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NOTES ON ESSENTIAL OILS

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NOTES ON ESSENTIAL OILS

NOTES ON
ESSENTIAL OILS

WITH SPECIAL REFERENCE TO

THEIR USE, COMPOSITION, CHEMISTRY, AND ANALYSIS

BY

T. H. W. IDRIS, F.C.S.

WITH TABLES OF CONSTANTS OF THE MORE COMMONLY OCCURRING OILS

SECOND EDITION

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PREFACE

The accompanying notes on Essential Oils are, as was pointed out in the first edition, in no sense intended as a Text Book on the subject. They are merely intended as a laboratory note-book, the utility of which has been demonstrated in the author's laboratory. Should they be found as useful elsewhere, as the cordial reception met with by the first edition indicates, the author will consider his trouble well repaid. Since the appearance of the first edition three comprehensive text-books on this subject have appeared, one very able work in English by E. J. Parry, one in German by Guildemeister and Hoffmann, and one in French by Charabot, Dupont and Pillet. To these works the reader is referred for fuller information on the subject. The author takes this opportunity of acknowledging the assistance he has derived from these works and to thank Messrs. Scott, Greenwood and Co., for permission to reproduce in full the table of constants from Parry, "The Chemistry of Essential Oils and Artificial Perfumes."

PRATT STREET,
CAMDEN TOWN, N.W.
1900.

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NOTES ON ESSENTIAL OILS

CHAPTER I.

THE CONSTITUENTS OF ESSENTIAL OILS.

THE bodies which are usually found in most essential oils may, with very few exceptions, be grouped under the following headings: (1) The Terpene and Camphor series; (2) Benzene derivatives; (3) Methane derivatives; (4) The Geraniol series. In this order they will be briefly described in the present chapter.

(I.)—THE TERPENE AND CAMPHOR GROUP.

The chemistry of the terpenes and the closely related oxygenated bodies is at present to a certain extent in a transition stage, and indeed the instability of many of the members of this group, and their consequent tendency to isomeric change have rendered their study exceedingly difficult. For the purpose in hand, a short and succinct account of the properties of the chief compounds whose chemical individuality is practically certain, will suffice. Many of the properties and relationships of some of these bodies are as yet somewhat hypothetical, so that much concerning this group must at present be received with caution. The hydrocarbons or terpenes, and the oxygenated bodies allied to them, here form two natural groups.

(α) THE TERPENES.

A large number of terpenes have from time to time been described, but a careful examination of the literature of the subject enables them to be reduced to something like a dozen well defined hydrocarbons of the formula $C_{10}H_{16}$. In addition to these the so-called hemiterpenes C_5H_8 and sesquiterpenes $C_{15}H_{24}$ are well defined, and the latter will be noticed later.

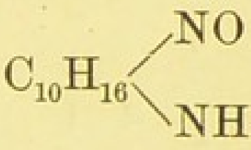
The present state of our knowledge of these compounds is very largely due to the systematic study of them undertaken by Wallach during the past ten years. Our own countrymen Armstrong and Tilden are well known for their valuable work on these bodies; but our more recent knowledge of them is chiefly due to Wallach, Tiemann, Baeyer, Bruhl and other Continental chemists. The most well defined hydrocarbons are the following:—Pinene, Camphene, Limonene, Dipentene, Sylvestrene, Carvestrene, Phellandrene, Fenchene, Terpinene, Terpinolene, and Thujene.

Pinene $C_{10}H_{16}$ is the chief constituent of French and American turpentine, and occurs in many other essential oils. It has from time to time been described under various names, such as terebenthene, australene, eucalyptene, laurene, olibene and eudesmene. But all of these bodies are merely more or less impure forms of the terpene which we now know as pinene. It occurs naturally in both optically active varieties, the chief source of dextro-pinene being American turpentine oil, whilst French turpentine consists chiefly of laevopinene; when obtained from natural sources by fractional distillation, however, pinene is never quite pure, so that its exact characteristics are matters of uncertainty. It is a colourless liquid of characteristic odour, and of specific gravity, about 0·860 at 15°, boiling at about 155°-156°. Wallach has prepared chemically pure *inactive* pinene by heating pinene nitrosochloride with aniline, when the following reaction occurs:—

$$\underset{\text{pinene nitrosochloride}}{C_{10}H_{16}NOCl} + \underset{\text{aniline}}{2C_6H_5NH_2} = H_2O + HCl +$$

$$\underset{\text{Amidoazobenzene}}{C_6H_5N_2C_6H_4NH_2} + \underset{\text{pinene}}{C_{10}H_{16}}$$

Pinene so obtained is an optically inactive liquid, boiling at 155°-156°, of specific gravity ·858 at 20° and ·854 at 25°. Its refractive index is 1·46553 at 21°. It is unsaturated and forms several well defined additive compounds. Thus, if dry hydrochloric acid be led into dry pinene, a molecule of the gas is added and a saturated compound, pinene hydrochloride $C_{10}H_{16}\cdot HCl$, is obtained, which melts at 125°. This body is commonly known as artificial camphor. It loses the molecule of hydrochloric acid by boiling with glacial acetic acid and sodium acetate, but the regenerated terpene is not pinene, but camphene, showing that an intramolecular change has taken place. Pinene also unites with a molecule of bromine, to form the compound $C_{10}H_{16}Br_2$, a crystalline compound melting at 169°-170°, and, according to Tilden, with 2 molecules to form a tetrabromide. This latter compound, however, requires confirmation. A characteristic nitrosochloride is obtained as a crystalline substance melting at 103° by acting on pinene with nitrosyl-chloride or amyl-nitrite, acetic and hydrochloric acids. This body has the formula $C_{10}H_{16}NOCl$, and is of great value in identifying pinene, on account of its sharp melting point. When the nitroso-chloride is treated with alcoholic solution of potash, nitroso-pinene results, of the formula $C_{10}H_{15}NO$. The pure compound melts at 132° and yields, on reduction, pinylamine $C_{10}H_{15}NH_2$. The action of organic bases on the nitroso-chloride and allied compounds, both of pinene and many of the other terpenes, gives rise to a series of compounds termed the nitrolamines. For example, with piperidine pinene forms a pinene-nitrolpiperidine, melting at 118°. These compounds possess sharp melting points, and are of use in identifying the terpenes. They have the general formula :—

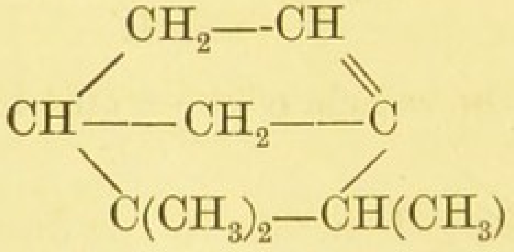


$$C_{10}H_{16}\begin{cases} NO \\ NHR' \end{cases}$$

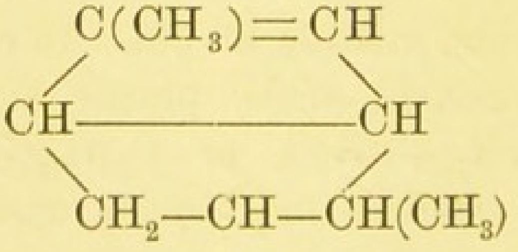
where R′ is the radicle of the amine base.

The prolonged action of hydrochloric acid appears to cause a re-arrangement of the molecule to dipentene, with the formation of dipentene dihydrochloride, melting at 50°. In contact with water and certain acids, pinene forms terpin hydrate $C_{10}H_{16}+3H_2O$, or $C_{10}H_{18}(OH)_2+H_2O$. This body crystallizes in rhombic crystals melting at 117°. At 100° they lose water and become terpin, $C_{10}H_{18}(OH)_2$, which by the separation of H_2O goes into terpineol $C_{10}H_{17}(OH)$.

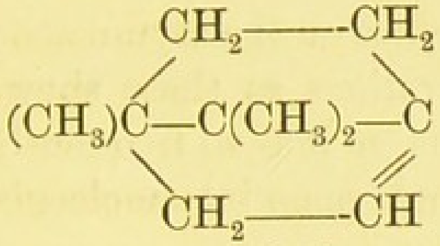
Many constitutional formulæ have been advanced by various workers for pinene, but none of them can at present be regarded as more than quite speculative, as practically no synthetical work has yet been effected on the body, and owing to the instability of the molecule, the apparent relationships between products of reactions cannot be depended upon. The formula of Tiemann, Wallach and Bredt are those which receive most support, but which is the one representing the true constitution of the terpene is by no means certain. Their formulæ are as follows :—



Tiemann.

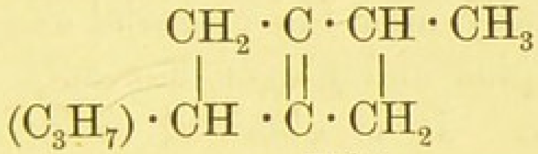


Wallach



Bredt

Quite recently Tilden has proposed the following formula to account for the combination of pinene with four atoms of bromine, which he maintains takes place :



$$\begin{array}{rcccl} & CH_2 & \cdot C \cdot & CH \cdot CH_3 \\ & | & \| & | \\ (C_3H_7)\cdot & CH & \cdot C \cdot & CH_2 \end{array}$$

Tilden

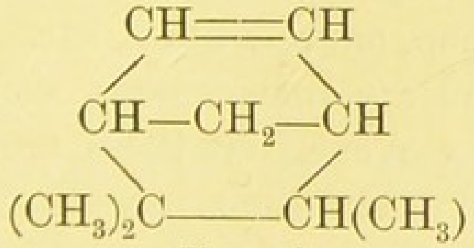
But this formula does not agree with the reactions of pinene as well as those quoted above.

The difficulty of arriving at any decision on the question has been well emphasized by Armstrong, who, in a note published in the Proceedings of the Chemical Society (1896. 161. 44) points out that it is certain that pinene must contain at least one asymmetric carbon atom—which cannot be one possessing an ethylenic linkage C=, for this at once destroys the asymmetry of the atom. Yet bromine and nitrosyl chloride give optically inactive derivatives capable of yielding inactive pinene. Thus apparently the addition of the two atoms at the point where a double linkage exists, appears to exert some peculiar influence on the asymmetric carbon atom. Such considerations as these show how difficult the question is, as it is so frequently uncertain as to what extent some intramolecular change has or has not gone on.

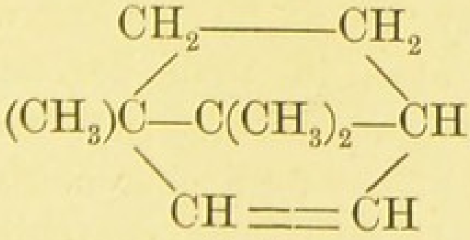
Camphene, $C_{10}H_{16}$, is the only solid terpene known, and, although occurring in nature to a very small extent, is important on account of its relations to the other terpenes and to camphor. It occurs naturally in a few essential oils such as citronella, camphor and ginger, but only in very small quantity. It is obtained artificially by eliminating hydrochloric acid from pinene hydrochloride as above mentioned, or from camphor by reducing it to borneol, converting this into bornyl chloride, $C_{10}H_{17}Cl$, and boiling this with aniline to abstract HCl. It is also formed by the action of heat in the presence of acetic acid on bornylamine, $C_{10}H_{17}NH_2$, which causes the withdrawal of ammonia, leaving camphene, thus:—

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

The latter method gives inactive camphene, whereas the pinenes give rise to dextro- or laevo-camphene according to their own rotation. Camphene melts at 49°-50°, or according to Brühl at 51°-54°, and has a specific gravity of about 0·860 and boils at about 160°. It forms a monohydrochloride $C_{10}H_{16}HCl$, which does not boil without decomposition. Bromine appears to form a substitution compound, $C_{10}H_{15}Br$, but quite recently Reychler has described a camphene dibromide, $C_{10}H_{16}Br_2$, forming doubly refracting prisms melting at 90°. The actual constitution of this compound is a matter of doubt, as no synthetic evidence has yet been adduced on the question; and, until the constitution of camphor and some of its allies is settled definitely, it is probable that that of camphene will remain a matter of doubt. The difficulty of the problems to be solved here is enhanced by the fact that the derivatives of camphene are less stable than those of pinene. Tilden has suggested a formula in harmony with that he gives for pinene, and many other chemists have done the same; but the most satisfactory, as far as can, at present, be judged, are those of Tiemann and Bredt as under :—



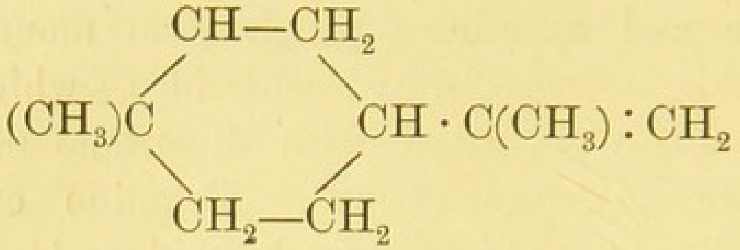
Tiemann



Bredt

Fenchene, $C_{10}H_{16}$, is a terpene which does not appear to exist in nature, or if so, only to a very small extent. It is a liquid boiling at about 160°, optically inactive, with a refractive index of 1·4690. Its specific gravity is ·864 at 20°. It unites with two atoms of bromine forming an oily dibromide, which has not been obtained in a state of purity. Fenchene bears the same relation to fenchone as camphene does to camphor. Fenchone $C_{10}H_{16}O$ on reduction yields fenchyl alcohol $C_{10}H_{18}O$. This can be converted into fenchyl chloride $C_{10}H_{17}Cl$ which on heating with aniline yields fenchene $C_{10}H_{16}$. This terpene is exceedingly stable, resisting the action of nitric acid in the cold far more than the other terpenes.

