carvacrol is thrown down as a finely divided white precipitate, giving the solution a milky appearance. In order to form a precipitate the liquid is vigorously shaken after the addition of iodine solution, and is subsequently filtered. Then the liquid is acidulated with hydrochloric acid, and subsequently the same procedure is followed as was described for thymol. The calculation is also the same.

Redman, Weith, and Brock[1] have modified the above-described method, by using sodium bicarbonate instead of sodium hydroxide. They proceed as follows:—

About 50 c.c. of *n*-sodium bicarbonate solution is placed in a glass-stoppered bottle of 500 c.c. capacity and diluted with 100 c.c. water. To this is added from a burette 15 c.c. of a solution containing as much of the phenol under examination as corresponds to about a decinormal

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[1] *Jour. Ind. Eng. Chem.*, **5** (1913), 831.

solution. To this is added $\frac{1}{30}$ normal iodine solution in excess until a permanent brown colour is obtained. The excess of iodine should amount to 20 c.c. The mixture is now vigorously shaken for one minute, diluted with 50 c.c. of *n*-sulphuric acid, and the excess of iodine titrated back with decinormal thiosulphate solution, 5 c.c. of a 20 per cent. potassium iodide solution being added. Starch is used as an indicator. The temperature should be from 20° to 25°.

In order that the reaction may proceed rapidly it is important to shake the mixture thoroughly after adding the iodine solution. When this is done the iodine compound is formed completely within one minute. With thymol it affords thymol di-iodide. In order to make sure that any iodine which may have entered into the hydroxyl-group is again liberated, care should be taken that a little hydriodic acid is always present; hence the addition of the potassium iodide solution before the excess of iodine is titrated back with thiosulphate. Titration can only be regarded as complete when the blue coloration does not return in 10 minutes.

For the determination of eugenol Thoms has elaborated the following method, the results of which are fairly accurate:—

About 5 grams of the oil are weighed into a beaker of about 150 c.c. capacity, 20 grams of 15 per cent. sodium hydroxide solution added, and then 6 grams benzoyl chloride. On stirring, the solid mass of eugenol sodium salt at first formed goes into solution again as it is converted into benzoic ester, with evolution of much heat. In the course of a few minutes the reaction ends, and on cooling a solid crystalline mass of benzoyl eugenol is obtained. To this 50 c.c. water is added, and the whole warmed on a water-bath until the ester is completely melted to an oil, well stirred, cooled, and the clear supernatant aqueous solution filtered off. The crystalline mass is again washed with two successive quantities of 50 c.c. water, and the resulting impure benzoyl eugenol is re-crystallised from alcohol, due allowance being made for its solubility in that medium. 25 c.c. of hot alcohol (90 per cent. by weight strength) are poured through the filter employed in the previous washing operations, in order to dissolve any adherent crystals, into the beaker, and the whole warmed upon the water-bath until complete solution is effected. The solution is then cooled to 17° C., and the crystalline precipitate thrown upon a small weighed filter paper, filtered into a 25 c.c. cylinder, and washed with 90 per cent. alcohol until the filtrate exactly measures 25 c.c. The filter and crystals are then removed to a weighing bottle, dried at 100° C. until constant, and then weighed. From the total weight the weights of the filter paper and of the weighing bottle are deducted, from which the benzoyl eugenol is calculated. To the latter weight 0·55 gram are added, being the weight of pure benzoyl eugenol dissolved by 25 c.c. 90 per cent. alcohol at 17° C. as determined by experiment.

This final quantity gives the amount of benzoyl eugenol, from which the amount of eugenol is easily calculated, eugenol having the formula $C_{10}H_{12}O_2$, and benzoyl eugenol $C_{17}H_{16}O_3$, so that $\frac{164x}{268y} \times 100 =$ the percentage of eugenol if x equals the weight of benzoyl eugenol obtained, and y the weight of oil used in the estimation. Under these circumstances the eugenol-content should not fall below 75 per cent., or if estimated by absorption with potash not below 82 per cent., usually from 85 to 90 per cent.