Limonene, $C_{10}H_{16}$, is one of the most widely diffused of the terpenes, and occurs largely in essential oils from plants of the Aurantiaceæ, such as oils of lemon, orange, limes, etc. It has been described under various names, such as citrene, hesperidene, carvene, but these are merely impure forms of dextro-limonene. Both dextro- and laevo-limonene are agreeably smelling liquids of specific gravity ·846 at 20°, boiling at 175°-176°. They differ, even in their derivatives, almost entirely in their optical activity, which is equal and opposite. They form characteristic dihydrochlorides $C_{10}H_{16}(HCl)_2$, in contradistinction to pinene and camphene which form monohydrochlorides. These dihydrochlorides, which are inactive, are identical with dipentene dihydrochloride, melting at 50°. Bromine converts both limonenes into tetrabromides, $C_{10}H_{16}Br_4$, crystallizing in large prisms, melting at 104°. Amyl nitrite and hydrochloric acid give rise to nitrosochlorides, $C_{10}H_{16}(NOCl)$. In both cases these melt at 103°. By crystallization from chloroform, each of these nitroso-chlorides can be separated into two isomeric bodies, the α and β forms, the latter having a smaller rotary power than the former. Whether these are stereoisomers or polymers, is hardly certain. Considerable light is thrown on the chemistry of limonene by the fact that the nitroso-chlorides when boiled with alcohol, give up HCl and yield nitroso-limonenes $C_{10}H_{15}(NO)$ melting at 72°. In the case of the dextro-body this is found to be identical with dextro-carvoxime obtained from carvone and hydroxylamine, whose constitution is fairly well understood as an oxycymene derivative. The laevo-compound corresponds in every way to this. Peculiarly enough, the dextro-nitroso chloride yields the laevo-nitroso limonene (carvoxime), and the laevo-nitroso-chloride yields dextro-nitroso limonene. The constitution of limonene is possibly

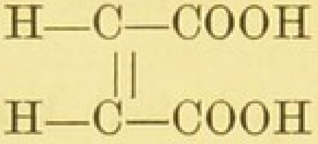


The following table gives the optical rotations of the various derivatives of limonene, showing how closely the experimental observations agree with the theoretical values (after Heusler).

	Prepared from – limonene.	 + limonene.
Limonene	– 105°	+ 106·8°
Limonene tetrabromide	– 73·45°	+ 73·27°
α limonene nitrosochloride . .	– 314·8°	+ 313·4°
β limonene nitrosochloride . . .	– 242·2°	+ 240·3°
α limonene nitrobenzylamine . .	– 163·6°	+ 163·8°
,, ,, hydrochloride .	+ 83·06°	– 82·26°
,, ,, nitrate	+ 81°	– 81·5°
,, ,, dextro-tartrate	+ 69·6°	– 69·9°
,, ,, laevo-tartrate .	+ 51°	– 49·9°
Carvoxime	+ 39·71°	– 39·34°
Limonene monohydrochloride . .	+ 39·5°	– 40°

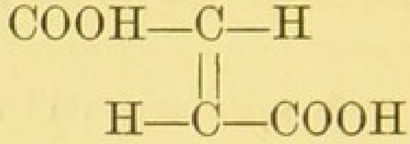
Dipentene was at first regarded as a distinct terpene of different constitution to those hitherto known. It is now certain, however, that dipentene, which is optically inactive, is merely inactive limonene. It can be obtained by mixing equal quantities of the two limonenes, and its derivatives, in the same way, result by mixing equal quantities of the oppositely active limonene derivatives. It therefore stands in the same relation to the limonenes as racemic acid does to the active tartaric acids. It occurs naturally in many oils, and results by heating many other terpenes either alone or with sulphuric acid to a moderately high temperature, which is, of course, quite in accord with the known properties of optically active bodies, many of which are rendered inactive by heat, and with the instability of the molecule of many terpenes. Its specific gravity is ·853, and its boiling point 176°-178°. Hydrochloric acid forms a dihydrochloride, melting at 50°, identical with that from both limonenes, as previously mentioned, and bromine gives a tetrabromide melting at 124°-125°. A direct mixture in equal quantity of dextro- and laevo-limonene tetrabromides melting at 104° yields this tetrabromide of higher melting point, which is most unusual with the so-called "racemic" isomers. The nitroso-chloride melts at 103°, whereas the nitroso-dipentene $C_{10}H_{15}(NO)$, identical with inactive carvoxime, melts at 93°, or 21° higher than either of its active isomers, which melt at 72°.

During the last few years Baeyer has extended his researches on the so-called "cis-trans" isomerism, that is, position isomerism of the maleic and fumaric acids type, to the terpenes, especially dipentene or as it is more correctly called, i-limonene. This isomerism covers compounds of the type—



$$\begin{array}{l}\mathrm{H{-}C{-}COOH}\\ \quad\ \ \|\\ \mathrm{H{-}C{-}COOH}\end{array}$$

Maleic acid



$$\begin{array}{r}\mathrm{COOH{-}C{-}H}\\ \|\qquad\qquad\\ \mathrm{H{-}C{-}COOH}\end{array}$$

Fumaric acid

Baeyer has found that the dihydrochloride and dihydrobromide of dipentene exist in the two forms, of which he provisionally designates those of the lower melting points the *cis*-series, and those of the higher melting points the *trans*-series. The usually occurring dipentene dihydrochloride melts, as mentioned above, at 50°. The *cis*-form, prepared from eucalyptol (cineol) and hydrochloric acid, melts at 25°. The usual dihydrobromide melts at 64°, while the *cis*-dihydrobromide, prepared from eucalyptol and hydrobromic acid, melts at 39°. From both forms ordinary dipentene is easily regenerated.

Sylvestrene, $C_{10}H_{16}$, is one of the most stable of the terpenes, and is a constituent of Russian and Swedish oils of turpentine. It boils at 175°-178° and is known only in the dextro-rotary form, unless, indeed, carvestrene is optically inactive sylvestrene, as is probable. It combines with two molecules of bromine or hydrochloric acid. The tetrabromide $C_{10}H_{16}Br_4$ melts at 135°. The dihydrochloride $C_{10}H_{16}(HCl)_2$ melts at 72°, and the dihydrobromide at the same temperature. The nitroso-chloride $C_{10}H_{16}NOCl$ melts at 106°.

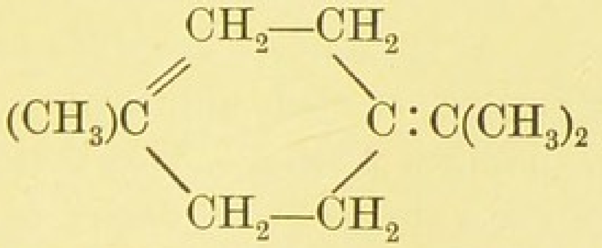
Carvestrene, mentioned above, is an optically inactive terpene prepared artificially from carone, and probably bears the same relation to the sylvestrenes as dipentene does to the limonenes. The constitution of these terpenes is unknown. Sylvestrene gives a very beautiful and characteristic blue colour with acetic anhydride and concentrated sulphuric acid.

According to Wallach, sylvestrene can be prepared in a state of approximate purity by diluting the fraction of Swedish oil of turpentine, which boils at 174°–178°, with an equal volume of ether, and saturating it with hydrochloric acid gas. The whole is allowed to remain for two days, the ether is then distilled off, and the residue crystallizes. The dihydrochloride $C_{10}H_{16} \cdot 2HCl$ is purified by re-crystallization, when it melts at 72°. From this the hydrocarbon is regenerated by heating with aniline. Carvestrene does not occur in nature, but may be prepared by distilling carylamine hydrochloride $C_{10}H_{17}NH_2 \cdot HCl$ in an atmosphere of dry hydrochloric acid gas. It is optically inactive, and boils at 178°. Its dihydrochloride melts at 52·5°.

Phellandrene, $C_{10}H_{16}$, a terpene boiling at 170° or thereabouts, was originally obtained and described by Pesci. Whilst the general properties given by this chemist were correct, it is most probable that he did not obtain it in a state of purity. Recent additions to the chemistry of this body are chiefly due to Wallach. The dextro-rotary variety is found in oil of water fennel (*Phellandrium aquaticum*), and the laevo-rotary in certain eucalyptus oils. The halogen addition products are not so well defined as are those of many of the terpenes, but it forms a very characteristic nitrite, $C_{10}H_{16}N_2O_3$. To prepare this derivative, the following directions are given by Wallach. The hydrocarbon, diluted with petroleum, is placed in a beaker surrounded by a freezing mixture. Dilute sulphuric acid is added, and solution of sodium nitrite slowly run in, the temperature being kept below 4°. Both the nitrites melt at 103°, and are identical in their properties, except in their optical activity. That from d-phellandrene is laevo-rotary and that from l-phellandrene is dextro-rotary. Numerous derivatives can be obtained from these nitrites, from a study of which it is clear that the constitution of phellandrene is closely related to that of carvone. The formation of the nitrite is now the official test of the British Pharmacopoeia for phellandrene in oil of eucalyptus.

Terpinene $C_{10}H_{16}$ is a very stable terpene, resulting from the isomerisation of other terpenes, and occurring in nature to a small extent. It forms a nitrosite $C_{10}H_{16}N_2O_3$, which melts at 155°. It also forms liquid products with the halogens. Terpinine boils at about 180°. It has been stated by Weber to occur in oil of cardamoms.

Terpinolene $C_{10}H_{16}$ also results from the isomerisation of other terpenes with sulphuric acid. It boils at 185°-190° and forms a tetrabromide melting at 116°. The dihydrochloride appears to be identical with that of dipentene. Baeyer considers the constitution of terpinolene to be



Thujene $C_{10}H_{16}$ is a terpene prepared from oil of thuja, but which, so far, appears not to exist naturally. It is prepared by submitting to dry distillation the hydrochloride of thujylamine, a base prepared from thujone, one of the constituents of oil of thuja. In all probability this terpene is identical with tenacetene, a terpene described by Semmler, which he prepared from one of the constituents of oil of tansy (*Tanacetum vulgare*).

Thujene boils at 170°-172°, has a specific gravity of ·836-·840, and a refractive index of 1·47145 at 20°. It contains two ethylenic unions, and differs from all the other terpenes, in yielding an intense red colouration, when a drop of concentrated sulphuric acid is added to its solution in acetic acid.

A number of bodies, having the same empirical composition as the terpenes, but differing in molecular weight, occurs in nature. Of these, the only ones of importance are the sesquiterpenes, compounds of the formula $C_{15}H_{24}$. A number of these have from time to time been described, but very little evidence in favour of their chemical individuality has, so far, been adduced, except in a few cases. A systematic classification will, in all probability, reduce their number to a comparatively few definite bodies. The better defined sesquiterpenes, which will be described here, are cadinene, cedrene, caryophyllene, clovene, humulene, ledene, and patchoulene; the others are of less importance and interest.

Cadinene $C_{15}H_{24}$ occurs in patchouli, galbanum, cade, and other oils. It is prepared by heating the dihydrochloride with aniline or sodium acetate. The boiling point of the pure sesquiterpene is 274°-275°, its specific gravity at 20° is ·918, and its optical rotation +98·6°. To prepare the dihydrochloride, the fraction of oil of cade (*Juniperus oxycedrus*) boiling at 260°-280° is dissolved in twice its volume of ether, and saturated with dry hydrochloric acid gas. After standing for a day, half the ether is distilled off; by further evaporation the dihydrochloride crystallizes out. This melts at 117°, and is laevo-rotary to the extent of $-36{\cdot}8°$. The dihydrobromide $C_{15}H_{24}2HBr$. melts at 124°, and is also laevo-rotary $[a]_d = -36{\cdot}13°$. The dihydriodide melts at 105°, is laevo-rotary $[a]_d = -48°$.

Caryophyllene $C_{15}H_{24}$ occurs in clove, copaiba and other oils. It is difficult to purify, and, indeed, it is very doubtful whether it has yet been obtained pure. The approximately pure sesquiterpene, obtained by fractional distillation of oil of cloves, boils at 258°–260°, and has a specific gravity of ·9085 at 15°. Its individuality was characterized by Wallach and Walker by converting it into caryophyllene alcohol $C_{15}H_{26}O$. This is best achieved by dissolving 25 grammes of the fraction of clove oil boiling at 250°–260° in a mixture of glacial acetic acid (1 kilo.) and concentrated sulphuric acid (20 gr.) and water (40 gr.) and heating the solution on the water bath for 12 hours. On distillation, at the end of the operation, the alcohol comes over and solidifies in the neck of the retort, and can be obtained pure by recrystallization from ethyl alcohol. It then melts at 96°. By heating with dilute acids or P_2O_5, it gives up a molecule of water and reforms a sesquiterpene. But a molecular re-arrangement takes place, so that instead of obtaining pure caryophyllene, one obtains *Clovene*, an isomeric sesquiterpene. Caryophyllene nitroso-chloride $C_{15}H_{24}NOCl$ forms a white powder melting at 161°–163°. The nitrosate $C_{15}H_{24}N_2O_4$ is formed by the action of amyl nitrite, acetic acid and sulphuric acid. It forms needles melting at 148°.

Clovene $C_{15}H_{24}$ is obtained as described above. It boils at 261°-263°, has a specific gravity of ·930 at 18° and a refractive index of 1·50066. It does not yield a crystalline alcohol, so that it is clearly not identical with caryophyllene.

Cedrene $C_{15}H_{24}$ occurs in cedar wood oil. It has so far been prepared only by fractional distillation of the oil, unless, indeed, the hydrocarbon obtained by heating cedar camphor (cedrol) with acetic anhydride is identical with it. According to Chapman the boiling point of cedrene is 261°-262°, the specific gravity at 15° is ·9359, and the optical activity $[a]_d = -60°$. According to Rousset, however, its rotation is only $-47·9°$. A hydrocarbon of a very similar nature is produced by the action of P_2O_5 on santalal, the aldehyde of sandal wood oil, but its alleged identity with cedrene is by no means established.

Humulene $C_{15}H_{24}$ occurs in oil of hops. It boils at 263°-266°, and has a specific gravity of ·9001 at 20°. It yields a liquid tetrabromide $C_{15}H_{24}Br_4$ and dihydrochloride $C_{15}H_{24}2HCl$. A crystalline nitrosochloride $C_{15}H_{24}NOCl$ has been obtained by Chapman, also a nitrosate $C_{10}H_{24}N_2O_4$ melting at 162°. This hydrocarbon has also recently been stated to occur in the oil of poplar buds.

Ledene $C_{15}H_{24}$ is a sesquiterpene which has not been found in nature, but is prepared by dehydrating ledum camphor $C_{15}H_{26}O$, a crystalline body obtained from *Ledum palustre*. The sesquiterpene boils at 255°, but its general properties are not well understood.

Patchoulene $C_{15}H_{24}$ is also obtained by dehydrating its corresponding alcohol, patchouli camphor $C_{15}H_{26}O$. This sesquiterpene boils at 254°, has a specific gravity of ·939 at 23° and a refractive index 1·5009. It resembles oil of cedar wood in odour.

Very little is understood of the exact chemical relationships of the sesquiterpenes, other than that they are intimately connected with the terpenes proper. The same remark applies to other "condensed" terpenes, such as the di-terpenes and tri-terpenes.

(β) THE CAMPHOR GROUP

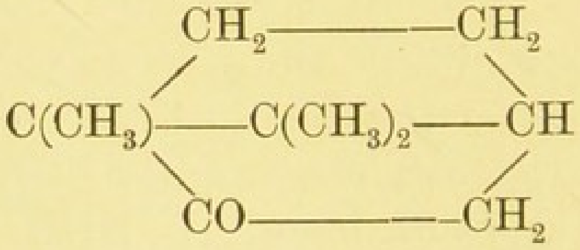
Under this head, those bodies containing oxygen, which show an intimate relationship with the terpenes, will be dealt with. It is necessary to preface this section, however, with the following remarks. There are so many of these bodies, both naturally occurring and artificially prepared, that only the more important can be dealt with here. Further, the chemistry of this group of compounds is in a transition stage, and so much work has recently been published on camphor and its allied compounds, that only the barest outlines of the most important work can be touched upon. In the hands of Tiemann, Bredt, Wallach, Beckmann, Brühl, Perkin, Marsh, Kipping and others, the camphor question has begun to assume something approaching a definite shape, but so many difficulties await clearing up, that we are still much in the dark as to the constitution and relationships of these bodies.

Camphor $C_{10}H_{16}O$ occurs in the dextro-rotary form in the wood and other parts of camphor tree (*Laurus camphora*), and as laevo-rotary camphor in the oil of *Matricaria parthenium*. It also results from the oxidation of borneol with nitric acid, and, in small quantities, from the oxidation of camphene. Inactive camphor results by mixing equal quantities of the optically active varieties.

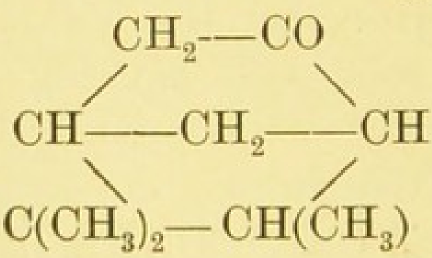
It forms a colourless, transparent mass, crystallizing well from alcohol, and easily sublimes in long shining prisms. The optically active varieties melt at 175°, and boil at 204°. $[a]_d = 44{\cdot}22°$, and specific gravity at $20° = {\cdot}985$. The inactive variety melts at 178°-179°. Distilled with P_2O_5 camphor yields cymene (methyl-propyl-benzene), and with iodine, carvacrol (oxycymene). Reduction with sodium and alcohol produces borneol, which is related to camphor as an alcohol to a ketone. By oxidation, various acids are produced, amongst which the most important are, camphoric and camphoronic acids. The following are amongst the most characteristic derivatives of camphor. Camphoroxime $C_{10}H_{16}{\cdot}NOH$, prepared by the action of hydroxylamine on camphor, melts at 118°. On reduction this yields bornylamine $C_{10}H_{17}NH_2$, a solid base melting at 160°. By the action of acetyl chloride it yields campholene nitrile, $C_9H_{15}{\cdot}CN$, which on hydrolysis yields campholenic acid $C_9H_{15}{\cdot}COOH$, a liquid acid boiling at 258°-261°, of specific gravity ·992 at 20°. Phenylhydrazine gives a hydrazide $C_{10}H_{16}(N_2H.C_6H_5)$. Isonitrosocamphor $C_{10}H_{14}O\ (NOH)$

is obtained by the action of amyl nitrite and sodium ethylate on camphor. It melts at 153°. Sodium camphor $C_{10}H_{15}NaO$ separates when metallic sodium acts on camphor dissolved in benzene.

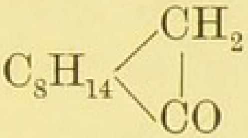
The chief products of the oxidation of camphor by nitric acid are, camphoric acid $C_{10}H_{16}O_4$, camphanic acid $C_{10}H_{14}O_4$, and camphoronic acid $C_9H_{14}O_6$. Of these, camphoric acid is the most important, as when its constitution is completely understood, that of camphor will become apparent. A study of these acids and their decomposition products induces Bredt, who has done a great deal of brilliant work in this group, to assign to camphor the formula



Tiemann, on the other hand, suggests



A recent partial synthesis of camphoric acid, by W. H. Perkin, lends support to Bredt's formula. Under any circumstances, it may be safely assumed that camphor is a ketone, containing the complex $\cdot CH_2\cdot CO$, of the formula



$$C_8H_{14}\left\langle \begin{array}{l} CH_2 \\ \ | \\ CO \end{array}\right.$$

Borneol is the alcohol corresponding to camphor and has the formula $C_{10}H_{17}OH$. This body, known commonly as Borneo camphor, occurs in nature both as dextro- and laevo- borneol, and in the racemic or inactive condition. It occurs both free and as esters. Dextroborneol is chiefly obtained from the wood of *Dryobalanops camphora.* The product from *Blumea balsamifera,* known as Ngai camphor, consists of laevoborneol. Valerian oil contains laevoborneol and inactive borneol. Reduction of camphor gives borneol, together with some isoborneol. Pure borneol melts at 203°-204°, and boils at 212°. On oxidation with nitric acid, camphor results. Bornyl chloride $C_{10}H_{17}Cl$, melting at 157°, is formed by the action of PCl_5 on the alcohol. Borneol forms a series of esters with the fatty acids, of which the boiling point increases, and the specific gravity and refractive index decrease, with a rise in the molecular weight of the fatty acid. The constitution of borneol is, of course, in intimate relationship with that of camphor. Isoborneol is also obtained by warming camphene with a mixture of sulphuric and acetic acids, and decomposing the resulting acetate with alcoholic potash. It crystallizes in laminae, melting at 212°. It forms compounds with chloral and bromal, as does borneol, the melting points of which are as follows :—

	Chloral.	Bromal.
Borneol,	55°	98°
Isoborneol,	liquid	71°

The relationship of borneol to isoborneol is not yet understood, but Jünger considers that they are geometrical isomers of otherwise identical constitution. This however is not probable. The following is a comparison of their properties, as given by Heusler :—

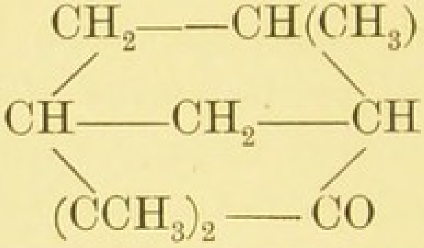
	Borneol.	Isoborneol.
Crystalline forms.	Hexagonal doubly refracting.	Hexagonal doubly refracting.
Melting point	203°	212°
Boiling point	212°	—
Solubility in benzene at 0° -	1 in 6·5 to 7	1 in 2·5 to 3
Solubility in petroleum ether at 0° - -	1 in 10 to 11	1 in 4 to 4·5
Chloral compound	melts at 55°	liquid
Bromal compound	melts at 98°	melts at 71°
Acetic ester -	melts at 29°, boils at 106° to 107° at 15 mm.	liquid; boils at 107° at 13 mm.

For further details of the compounds of camphor and borneol, references must be made to the original papers which have appeared in various chemical journals during the last few years.

There are numerous isomeric so-called camphors found in various essential oils, but little is yet known of them. The other bodies of this formula with which we shall deal are the better defined compounds, fenchone, thujone ("tanacetone") and pulegone, and the allied ketone, menthone $C_{10}H_{18}O$, with their corresponding alcohols. Cineol (eucalyptol) will also be noticed here.

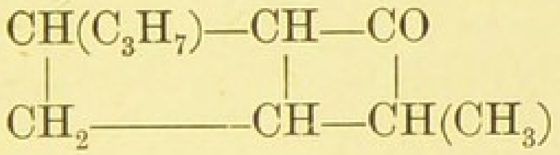
Fenchone $C_{10}H_{16}O$ occurs in oil of fennel as dextrofenchone and in oil of thuja as laevofenchone. In the former it is dextrorotary, in the latter laevorotary. Dextrofenchone is described by Wallach as a liquid isomeride of camphor, of specific gravity ·9465 at 19°, and boiling at 192°-193°. It forms a well defined oxime, $C_{10}H_{16}: NOH$, melting at 140°-149°, or, if quickly heated, at 161°. When kept at a low temperature, fenchone solidifies to a mass of hard crystals, melting at 5°. Its rotary power is +71·83°. To purify fenchone it is best converted into fenchyl alcohol $C_{10}H_{17}OH$, by reduction with sodium. This is a colourless crystalline compound, which can be purified by recrystallization, and then melts at 40°-41°. Oxidation converts it into fenchone. A chloride is obtained by treating the alcohol with PCl_5, which on heating with aniline yields a terpene, fenchene, already described.