Thom has recognised that the foregoing process is only approximately accurate and now recommends the following modification. This consists in heating 5 grams of the oil in a water-bath with 20 c.c. of a 15 per cent. soda solution for thirty minutes. After allowing the hydrocarbons to separate, the eugenol soda solution is run off, and the hydrocarbons washed with dilute soda solution twice, the washings being added to the original soda solution. The reaction is now effected at water-bath temperature with 6 grams of benzoyl chloride. The whole is allowed to cool, and the crystalline mass transferred to a beaker with 55 c.c. of water. It is heated in order to melt the crystals, and well agitated with the water to wash the benzoyl eugenol. This washing is repeated twice. The crystalline mass is then transferred to a beaker with 25 c.c. of 90 per cent. alcohol, and warmed till complete solution takes place. The solution is allowed to stand till the bulk of the crystals have separated out, and is cooled to 17° and filtered through a paper 9 cm. in diameter, previously dried and tarred. The filtrate measures about 20 c.c. and the crystals are washed with more alcohol until it measures 25 c.c. The paper and crystals are then dried in a weighing-glass and weighed, the temperature of drying being not more than 101° C. The solubility allowance for 25 c.c. of alcohol is 0·55 gram. The total eugenol is calculated from the formula

$$P = 4100\frac{a + 0{\cdot}55}{67b}$$

where P is the percentage, *a* the weight of benzoyl eugenol obtained, and *b* is the weight of clove oil used.

Verley and Bolsing propose the following method. It depends on the fact that acetic and other anhydrides react with phenols in excess of pyridine. Eugenol reacts readily forming eugenol acetate and acetic acid, the latter combining with pyridine to form pyridine acetate. This compound reacts towards indicators such as phenol-phthalein in the same way as acetic acid, and therefore a titration is possible. Verley and Bolsing use from 1 to 2 grams of the oil, which is placed in a 200 c.c. flask, and 25 c.c. of a mixture of acetic anhydride (15 parts) and pyridine (100 parts). The mixture is heated for thirty minutes on a water-bath, the liquid cooled, and 25 c.c. of water added. The mixture is well shaken and titrated with normal potash, using phenolphthalein as indicator. A blank experiment is carried out without the eugenol, and the difference between the titration figures in c.c. of normal alkali, multiplied by 0·582, gives the amount of eugenol in the sample taken.

Determination of the Methyl Number.

Benedikt and Grüssner[1] have proposed the determination of the methyl number in the analysis of essential oils. Whilst this process may have some value in the examination of the constitution of a compound, it is very rarely necessary to use it in the analysis of essential oils. The methyl number (which is a somewhat fallacious term as it includes other alkyl radicles) is understood as the number of milligrams of methyl yielded by the gram of the substance when heated with hydriodic acid. From 0·2 to 0·3 gram of the oil is heated with hydriodic acid of specific gravity 1·7 and the methyl iodide formed collected in a suitable receiver,

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[1] *Chem. Zeit.*, 13 (1899), 872, 1087.

free iodine being absorbed by phosphorus. The methyl (or alkyl) iodide is decomposed by alcoholic solution of silver nitrate, and the silver iodide weighed, from which the amount of alkyl radicle, calculated as CH_3 is found.

THE DETECTION OF CHLORINE IN ESSENTIAL OILS.

A few essential oils contain substances which can be easily synthesised by processes in which the use of chlorine is involved. Such oils are frequently adulterated with the synthetic product. If this contains chlorine—which is very frequently the case, on account of the difficulty in removing the last traces of this body—its detection becomes of importance, as the presence of a trace of chlorine is evidence of the presence of the artificial compound.

The Determination of Chlorine.—Many methods have been suggested for the detection and determination of chlorine, but most of them are merely qualitative. Of these the following are useful:—

(*a*) By simple combustion. This method depends on the fact that on combustion a portion of the chlorine present in the organic compounds existing as impurities forms hydrochloric acid, which can be detected by means of silver nitrate.

A piece of filtering paper about 2 inches by 1 inch, and rolled in the shape of a spill, is saturated with the oil, the excess of oil is thrown off and the paper is placed in a small porcelain dish which in its turn reposes in a larger dish, measuring about 8 inches in diameter. The paper is ignited, and a beaker, of a capacity of about 2 litres, moistened inside with distilled water, is quickly placed over the paper. The sizes of the dishes used must be such that the rim of the larger dish must stand out well all round from the beaker. After the flame is extinguished the beaker should be left in position for about one minute, after which the products of combustion which have been deposited against the moist sides of the beaker are rinsed out with a little distilled water, and filtered. The filterate, acidulated with a drop of nitric acid, must remain clear when silver nitrate solution is added.

Care must be taken that the filter paper is free from chlorine. This should be determined by a blank experiment. This process has been strongly recommended by Schimmel & Co., but there is considerable doubt whether it will detect minute quantities of chlorine.