Laevofenchone is easily obtained from oil of thuja. It melts at 5°, boils at 192°-194°, has a specific gravity of ·948 at 20°, and is laevorotary $[a]_d = -66{\cdot}94°$. By mixing equal quantities of the two modifications the inactive variety is obtained. Many of the compounds of fenchone are quite analogous to those of camphor; for example, fencholene nitrile $C_9H_{15}CN$, and fencholenic acid $C_9H_{15}COOH$, are formed in a similar way to the corresponding camphor compounds. A study of their derivatives leads Tiemann to assign to fenchone the formula



Wallach, however, considers that this body contains a four carbon and a five carbon ring.

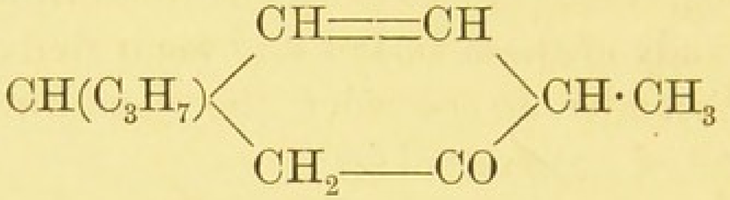
Thujone $C_{10}H_{16}O$ is a ketone isomeric with camphor and fenchone. It was first separated from oil of thuja by Jahns, and afterwards studied by Wallach. It is apparently identical with tanacetone, described by Semmler, from oil of tansy, and with salvone from oil of sage. It also occurs in oil of wormwood. It boils at 203°, has a specific gravity of ·9126 at 20°, and refractive index 1·4495. Its rotary power is about + 68°. It has the general characteristics of a saturated ketone. It forms several isomeric oximes, $C_{10}H_{16}:NOH$, of which the most stable melts at 55°, and yields, on reduction, thujonamine. On oxidation, thujone gives two isomeric ketonic acids, and a study of these bodies and their derivatives, leads Semmler to consider the constitution of thujone to be expressed by



$$\begin{array}{lll} \mathrm{CH(C_3H_7)} & \text{—}\mathrm{CH} & \text{—}\mathrm{CO} \\ | & \quad | & \quad | \\ \mathrm{CH_2} & \text{————}\mathrm{CH} & \text{—}\mathrm{CH(CH_3)} \end{array}$$

A tribromo-derivative $C_{10}H_{13}Br_3O$ is formed by the action of bromine on thujone. This melts at 121°. A characteristic semicarbazone has also been prepared, melting at 171°. Thujone can be prepared in a fairly pure state from oil of wormwood. 200 grammes of this oil and 200 cc. of a saturated solution of sodium bisulphite are well shaken with 75 cc. of water, and 300 cc. of alcohol, at intervals for a fortnight, and the resulting crystals separated and washed with alcohol-ether and the ketone set free by means of soda solution. It can be almost quantitatively converted into thujyl alcohol $C_{10}H_{17}OH$, by reduction with sodium and alcohol. This body has a specific gravity of

·9249, and refractive index 1·4635 at 20°. It boils at 93° under a pressure of 13 mm. When thujone is heated with strong sulphuric acid for 8 or 10 hours it is converted into isothujone, of the same formula, boiling at 232°, of specific gravity ·927, and refractive index 1·4822 at 20°. For this body Wallach suggests the formula



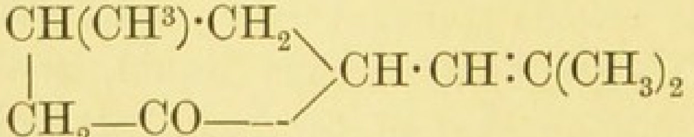
By heating to 280°, thujone is converted into an isomer, which has been termed carvotanacetone.

The properties of these three bodies are contrasted in the following short table :—

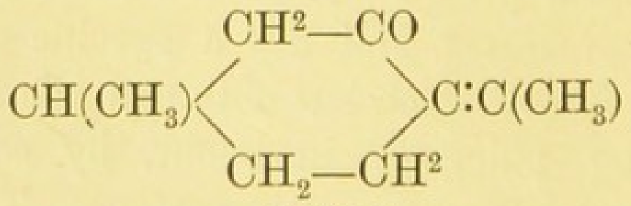
	Boiling point.	Sp. gravity.	Refractive index.
Thujone	200°–203°	·9175	1·45109
Isothujone . . .	231°–232°	·9285	1·48217
Carvotanacetone .	228°	·9373	1·48350

Pulegone $C_{10}H_{16}O$ is a ketone contained in the oils of *Mentha pulegium* and *Hedeoma pulegoides*. Beckman isolated it by distilling the oil and repeatedly fractionating under reduced pressure that portion boiling at 212°-216°. It was described by him as a colourless liquid, boiling at 130°, under a pressure of 60 mm., of specific gravity ·9323, and refractive index 1·4702 at 20°. Its rotary power is +22·89°. When purified, however, by means of the bisulphite compound, it boils, according to Wallach, at 221°-222°, has a specific gravity of ·936, and a refractive index of 1·4868 at 20°.

Amongst the more characteristic derivatives of pulegone may be mentioned the following. Pulegone hydrochloride $C_{10}H_{16}O.HCl$ is formed by acting on pulegone in acetic acid solution, with dry hydrochloric acid. It melts at 24°-25°. Pulegone oxime $C_{10}H_{16}:NOH$ melts at 118°-119°, and yields pulegoneamine on reduction with sodium. This latter body melts at 49°-50°. There appears also to be a liquid oxime isomeric with that just mentioned. When pulegone is reduced it yields pulegol, the corresponding alcohol, $C_{10}H_{17}OH$, a viscous liquid, with an odour resembling that of terpineol. It boils at 103°, under a pressure of 15 mm., and at 215° at ordinary pressures, and has a specific gravity of ·912 at 20°. Wallach has obtained a body closely resembling pulegone in odour, by condensing methyl-cyclohexenone with acetone. This body is isomeric with pulegone, and is termed pseudopulegone. Conversely, when pulegone is heated with formic acid, it yields acetone, and an isomeric methylcyclohexenone. A second closely related isomer, isopulegone, has been obtained by Tiemann and Schmidt. Citronellaldehyde is heated with acetic anhydride to 200° for 12 hours, when it yields an alcoholic body, isopulegol $C_{10},H_{18}O$, which has a strong odour of menthol. On oxidation this yields isopulegone $C_{10},H_{16}O$, which differs from pulegone in not forming a crystalline compound with sodium bisulphite. Further, pulegol and pulegone readily yield menthol when reduced with sodium, whilst isopulegone does not. Isopulegone has a specific gravity of ·921 at 18°, refractive index 1·4690, and rotary power +10·25°. By agitating it with barium hydroxide it is completely converted into pulegone, identical with the natural body. The formulae which most probably express the constitutions of these two ketones, are :—



Isopulegone.



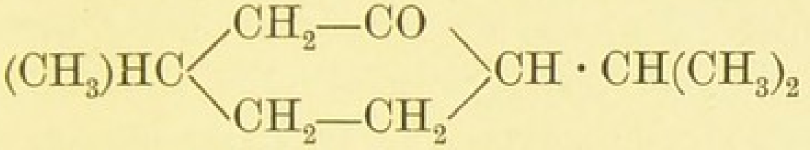
Pulegone.

The physical characters of the isomeric bodies referred to are contrasted in the following table :—

	Boiling point.	Sp. gravity.	Rotation.
Pulegol	215°	·912	–
Isopulegol . . .	91° (at 12 mm.)	·916	– 2° 7′
Pulegone . . .	221°	·936	+22° 9′
Isopulegone . .	90° (at 12 mm.)	·921	+10° 25′
Pseudopulegone .	215°	·918	–

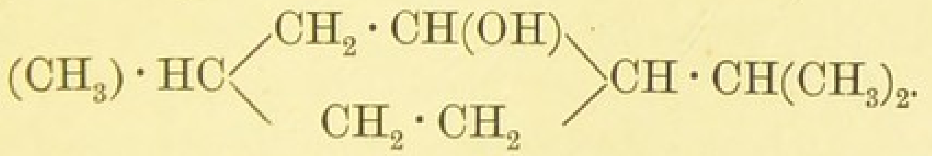
Menthone $C_{10}H_{18}O$ is by far the most important of the ketones of the formula $C_{10}H_{18}O$, on account of its intimate relationship with menthol. It occurs in nature in peppermint oil (in American oil to the extent of about 10 or 12 per cent.). Moriya obtained menthone by the oxidation of menthol with chromic acid, and described it as being optically inactive. This observation was shown to be incorrect by Atkinson, menthone obtained by him by Moriya's method having an activity of about + 21°. Beckmann prepared laevo-menthone by the oxidation of laevo-menthol. Laevo-menthone is easily converted into dextro-menthone by the action of acids, and *vice versa.* Neither isomer combines with sodium bisulphite. On reduction, menthone yields menthol, the corresponding alcohol, $C_{10}H_{20}O$. Atkinson described menthone as an oily liquid, boiling at 206°, and smelling like diluted peppermint oil. Its rotary power was given as $+21°$ (Beckmann gives it as $+26°$ to $+28°$), its specific gravity as ·897 at 20°, and its refractive index as 1·4528. Pure laevo-menthone boils at 208°, has a specific gravity of ·894, refractive index 1·4496 at 20°, and rotary power $+26°$. Menthone forms an oxime $C_{10}H_{18}:NOH$, in the case of dextromenthone a slightly laevorotary oil, and in the case of laevo-menthone a laevorotary solid, melting at 59°. It is possible that stereo-chemical relationships exist here, which are as yet not understood. On reduction, the oximes yield bases $C_{10}H_{19}NH_2$. These are both liquids, boiling at 206°, and as far as can be judged, both laevorotary. The action of P_2O_5 on the oximes gives the nitriles $C_9H_{17}CN$, which, in the case of the dextrorotary base, is of great interest, as Wallach has succeeded in preparing from menthone, by means of the nitrile, an open chain alcohol, which he terms mentho-citronellol. The semicarbazone of d-menthone $C_{10}H_{18}:N \cdot NH \cdot$

$CONH_2$ melts at 184°. In all probability menthone has the following constitution:—



$$(CH_3)HC\left\langle\begin{array}{l}CH_2—CO\\CH_2—CH_2\end{array}\right\rangle CH\cdot CH(CH_3)_2$$

Menthol, $C_{10}H_{19}OH$, the alcohol corresponding to menthone, occurs in peppermint oil, and is obtainable as mentioned previously, from menthone, by reduction. According to Beckmann it also results from the reduction of pulegone. Menthol from oil of peppermint is laevorotary $[a]_d = -59{\cdot}1°$. It forms colourless crystals, melting at 42°, boiling at 212°, and of specific gravity ·890 at 20°. Heated with anhydrous $CuSO_4$ it gives cymene $C_{10}H_{14}$. It is related to menthone as an alcohol to a ketone. and has, therefore, in all probability, the formula:—

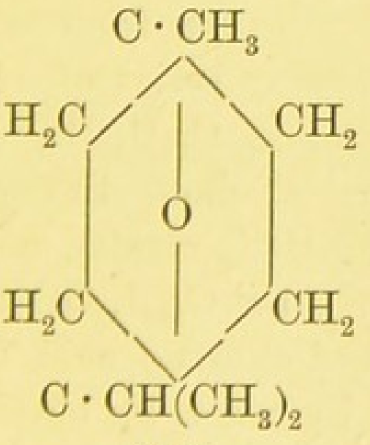


$$(CH_3)\cdot HC\left\langle\begin{array}{l}CH_2\cdot CH(OH)\\CH_2\cdot CH_2\end{array}\right\rangle CH\cdot CH(CH_3)_2.$$

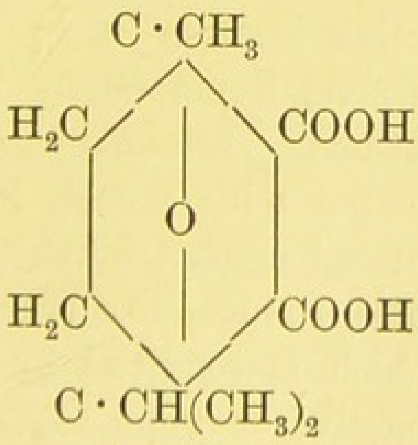
Menthol forms a series of well characterised esters with organic acids, some of which are found in nature. Of these, the more important are the following:—Menthyl acetate, $C_{10}H_{19}\cdot CO_2CH_3$; liquid, boils at 224°, laevorotary. Menthyl butyrate $C_{10}H_{19}CO_2\cdot C_3H_7$, liquid, boils at 230°, laevorotary. Menthyl benzoate, $C_{10}H_{19}\cdot CO_2C_6H_5$, crystals melting at 54°, laevorotary. Menthyl phthalate $(C_{10}H_{19}\cdot CO_2)_2C_6H_4$, crystals melting at 133°, laevorotary. Dehydrating agents convert menthol into a hydrocarbon of the formula $C_{10}H_{18}$, menthene, which, on treatment with hydriodic acid, gives tertiary menthyl iodide $C_{10}H_{19}I$. This body, on treatment with silver acetate, gives tertiary menthyl acetate, which is hydrolysed with potash, yielding tertiary menthol $C_{10}H_{19}OH$, isomeric with ordinary menthol. Carvomenthone and thujamenthone, with their corresponding alcohols, carvomenthol and thujamenthol, are isomeric with menthone and menthol. They can be prepared from carvone and thujone respectively. The carvomenthone series can also be prepared from phellandrene, with which they are closely allied.

CINEOL $C_{10}H_{18}O$.

This body has been described under several different names from that which is now generally used. The chief of these are eucalyptol and cajuputol, the derivations of which are obvious. The compound occurs in many essential oils, for example, eucalyptus, cajuput, spike, lavender, etc. It can also be produced by heating terpin hydrate with dilute acids. It can be obtained in a fairly pure condition by passing dry hydrochloric acid gas into rectified wormseed oil. The resulting crystalline magma is pressed, and the hydrochloride decomposed by hot water, and the cineol distilled in a current of steam, the acid being retained by an alkali. Scammell has also devised a process, by means of which pure cineol may be prepared (called eucalyptol in the patent specification). The oil containing the cineol in high proportion is treated with phosphoric acid (sp.gr.1·8). A crystalline cineol phosphate, $C_{10}H_{18}O \cdot H_3PO_4$ is obtained. The phosphate, after separation from adherent impurities, is decomposed by hot water, and the cineol is distilled with steam. This is a liquid of characteristic camphoraceous odour, of specific gravity, ·930 at 15°. It solidifies at low temperatures, and melts at —1°. It boils at 176°, and has a refractive index of 1·4559. It is optically inactive. It forms additive compounds with chlorine, bromine and iodine, as well as with hydrochloric and hydrobromic acid. It is easily oxidized to cineolic acid, $C_{10}H_{16}O_5$. The relations of cineol and cineolic acid to the terpene and camphor compounds are seen from the following formulæ, suggested by Wallach :—



Cineol.



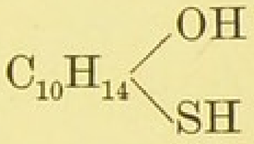
Cineolic Acid.

(II.)—BENZENE DERIVATIVES.

In addition to the compounds belonging to the series already described, there are a number of bodies occurring to a very large extent in many essential oils, which are well characterised simple derivatives of benzene. In this section, the more important benzenoid phenols, aldehydes, and allied bodies occurring in essential oils, will be briefly described.

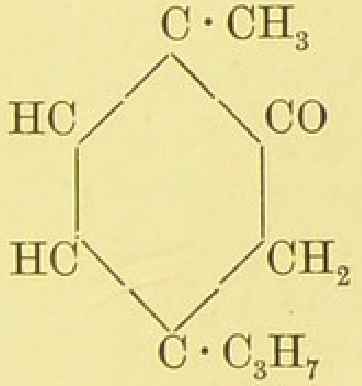
(α) KETONES.

The most important ketone of the benzene series, indeed the only one which is found to any considerable extent in essential oils, is carvone $C_{10}H_{14}O$. which is an oxy derivative of dihydrocymene. This compound occurs as *dextro*carvone in the oils of caraway and dill, and as *laevo*-carvone to a small extent in several oils. The inactive variety results by mixing the optically active isomers in equal quantities, or from the terpene limonene by the following series of reactions. Limonene tetrabromide $C_{10}H_{16}Br_4$ is heated with potash in methyl alcohol. Bromocarveol methyl ether $C_{10}H_{14}BrOCH_3$ results, and this is reduced to carveol methyl ether $C_{10}H_{15}OCH_3$. which is oxidized by means of chromic acid to inactive carvone $C_{10}H_{14}O$. In order to obtain this body in a pure state, sulphuretted hydrogen is added to a strongly ammoniacal solution of the carvone-containing fractions of ethereal oils. A compound of the constitution



$$C_{10}H_{14}\begin{matrix}\diagup OH\\ \diagdown SH\end{matrix}$$

separates in crystals, which can be purified by recrystallization from a mixture of alcohol and chloroform. It then melts at 187°. Pure carvone boils at 223°, and has a specific gravity of ·9598 at 0°. Its constitution (omitting double linkages in the benzene nucleus), is :—

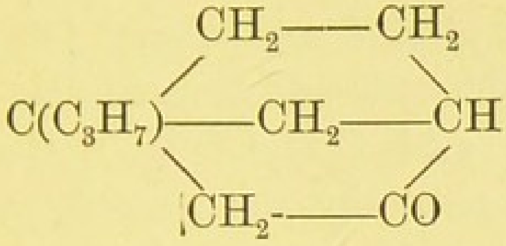


It forms characteristic ketone derivatives, such as the oxime $C_{10}H_{14}NOH$, and the semicarbazone $C_{10}H_{14} : N{\cdot}NH{\cdot}CONH_2$. The latter melts at 162° (active) and 154° (inactive). The former, carvoxime, is identical with nitroso-limonene, produced by the action of potash on the nitrosochlorides of limonene. The active isomer melts at 72°, the inactive at 93°. A comparison of the derivatives of the active carvones is given in the following table :—

Optical Activity $[a]_d$

Compound.	Derivative of + Carvone or − Limonene.	 —Carvone or + Limonene.
Carvone . .	+ 62°	− 62°
H_2S compound .	+ 5·53°	− 5·55°
Carvoxime .	+ 39·71°	− 39·34°
Benzoyl-carvoxime	+ 26·47°	− 26·97°
Benzoyl-hydrochlor-carvoxime .	− 10·58°	+ 9·92°

When Carvone is reduced, it takes up four atoms of hydrogen, forming an alcoholic body of the formula $C_{10}H_{17}OH$, dihydrocarveol, which on oxidation gives dihydrocarvone $C_{10}H_{16}O$. By isomerisation with hydrobromic acid in acetic acid, this yields carone $C_{10}H_{16}O$, a liquid of peppermint-like odour. This change is brought about as follows. Dihydrocarvone unites with hydrobromic acid, to form a hydrobromide, which, on treatment with potash, gives up HBr, yielding the isomer, carone. No bisulphite compound of carone has been prepared, although it is of a ketonic nature. Baeyer, who has worked on this compound for some years past, considers its constitution to be :—



Dextro-carone is obtained from caraway oil, and laevo-carone from the oil of *Mentha Crispa*. The former has a specific gravity of ·957, and rotary power $[a]_d = +173·8°$, the latter, specific gravity ·957, and rotary power $[a]_d = -169·5°$. Each forms a liquid oxime, and when equal quantities of the two are mixed, the oxime of inactive carone is formed, melting at 77°–79°. The semicarbazones of *dextro-* and *laevo-* carone melt at 167° and that of inactive carone at 178°.

(β) ALCOHOLS, ALDEHYDES AND ACIDS.

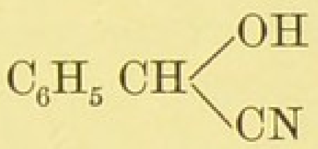
Under this head may be described the more important of the benzene alcohols which are found in essential oils, together with their corresponding aldehydes and acids.

Benzyl alcohol, $C_6H_5(CH_2OH)$, occurs as benzyl benzoic ester in the balsams of Peru and Tolu, and in storax. It can also be readily obtained from benzaldehyde by reduction with sodium. It is a colourless liquid, with a faint aromatic odour, boiling at 206° and having a specific gravity at 0° of 1·062. It is very slightly soluble in water, but readily so in alcohol and ether. On oxidation it yields benzaldehyde and benzoic acid. The ester of benzoic acid $C_6H_5{\cdot}CO{\cdot}OCH_2{\cdot}C_6H_5$, besides being found naturally, can be easily obtained from the interaction of sodium ethylate and glacial acetic acid and benzaldehyde. It is a crystalline compound melting at 21° and boiling at 324°.

Benzaldehyde, $C_6H_5(CHO)$, is the chief constituent of essential oil of almonds. Indeed the remaining constituents of this oil may almost be regarded as impurities, and pure benzaldehyde is very frequently used in place of natural oil of almonds when a particularly delicate odour is not needed. It occurs in bitter almonds and in the kernels of various fruits as amygdalin, a glucoside, which, under the influence of the natural ferment emulsin, or by boiling with dilute acid, decomposes as follows,

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde}}{C_7H_6O} + \underset{\text{Dextrose}}{2C_6H_{12}O_6}$$
$$+ \underset{\text{Hydrocyanic acid.}}{HCN}$$

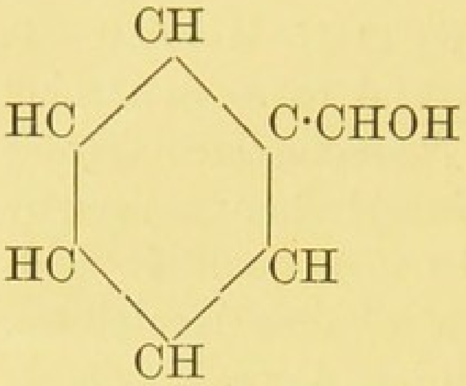
It results also from the oxidation of benzyl alcohol, and is made on a large scale from benzyl chloride, $C_6H_5(CHCl_2)$, by heating it under pressure with lime, or by boiling it with sulphuric acid. It is a practically colourless liquid of characteristic almond odour; of high refractive power. It boils at 179°. Its specific gravity at 15° is 1·050. It is slightly soluble in water, and easily in alcohol and ether. It gives all the characteristic reactions of aldehydes; it forms benzoic acid when oxidized by the air, and benzyl alcohol by reduction. It yields a crystalline compound with alkaline bisulphites. Hydrocyanic acid converts it into a cyanhydrin,



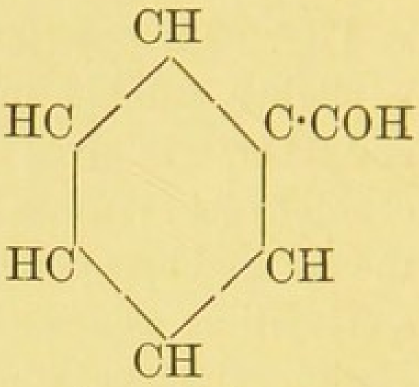
$$C_6H_5\ CH\begin{cases} OH \\ CN \end{cases}$$

a yellow oil, solidifying at low temperatures.

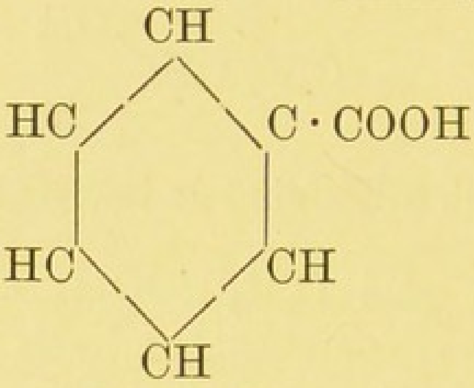
Benzoic acid $C_6H_5(COOH)$ occurs naturally both free and combined, and can be obtained by many synthetic methods. It results from the oxidation of either of the two preceding compounds, and also of numerous other derivatives of benzene. It can even be obtained by acting on benzene with carbon dioxide, in the presence of aluminium chloride. It crystallizes in white needles, melting at 120°, boiling at 250°. It is easily sublimable, or can be distilled with steam. It is soluble in 600 times its weight of cold water. When heated with lime it gives up CO_2, and yields benzene. The benzoates are mostly soluble in water. Potassium benzoate $2C_7H_5O_2K + H_2O$ crystallizes in concentrically grouped needles. The relations of the alcohol, aldehyde and acid, are seen from the following constitutional formulæ :—



Benzyl Alcohol



Benzaldehyde.



Benzoic Acid.

Salicylic aldehyde $C_7H_6O_2$ is an aldehyde phenol of the constitution $C_6H_4(\overset{1}{OH})(\overset{2}{CHO})$. It occurs in the volatile oils of varieties of Spiræa. It can also be obtained by oxidising saligenin, its corresponding phenol-alcohol $C_6H_4(OH)(CH_2OH)$ or salicin, a glucoside occurring in willow and poplar bark. It can also be readily prepared by the action of chloroform on phenol, in the presence of potash. It is then, however, contaminated with the corresponding *para*-compound, *p*-oxybenzaldehyde. It is an oil with a pleasant aromatic odour, solidifying at about $-20°$. It boils at 196°, and has a specific gravity of 1·172 at 15°. It is fairly soluble in water, and the solution is coloured deep violet by ferric chloride. By reduction with sodium amalgam, it yields its alcohol, saligenin; by oxidation, it yields salicylic acid.