(*b*) The sodium test is distinctly more delicate, and is carried out as follows:—

A piece of pure metallic sodium about half the size of a pea is dropped into 0·5 c.c. of the oil in a dry test tube, and heated until all chemical action has ceased. The test tube and contents are immersed whilst still hot in 10 c.c. of distilled water in a porcelain dish. The solution is filtered, acidulated with nitric acid, and silver nitrate solution added. Any turbidity or opalescence indicates the presence of chlorine compounds.

A blank test should be performed to ensure the absence of chlorine in the materials employed.

(*c*) The lime combustion method gives good results as a qualitative test, although it will often fail to detect very minute traces, say below 0·08 per cent. It is carried out as follows:—

A mixture of 1 c.c. of benzaldehyde and 5 grams of lime are placed in the bottom of a platinum crucible about 3 ins. in depth, a layer of lime placed on the top and the crucible covered and gently heated; a considerable escape of benzaldehyde takes place, so that it is obvious that the results can have no quantitative value.

The temperature is then gradually increased until no further vapours are driven off. The mixture is then dissolved in dilute nitric acid, filtered and tested in the usual manner with silver nitrate.

The method of Carius for the determination of chlorine in organic compounds is, of course, absolutely quantitative, but is very tedious, and is scarcely suitable for the detection of very small traces of chlorine, as the weight of oil taken in a Carius determination never exceeds 0·5 grams.

Salamon has recommended the following method, and appended are the results obtained compared with those yielded by the Carius' method and the obviously inadequate lime method.

About 2 grams of benzaldehyde are heated in a retort with 40 c.c. of concentrated sulphuric acid, the fumes collected in a solution of silver nitrate, and the heating continued until no further precipitate insoluble in hot dilute nitric acid is obtained in the silver nitrate solution. This takes about three hours.

The solution of silver nitrate is acidified with dilute nitric acid, boiled so as to decompose any silver sulphite that might have been formed, and the precipitate filtered, washed, etc.

A slight modification consists in using a mixture of 40 c.c. concentrated sulphuric acid and 5 c.c. concentrated nitric acid, the nitric acid being added last to the mixture of sulphuric acid and benzaldehyde.

The hydrochloric acid was evolved more rapidly, and slightly higher results were obtained in certain cases, due probably to better oxidation. By using this modification, a test can be easily carried out in one hour.

In using this method the heating must be very gradual, the mixture should not be allowed to froth until the end of the operation, and a blank should be carried out on the reagents used.

In cases where the amount of chlorine is very small such as ·005 per cent., it is advisable to carry out, say, distillations on 5 separate quantities of about 2 grams each, collecting them all in the same receiver.

By this means an appreciable amount of precipitate can be obtained, and definitely identified.

No.	Lime Method, Chlorine, per Cent.	Sulphuric Acid Method, per Cent.	Nitro-sulphuric Acid Method, per Cent.	Carius Method, per Cent.
1	·19	1·83	2·14	2·2
2	Not weighable.	0·13	0·13	0·15
3	·20	1·8	1·9	2·0
4	·19	1·7	1·7	1·9
5	nil.	trace	trace	trace
6	·17	—	1·63	—
7	·28	—	2·66	—
8	·17	—	1·42	—

THE DETERMINATION OF HYDROCARBONS.

The determination of hydrocarbons is not often required, but is a matter of some importance in the case of the so-called terpeneless and sesquiterpeneless oils, especially those of lemon, many commercial samples of which contain appreciable quantities of hydrocarbons.

Böcker[1] has elaborated the following method for the determination of the hydrocarbons present in concentrated oils of lemon —

Citral is first estimated in 10 c c of oil by the sulphite method. When the oil which has not entered into reaction is less than 6 c c, the estimation is repeated with another 5 or 10 c c The oil left over from these tests is bulked, and 5 c c of this citral-free oil is placed in a 600 to 700 c c separator, into which, immediately previously, 500 c c. of alcohol of precisely 51 per cent by volume, cooled down to from 0 to – 2° C., has been introduced The separator is closed with a cork and the contents are repeatedly shaken, when the aromatic bodies of the oil are dissolved by the alcohol, while the hydrocarbons are left behind almost quantitatively The separator is then placed in a cooling-bath at 0° C, cork downwards, for six to ten hours It is then taken out of the freezing mixture, carefully turned back to its proper position, and placed in a stand When the alcoholic solution has cleared to a point at which only a slight film remains (which in certain conditions may take up to two days) it is drawn off to about 10 c c, any oil-drops which may still adhere to the sides of the funnel being rinsed down with ice-cold 51 per cent alcohol, so that all the oil which has remained undissolved is brought together When the mixture has become perfectly clear, the oil, being freed as far as possible from the last traces of alcoholic solution, is transferred to a measuring tube calibrated to $\frac{1}{10}$ c c, and the vessel rinsed out with a little more ice-cold 51 per cent alcohol It is advisable to use a separating funnel of which the lower part ends in a narrow graduated tube As soon as the oil is completely cleared (when the froth is very persistent a few drops of dilute acetic acid should be added), the volume is read off and calculated to the original oil

The method may be completed by estimating not only the quantity but also the character of the hydrocarbons Thus, from 100 to 200 c c of oil is fractionally distilled *in vacuo* The distillation is only continued up to the point where the separate fractions of about 10 c.c each still show dextro-rotation These fractions are put together as the "terpene-containing portion" of the oil, the rest constituting the "sesquiterpene-containing portion" Each of these portions is then freed from citral by means of Na_2SO_3, and in both cases the residue is treated with 100 times its quantity of ice-cold 51 per cent alcohol, as described above, a large glass flask being, if necessary, substituted for the separator. The alcohol solution is separated by means of a siphon from the portion which has remained undissolved The oils which have been separated are estimated quantitatively and from the values thus obtained the percentage of terpenes and sesquiterpenes in the original oil is calculated For purposes of further identification the rotation is estimated, and, if necessary, the characteristic derivatives are prepared The terpenes, of which the principal constituen is *d*-limonene, are characterised by a pronounced dextro-rotation, they yield a liberal proportion of limonene tetrabromide, whereas the sesquiterpenes, which consist chiefly of bisabolene, are laevo-rotatory and may be identified from the bisabolene trihydrochloride

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[1] *Jour Prakt. Chem* (**1914**), 89, 199

THE HYDROGEN NUMBER OF ESSENTIAL OILS.

A new method for the examination of certain oils has recently been described by Allan R. Albright.[1]

Some unsaturated compounds are capable of quantitative hydrogenation in a solution of colloidal palladium. It has been found that a "hydrogen number" corresponding to the iodine number of fatty oils may be ascribed to some ethereal oils.

The colloidal palladium solution is prepared as follows: A solution of a palladium salt is added to a solution of an alkali salt of an acid of high molecular weight, the sodium salt of protalbinic acid being suitable. An excess of alkali dissolves the precipitate formed, and the solution contains the palladium in the form of a hydrosol of its hydroxide. The solution is purified by dialysis, and the hydroxide reduced with hydrazine hydrate. On further dialysis and evaporation to dryness a water-soluble product is obtained, consisting of colloidal palladium and sodium protalbinate, the latter acting as a protective colloid.

A substitute may be prepared thus: 0·05 gram palladous chloride is placed in a special shaking flask with 50 c.c of 50 per cent. alcohol and 1 or 2 c c. of 1 per cent. aqueous solution of gum-arabic, the weight of gum being about one-fourth the weight of the palladous chloride. On shaking this mixture in an atmosphere of hydrogen the chloride is reduced with formation of a black solution of colloidal platinum, which is rendered stable by the small quantity of gum present.

The apparatus used is somewhat complicated, and consists of shaking baskets containing the absorption flasks, which are connected with a gas burette and a hydrogen supply, the latter being purified by passing through a wash bottle containing alkaline permanganate, and afterwards washing with water. Arrangements are made to correct errors due to absorption of hydrogen by the catalyser, the solubility of the gas in the solvent, and the consumption of hydrogen by oxygen dissolved in the solvent. The weight of the substance taken is adjusted so that 100 c.c. or less of hydrogen is absorbed.

Every essential oil contains at least small quantities of unsaturated substances, such as terpenes (limonene phellandrene, etc.), but not all bonds are hydrogenated with equal ease. For instance, limonene is first reduced to carvomenthene, citral to citronellal, carvoxime to carvotanacetoxime, the second bond in each case requiring a considerably longer treatment for complete saturation. For such substances a quantitative determination is unsatisfactory. Some oils, however, contain substances which are completely and rapidly reduced, notably those containing the allyl or propenyl group. Safrol, anethol, and eugenol are the chief substances which have been studied, and these are reduced to dihydro-safrol, dihydro-anethol, and dihydro-eugenol. The pure substances have been compared with the natural oils of sassafras, anise, fennel, clove, and pimento, and with imitation oils made up of the active constituent and limonene.

The hydrogen number is defined as the number of c.c. of hydrogen corrected to normal temperature and pressure absorbed by 1 gram of the material during the period of rapid absorption. This number gives a measure of the proportion of active constituent present, but the results

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[1] *Jour. Amer. Chem. Soc.*, **1914**, 2188; through *P. and E.O.R.*

are generally too high because of the absorption of hydrogen by other constituents.