Salicylic acid $C_7H_6O_3$ is ortho-oxybenzoic acid, of the formula $C_6H_4\overset{1}{(OH)}\overset{2}{(COOH)}$. It occurs in the free state in the buds of *Spiræa ulmaria*, and as methyl ester in the oil of *Gaultheria procumbens* and other plants, from which it can easily be obtained by saponification. It can be prepared artificially by oxidizing saligenin and salicylic aldehyde; from the *ortho*chlor- or *ortho*brombenzoic acids by fusion with potash; or by the action of carbon dioxide on phenol-sodium. This latter process formed the subject matter of Kolbe's well-known patent:—

$$\underset{\text{Phenol-sodium.}}{2C_6H_5ONa} + CO_2 = \underset{\text{Di-sodium salicylate.}}{C_7H_4O_3Na_2} + C_6H_5OH$$

Usually, *para*-oxybenzoic acid is formed at the same time. Various other reactions yield salicylic acid with great ease. It is a white crystalline powder, consisting of four-sided prisms. It melts at 155°-156°, and is sublimed when heated carefully. It is soluble in 400 parts of water at 15°, and in 12 parts at 100°, and its solution is coloured violet by ferric chloride. The methyl ester of salicylic acid is important on account of its extensive natural occurrence. It can also be formed by passing dry hydrochloric acid into a solution of the acid in methyl alcohol.

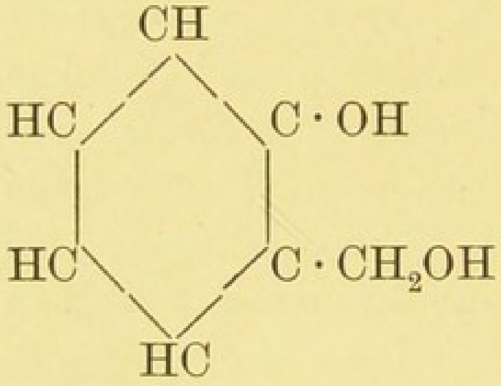
$$C_6H_4(OH)(COOH)+CH_3OH=$$

Salicylic Acid.

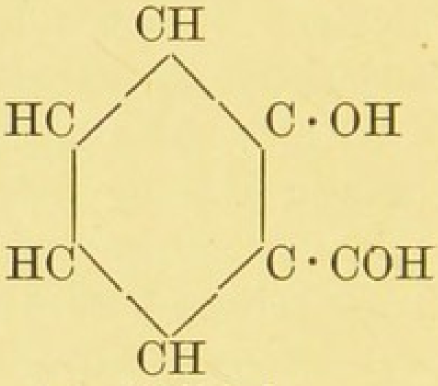
$$C_6H_4(OH)(CO_2CH_3)+H_2O$$

Methyl Salicylate.

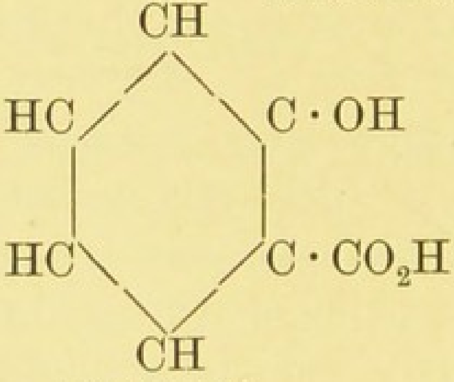
It is a pleasant smelling liquid, of specific gravity 1·197 at 0°, and boils at 224°. The relations of these bodies are seen from the following formulæ :—



Saligenin.

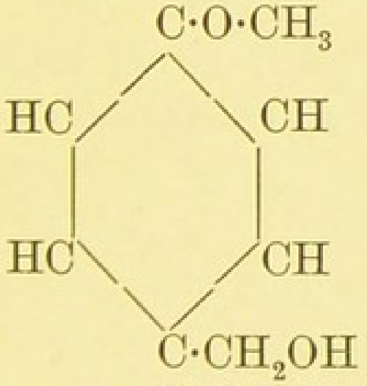


Salicylic Aldehyde.

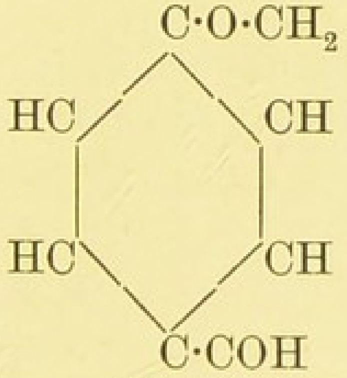


Salicylic Acid.

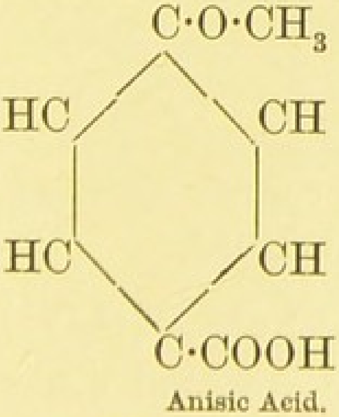
Anisyl alcohol, anisic aldehyde and anisic acid have the same relations to one another as the bodies just described. The aldehyde results from the oxidation of constituents of various essential oils, especially those of anise and fennel. Reduction converts it into anisyl alcohol and oxidation gives anisic acid. Anisyl alcohol $C_6H_4(O.CH_3\overset{1}{)}(CH_2OH\overset{4}{)}$ crystallizes in needles melting at 25°, and boiling at 259°. Anisic aldehyde $C_6H_4(O.CH_3\overset{1}{)}(CHO\overset{4}{)}$ is a colourless oil, of specific gravity 1·123 at 15°, boiling at 248°. It forms a crystalline bisulphite compound and two isomeric oximes. Anisic acid $C_6H_4(O.CH_3\overset{1}{)}(COOH\overset{4}{)}$ forms rhombic prisms melting at 185° and boiling at 280°. The constitution of these bodies is as follows:—



Anisyl Alcohol.

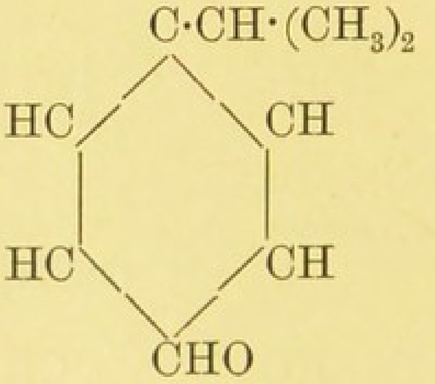


Anisic Aldehyde.



Anisic Acid.

Cuminol, or cumic aldehyde $C_{10}H_{12}O$ is a constituent of Roman caraway oil and of the oil of *Cicuta virosa.* It is *p*-isopropyl benzaldehyde $C_6H_4\overset{1}{(C_3H_7)}\overset{4}{(CHO)}$. It can be separated from the oils by shaking that portion boiling above 190°, with sodium bisulphite, and pressing the separated crystalline mass, washing the crystals with alcohol-ether and distilling with sodium carbonate. Cumic aldehyde is an oil of aromatic odour, of specific gravity ·973 at 13°, boiling at 235°. Oxidation with dilute nitric acid converts it into cumic acid, $C_6H_4\overset{1}{(C_3H_7)}\overset{4}{(CO_2H)}$, a crystalline acid melting at 116° and boiling at 290°, and reduction gives cumic alcohol, $C_6H_4\overset{1}{(C_3H_7)}\overset{4}{(CH_2OH)}$, an oil boiling at 246°. The constitution of cuminol is:—

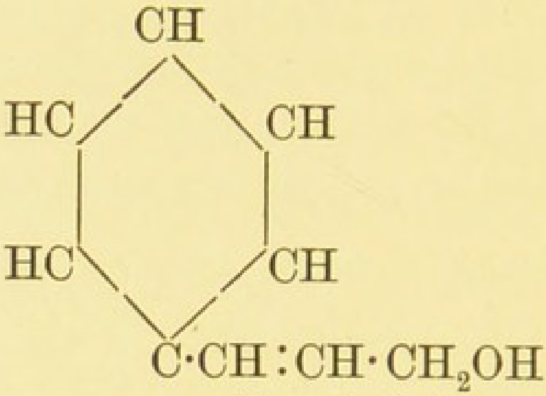


from which, of course, those of the alcohol and acid are easily deduced.

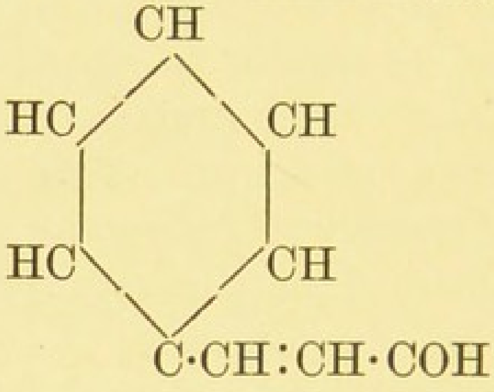
Cinnamic aldehyde C_9H_8O is the chief ingredient of the essential oils of cinnamon and cassia. It can be obtained from these oils by the usual bisulphite of sodium process. It can also be prepared by acting on a mixture of benzaldehyde and acetaldehyde with sodium ethylate :—

$$\underset{\text{Benzaldehyde.}}{C_6H_5COH} + \underset{\text{Acetaldehyde.}}{CH_3COH} = \underset{\text{Cinnamic Aldehyde.}}{C_6H_5CH{:}CH{\cdot}COH} + H_2$$

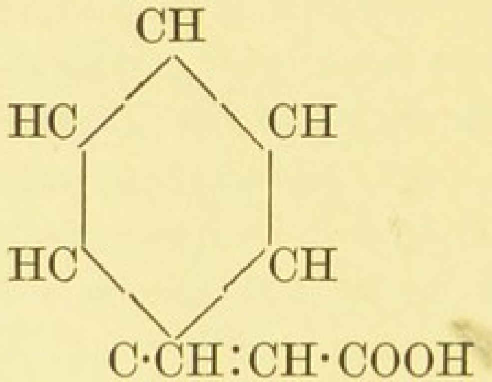
It is a colourless aromatic oil, boiling at 247°. It is oxidized by the air to cinnamic acid $C_9H_8O_2$, which also occurs naturally in Peru and Tolu balsams and in storax. This acid forms fine needles if crystallized from water, and thick prisms if crystallized from alcohol. It melts at 133°. The alcohol corresponding to these bodies is cinnamic alcohol or stryol, $C_9H_{10}O$. This body cannot be obtained from cinnamic aldehyde by reduction as there is an unsaturated radicle which easily takes up hydrogen. It occurs however as a cinnamic ester, styracine, in storax, and can be obtained from this by hydrolysis with potash. It forms shining needles, sparingly soluble in water and has an odour recalling that of hyacinths. It melts at 33°. These compounds are unsaturated, cinnamic aldehyde being phenyl-allyl-aldehyde. Their constitutions are :—



Cinnamic Alcohol.



Cinnamic Aldehyde.



(γ) PHENOLS AND THEIR ETHERS.

The most commonly occurring of these bodies are the following :—anethol, apiol, asarol, carvacrol, carvol, chavibetol, chavicol, diosphenol, eugenol, safrol and thymol.

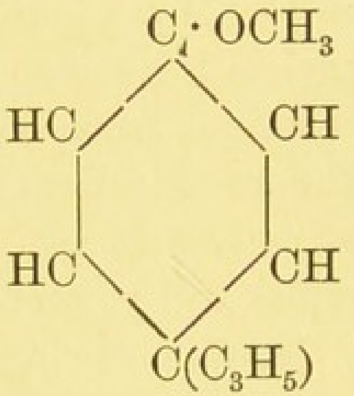
Anethol $C_{10}H_{12}O$ is the methyl ether of the phenol anol, which has the constitution of *para*-propenyl-phenol.

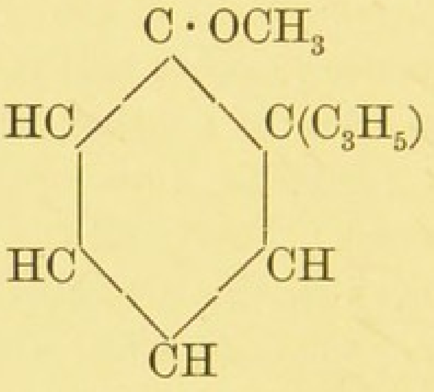
Anethol forms white shining scales, melting at 21°, and boiling at 232°. It has been prepared synthetically. Further, it can be prepared from methyl-chavicol (*vide infra*), by heating it with alcoholic potash, which brings about a molecular re-arrangement of the allyl to the propenyl group. (Grimaux asserts that methyl-chavicol is a stereo-isomeride of anethol, and that estragol, from oil of *Artemisia Dracunculus*, is the constitutional isomer). Nearly all the allyl derivatives of benzene suffer this alteration. Examples will be seen under eugenol, safrol and apiol. Anethol, being an unsaturated compound, readily combines with bromine, forming monobrom-anethol dibromide, in which two atoms of bromine have been added to the unsaturated side chain, and one atom has been substituted in the nucleus, thus—

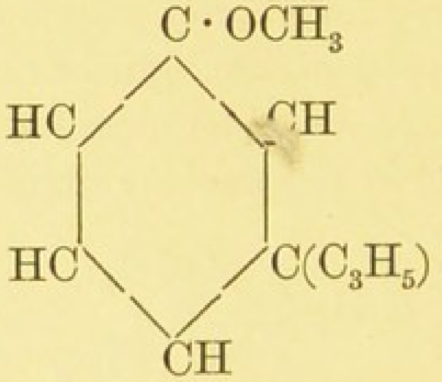
$$C_6H_3Br\left\langle\begin{matrix}OCH_3\\C_3H_5Br_2\end{matrix}\right.$$

This body forms compact needles, melting at 107°-108°. Closely allied to anethol are the corresponding *ortho*- and *meta*- compounds, which Mourew has prepared by acting on salicylic and *meta*-oxybenzoic aldehydes respectively, with propionic anhydride and sodium propionate. These bodies have the following properties:—*Ortho*-anethol, liquid, boiling at 220°-223°, specific gravity at 0° 1·0075, odour resembling veratrol; *meta*-anethol, liquid, boiling at 226°-229°, specific gravity at 0° 1·0013, odour resembles elemi.

The relations of the three isomers are seen from the following constitutional formulæ.


Natural Anethol


Ortho-anethol


Meta-anethol

Apiol $C_{12}H_{14}O_4$ is a constituent of oil of parsley. It is the methylene-dimethyl ester of allyl-tetroxy-benzene, of the constitution $C_6H(C_3H_5)(O_2:CH_2)(OCH_3)_2$. It crystallizes in long needles, melting at 30°, and boiling at 294°. When oxidized with potassium permanganate, it yields apiolic-aldehyde, and finally, apiolic acid, $C_6H(O_2:CH_2)(OCH_3)_2CO_2H$, melting at 175°. Boiling alcoholic potash converts it into isapiol, in which the allyl group $\cdot CH_2 \cdot CH : CH_2$ has been re-arranged to the propenyl group $\cdot CH:CH\cdot CH_3$. This body crystallizes in leaflets, melting at 56°, and boiling at 304°. In dill oil there occurs an isomer of apiol, which may be termed dill-apiol. It differs, probably, only in the orientation of the side chains attached to the benzene nucleus. It is a thick, oily liquid, boiling at 162° under a pressure of 11 mm, and at 285° under ordinary pressure. This body is also altered by alcoholic potash to iso-dill apiol, by a re-arrangement of the allyl to the propenyl group. This body forms colourless prisms, melting at 44°, and boiling at 296°, with slight decomposition. The orientation of the substituting groups of the two apiols is probably as follows, but which represents apiol and which dill-apiol is uncertain :—$C_6H\overset{1}{(C_3H_5)}\overset{2}{(OCH_3)}\overset{3}{(OCH_3)}\overset{4\cdot5}{(O_2CH_2)}$ and $C_6H\overset{1}{(C_3H_5)}\overset{2}{(OCH_3)}\overset{3\cdot4}{(O_2CH_2)}\overset{5}{(OCH_3)}$. This is proved by the fact that both can be made to yield the same tetramethyl apionol $C_6H_2(O\cdot CH_3)_4$, in which it is known that the four phenolic groups are adjacent.

Bromine in excess converts both apiols into the dibromide of the corresponding bromapiol, $C_{12}H_{13}Br_3O_4$. The following table gives a comparison of the two bodies :—

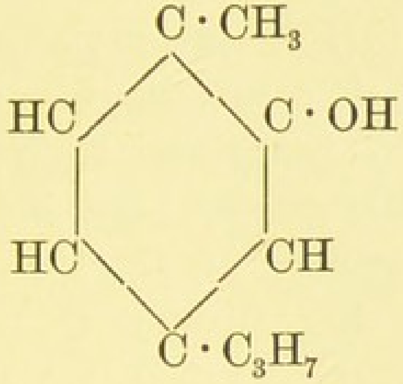
	Apiol from	Isapiol Parsley.	Apiol from	Isapiol Dill.
Melting point	30°	55°-56°	liquid	44°
Boiling point	294°	304°	285°	296°

Melting points of Derivatives.

	From Parsley.	From Dill.
Bromapiol dibromide	88°-89°	110°
Bromisapiol dibromide	120°	115°
Apiolic Aldehyde	102°	75°
Apiolic acid	175°	151°-152°
Apione	79°	——

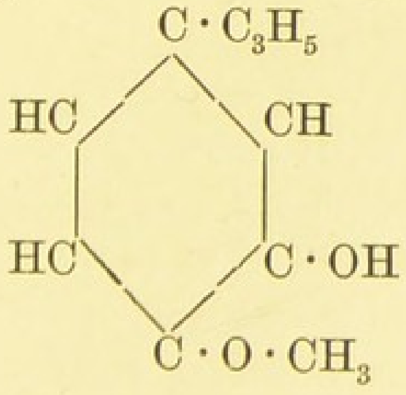
Asarol is the solid constituent of the essential oil of *Asarum europæum.* Its formula is $C_{12}H_{16}O_3$. It forms monoclinic prisms, melting at 67°, and boiling at 295°. Its constitution is that of trimethoxy-propenyl-benzene $C_6H_2(C_3H_5)(OCH_3)_3$. Oxidation with potassium permanganate converts it into trimethoxy-benzoic acid.

Carvacrol is one of the many methyl-propyl-phenols. It is isomeric with thymol, both being derivatives of *para*-cymene. The position of the substituting groups is as follows :—



It occurs in several essential oils, notably those of the Thyme family, and can be obtained by heating the isomeric ketone, carvone with alcoholic potash, by which means a molecular rearrangement of the $\cdot CO \cdot CH$ group to $\cdot C\ (OH) : C.$ takes place. It can also be obtained from pinene, by converting this body into nitrosopinene, and then acting upon this with hydrochloric acid. It is a thick oil, solidifying at low temperatures melting at 0°, and boiling at 236°. With P_2O_5 it yields propylene and *para*-cresol.

Chavibetol, $C_{10}H_{12}O_2$ is an isomer of eugenol. It occurs in oil of betel, and its constitution is, in all probability :—

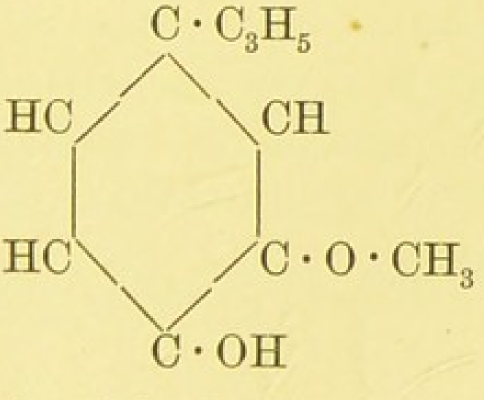


Chavicol, $C_9H_{10}O$ is *para*-allyl phenol $C_6H_4(C_3H_5)(OH)$. It occurs together with chavibetol in oil of betel. It is a colourless oil, of characteristic odour, of specific gravity 1·035 at 20°, boiling at 237°. It is soluble in all the usual organic solvents, but only slightly so in ammonia or water. The ethyl ether $C_9H_9 \cdot O \cdot C_2H_5$ is prepared by heating chavicol with KOH and ethyl iodide in alcoholic solution. It is a colourless liquid, boiling at 232°. The methyl ether $C_9H_9 \cdot O \cdot CH_3$ prepared in a similar manner, boils at 226°.

Diosphenol $C_{10}H_{16}O_2$ is a constituent of essential oil of buchu, originally discovered by Fluckiger. It forms lustrous, colourless crystals, melting at 82°, and boiling at 232°. It possesses an odour resembling camphor. It was originally regarded as an oxycamphor, but recent investigations tend to show that it is an aldehyde phenol of the constitution $C_9H_{14}(OH)(COH)$. Further than this its constitution is not yet known. It forms an oxime $C_9H_{14}(OH)(CH{:}NOH)$ melting at 159°. Methyl-diosphenol, obtained by the action of KOH and methyl-iodide, is a colourless liquid, which boils at 232°-235°, and has a specific gravity of ·985 at 15°. When dissolved in carbon bisulphide and treated with bromine, diosphenol gives a di-bromo compound $C_{10}H_{14}Br_2O_2$

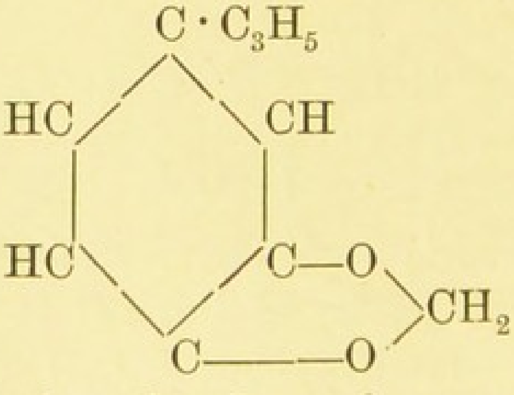
forming yellow needles, melting at 43°. The phenol may be extracted from the oil by means of potash, which is then separated and acidified. It gives a green colour with ferric chloride.

Eugenol $C_{10}H_{12}O_2$ is a phenol which occurs chiefly in oil of cloves. To extract it, the oil is shaken with alcoholic solution of potash, and the resulting mass pressed, washed with alcohol, and decomposed with an acid. It is an aromatic oil, boiling at 247°. It is coloured blue with ferric chloride. Potassium permanganate oxidizes it to homovanillin, vanillin and vanillic acid. Eugenol $C_{10}H_{12}O_2$ is the methyl ether of allyl-di-oxybenzene, of the following constitution :—



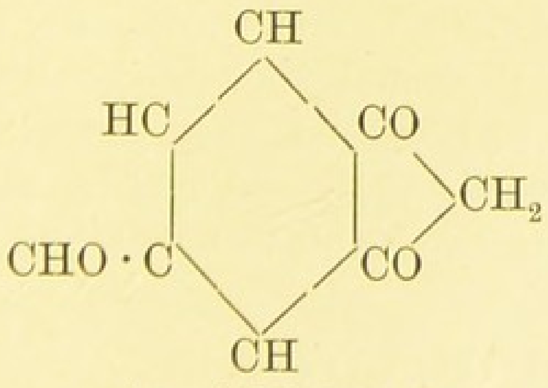
and is isomeric with chavibetol. Pure eugenol has a specific gravity of 1·070 at 15°, and boils at 253°-254°. Methyl-eugenol, $C_6H_3(C_3H_5)(OCH_3)_2$ is a constituent of several essential oils, and is formed by heating eugenol with methyl iodide and KOH. It is a liquid boiling at 237°-239°. It is also formed by the action of allyl iodide on veratrol, (dimethyl catechol) $C_6H_4(OCH_3)_2$. When boiled with caustic potash, eugenol is converted into isoeugenol, which has the same constitution as eugenol, except that the allyl group has been altered to the propenyl group $\cdot CH : CH \cdot CH_3$. This body boils at 260°, and is coloured olive green by ferric chloride. When bromine acts upon eugenol, dibrom-eugenol-dibromide $C_6HBr_2(OH)(OCH_3)(C_3H_5Br_2)$ is formed. Two bromine atoms in the allyl radicle can be removed by means of zinc dust, with the result that dibrom-eugenol $C_6HBr_2(OH)(OCH_3)(C_3H_5)$ is formed. By treating isoeugenol in the cold with bromine, momobrom-isoeugenol dibromide $C_6H_2Br(OH)(OCH_3)(C_3H_5Br_2)$ is formed, which does not give up bromine by the action of zinc dust.