The results obtained are summarised in the following table:—

Substance.	Hydrogen Number.	Equivalent per Cent. of Active Constituent.	Theoretical per Cent. of Active Constituent.
Safrol	135·6	98·3	100·0
Limonene	—	—	—
Imitation sassafras oil . .	111·9	81·1	80·0
Authentic „ „ . .	103·1	74·8	—
	102·0	74·0	—
Anethol	150·5	99·6	100·0
Imitation anise oil . . .	125·1	82·4	80·0
	127·0	83·7	80·0
Commercial anise oil . . .	125·8	82·9	—
	127·3	83·9	—
„ fennel oil . .	101·3	66·8	—
	102·7	67·7	—
Eugenol	134·4	98·3	100·0
Imitation clove oil . . .	113·2	82·8	80·0
	113·3	82·8	80·0
Commercial clove oil . . .	114·6	83·8	—
	114·0	83·3	—
„ pimento oil . .	97·8	71·5	—
	97·8	71·5	—

THE DETECTION OF SOME COMMON ADULTERANTS.[1]

Turpentine Oil.—This is readily recognised in oils which contain no pinene, as this is the main constituent of turpentine oil. It is usually found in the first distillates, and generally reduces the specific gravity and effects the solubility and optical rotation. Its presence is proved by the formation of pinene hydrochloride (melting-point 125°) and the nitrosochloride (melting-point 103°). If pinene is a constituent of the oil itself, the addition of turpentine can only be proved by comparison with an authentic sample.

Cedarwood, Copaiba and Gurjun Balsam Oils.—These adulterants are usually found in the last fractions owing to their high boiling-points. They have a high specific gravity (·900 to ·950) and high refractive index, and are only soluble in strong alcohol. Copaiba oil rotates − 7° to − 35° (African up to + 20°), cedarwood − 25° to − 45°, and gurjun balsam − 35° to − 130°. No definite characteristic derivatives can be obtained. Gurjun balsam oil gives an intense violet colour when a few drops of nitric acid are added to a solution of the oil in glacial acetic acid.

Fatty Oils may be detected by leaving an oily stain on blotting paper after evaporation by gentle heat. With the exception of castor oil they are insoluble in alcohol. Castor oil dissolves in a small quantity of petroleum ether, but on further dilution with petroleum ether, it separates. Fatty oils usually increase the ester value of an oil, and a greater proportion of non-volatile residue is found on evaporation over a water-bath. Some volatile oils leave a residue on evaporation, *e.g.* bergamot, lemon, orange, nutmeg, ylang-ylang, and cassia oils. The fatty oils do not distil

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[1] *P. and E.O.R.* (June, **1915**), 148.

without decomposition, and their presence may be proved by the acrolein test (heating with potassium bisulphate). Cocoanut oil may be detected by freezing.

Fatty acids may readily be detected by the increase in acid value.

Petroleum or mineral oil (kerosene, etc.) are less soluble in alcohol than most oils. They have a low specific gravity and refractive index, and are not saponified by alcoholic potash. The lower boiling fractions can usually be detected by their odour, and the higher boiling fractions remain in the residue on fractional distillation. They are unaffected by fuming nitric acid.

Alcohol and acetone may be detected by their low boiling-point and by the iodoform test. Oils containing alcohol form milky mixtures with water. It may be extracted by washing with water, when the refractive index of the washed oil is found to be distinctly higher than that of the original oil.

Chloroform is readily recognised by its odour and by the phenyl isonitrile test. It is found in the first fractions distilled.

Resin is frequently found in cassia oil. It interferes with the accurate determination of the aldehyde by making it difficult to read off the uncombined oil. It may be detected by adding a solution of lead acetate in 70 per cent. alcohol to a solution of the oil in alcohol of the same strength. The presence of resin increases the amount of non-volatile residue, and also increases the acid value of the oil.

The proportion of resin can be determined by weighing the precipitate formed with solution of lead acetate in 70 per cent. alcohol.[1]

Terpenes are commonly employed for diluting lemon, orange, and bergamot oils. The addition lowers the specific gravity, increases the optical rotation, and lowers the proportion of oxygenated constituents. Terpinolene, a by-product in the manufacture of terpineol, has been detected in some oils, notably citronella and spike, lavender. It can be detected by its odour in the fractionated oils.

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[1] *P. and E.O.R.*, **1914**, 264.

THE END.

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