Safrol. $C_{10}H_{10}O_2$ is the methylene ether of allyl di-oxybenzene, of the constitution:—

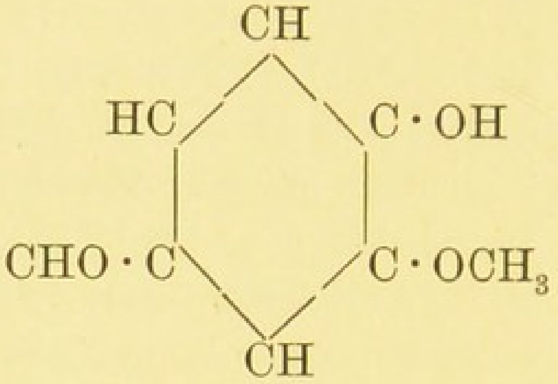


It occurs in the oils of sassafras, camphor, and in that of *Ilicium religiosum.* It forms a white crystalline mass, melting at about 8°. At ordinary temperatures it forms a colourless oil, possessing a sharp taste and characteristic odour. Its specific gravity is 1·096 at 18°. It is neutral in reaction, optically inactive, and boils at 232°. When warmed with alcoholic potash, it is converted into iso-safrol, a liquid boiling at 246°-248°, and solidifying at very low temperatures. Both bodies dissolve in concentrated sulphuric acid, with an intense red colouration. The C_3H_5 group in safrol is the allyl radicle, which is converted into the propenyl group, with the formation of isosafrol, as in the cases mentioned above. Safrol resists reduction with sodium, whereas isosafrol is easily reduced to dihydrosafrol $C_{10}H_{12}O_2$.

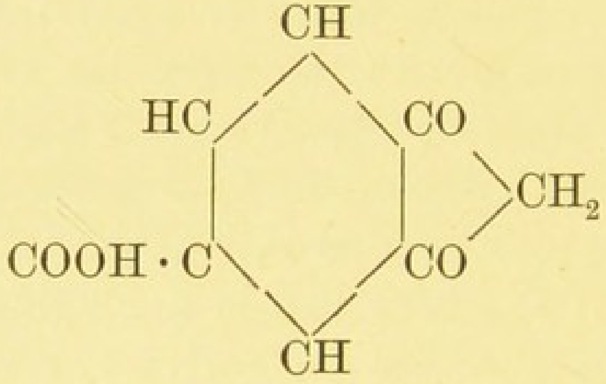
Safrol is closely related to the highly aromatic compounds piperonal (heliotropine) and vanillin. The chief products of oxidation of both safrol and isosafrol are piperonal and piperonic acid, the former being the methylene ether of protocatechuic aldehyde, and the latter, the methylene ether of the corresponding acid. The constitutions of these bodies and vanillin, are :—



iperonal (heliotropine)

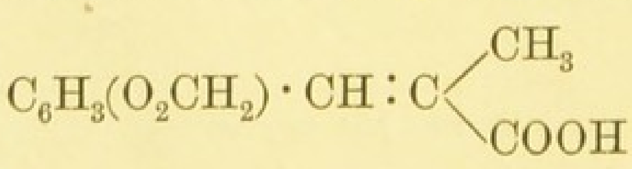


Vanillin.



Piperonic Acid.

Besides piperonal and piperonic acid, Tiemann has obtained another acid by oxidizing safrol with potassium permanganate, which he terms homopiperonic acid $C_9H_8O_4$, crystallizing in needles, melting at 127°. Mourew has recently synthesised isosafrol, definitely establishing its constitution thereby. Piperonal is heated with propionic anhydride and sodium propionate. Methylene homocaffeic acid is formed, melting at 198°–199°. The constitution of this body is known to be :—



$$C_6H_3(O_2CH_2) \cdot CH : C \Big\langle \begin{matrix} CH_3 \\ COOH \end{matrix}$$

and this, on giving up carbon di-oxide under the influence of heat, yields isosafrol, $C_6H_3(O_2 \cdot CH_2) \cdot CH : CH \cdot CH_3$.

Thymol $C_{10}H_{14}O$ is a methyl-propyl-phenol, isomeric with carvacrol. It is found in various essential oils, especially those of the Thyme family. To obtain thymol in a fairly pure condition, the oil is shaken with solution of potassium hydroxide, and to the separated aqueous solution, hydrochloric acid is added. The precipitated thymol can be purified by re-crystallization. The constitution of thymol is $C_6H_3\overset{1}{(CH_3)}\overset{4}{(C_3H_7)}\overset{3}{(OH)}$. It crystallizes in large colourless plates, melting at 44° and boiling at 230°. It is artificially prepared from nitro-cumic aldehyde, $C_6H_3(NO_2)(C_3H_7)(CHO)$ by converting it into its di-chloride $C_6H_3(NO_2)(C_3H_7)CHCl_2$, and reducing this to cymidine, $C_6H_3(NH_2)(C_3H_7)CH_3$, with zinc and hydrochloric acid. By means of the diazo reaction (sulphuric acid, sodium nitrite and water) the amido group is replaced by OH and thymol is obtained. Carvoxime (vide *carvol*) $C_{10}H_{14}N.OH$, on heating with sulphuric acid, undergoes certain molecular re-arrangement, yielding amido-thymol from which, by means of the diazo reaction (using alcohol in place of water) the amido group can be replaced by hydrogen, yielding thymol. With nitrous acid, thymol forms a characteristic nitroso-thymol $C_{10}H_{12}(NO)OH$, melting at 160°. On reduction this body yields the same amidothymol as is obtained from carvoxime. Thymol forms numerous well defined crystalline substitution products but they need not be discussed here.

(III.)—METHANE DERIVATIVES.

Under this heading only a few of the more important compounds which are characteristic of certain essential oils will be described.

(α) ALCOHOLS.

Esters of several of the alcohols of the Methane series are found in several oils (*e.g.* chamomile oil), of which the following are the most important.

Methyl alcohol, CH_3OH, a liquid of characteristic odour, boiling at 66°, of specific gravity ·795. It is soluble in water in all proportions, and a good solvent for most essential oils. It is found in traces in the free state (in oil of cloves), but generally in the combined state in the form of esters.

Ethyl alcohol, C_2H_5OH, is a liquid boiling at 78°. Its specific gravity is ·806 at 0°. It is very similar in all respects to methyl alcohol.

Propyl alcohol, C_3H_7OH, the next higher homologue, boils at 97° and has a specific gravity

·804 at 20°. The isomeric **isopropyl alcohol**, $(CH_3)_2CH \cdot OH$ boils at 83° and has a specific gravity ·789 at 20°.

Butyl alcohol C_4H_9OH boils at 117° and has a specific gravity ·810 at 20°. **Isobutyl alcohol** $(CH_3)_2CH \cdot CH_2OH$ boils at 108° and has a specific gravity ·802 at 20°.

Isoamyl alcohol $(CH_3)_2CH \cdot CH_2 \cdot CH_2OH$ boils at 131° and has a specific gravity ·810 at 20°.

Hexyl alcohol $C_6H_{13}OH$ boils at 157°; specific gravity ·820 at ·20°.

Octyl alcohol $C_8H_{17}OH$ boils at 191°; specific gravity ·830 at 15°.

(β) ALDEHYDES.

Acetic aldehyde $CH_3 \cdot COH$ is the aldehyde corresponding to ethyl alcohol and acetic acid. It is a liquid of peculiar and somewhat unpleasant odour, boiling at 21°, of specific gravity ·794. It is found in traces in a few oils.

Valeric aldehyde $(CH_3)(CH_2)_3COH$; liquid boiling at 102°.

Isovaleric aldehyde $(CH_3)_2CH \cdot CH_2 \cdot COH$; liquid boiling at 92°

(γ) ACIDS.

The acids as a rule are found in essential oils in the form of esters, that is, combined with the alcoholic radicals. The most important of these are the following:—

Acetic acid $CH_3 \cdot COOH$, a liquid of penetrating odour, known commonly in the dilute form as vinegar. Boiling point 119°, specific gravity 1·055 at 15°. When quite free from water it is a crystalline solid melting at 16·5°.

Propionic acid C_2H_5COOH boils at 140°; specific gravity ·992 at 15°.

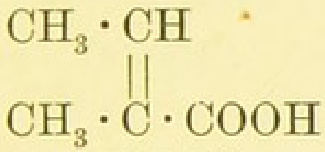
Butyric acid $CH_3 \cdot CH_2CH_2COOH$; boils at 162°; specific gravity ·961.

Isobutyric acid $(CH_3)_2CH \cdot COOH$; boils at 155°; specific gravity ·953.

Valeric acids $C_5H_{10}O_2$. Ordinary normal valeric acid has not been found in any essential oil. Isovaleric acid, of the formula $(CH_3)_2CH \cdot CH_2 \cdot COOH$ has been found. This is a liquid boiling at 174° and of specific gravity ·948. An isomeric acid, methyl-ethyl-acetic acid $(C_2H_5)(CH_3) \cdot CH \cdot COOH$ is an optically active liquid boiling at 175°, of specific gravity ·945.

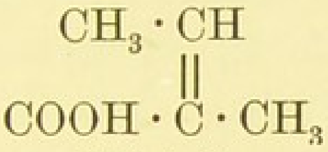
Caproic acid, $C_5H_{11}COOH$, is a liquid boiling at 205°. When cooled it solidifies at -2°. Its specific gravity is ·9315.

Tiglic and angelic acids, $C_5H_8O_2$, are two stereoisomeric acids found as esters in Roman chamomile oil. Tiglic acid melts at 65°, angelic acid at 45°. The relations of these two acids are expressed by the formulae :—



$$\begin{array}{l} CH_3\cdot CH \\ \quad\;\, \| \\ CH_3\cdot C\cdot COOH \end{array}$$

Angelic Acid.



$$\begin{array}{r} CH_3\cdot CH \quad\;\; \\ \| \qquad\quad\;\; \\ COOH\cdot C\cdot CH_3 \end{array}$$

Tiglic Acid.

Hydrocyanic acid, HCN, is found in several oils of the *Rosaceae*, such as bitter almond oil. When pure and anhydrous it is a liquid of specific gravity ·699 and boils at 27°. It is intensely poisonous.

(δ) KETONE.

Methyl-nonyl-ketone is the only ketone of importance belonging to this series, which is found in any quantity in essential oils. It forms the chief part of oil of rue. It is a liquid boiling at 225°, of very powerful odour. If cooled to a low temperature it solidifies, and then melts at 13°.

(IV.)—THE GERANIOL SERIES.

Amongst the most important of the constituents of essential oils possessing agreeable odours, are the bodies belonging to this open-chain series.

The well known members of the series are few in number, comprising three alcohols (and their esters) and two aldehydes. These are the alcohols, geraniol, linalol and citronellol and the aldehydes, citral and citronellol. A very large number of bodies have been described under various names, such as rhodinol, aurantiol, coriandrol, etc., but they have invaribly been shown to be impure forms of one or other of the above named alcohols.

Geraniol, $C_{10}H_{18}O$, is the typical constituent of the oils of rose and geranium. It is a colourless oil of sweet odour, boiling at 230° at ordinary pressure, and at 120° under a pressure of 16 mm. Its specific gravity is ·881, and its refractive index 1·4777. It is optically inactive. On oxidation it yields its aldehyde, citral or geranial. By heating with acetic anhydride it yields an acetic ester, $C_{10}H_{17}O, C_2H_3O$, a fragrant oil of specific gravity ·917 boiling at 129° at 16 mm.

To isolate geraniol in a state of purity, Tiemann and Kruger dissolve sodium in the alcohol and treat the resulting alcoholate with ether and phthalic anhydride. The geraniol sodium phthalate is saponified and pure geraniol is precipitated by the addition of water. To detect this body in oils containing it, the oil is rubbed in a mortar with dry powdered calcium chloride, and the mixture kept in a desiccator for 12 hours at −12°. The mass is then rubbed with benzene and the liquid portion is removed by a suction filter. The calcium chloride compound of geraniol is then decomposed by water and the oil separated, washed, and distilled; pure geraniol passes over at 229°. According to Tiemann and Semmler, geraniol has the constitution

$$(CH_3)_2C : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3) : CH \cdot CH_2OH.$$

Linalol $C_{10}H_{18}O$ is an alcohol isomeric with geraniol. It is a sweet-smelling oil of specific gravity ·875 and refractive index 1·4611; it boils at 198° and is known in both optically active forms, the rotation being about 20° in either direction. On oxidation linalol yields citral, which is actually the aldehyde of geraniol. By the action of acetic anhydride, it yields an acetic ester, which is a fragrant oil, with a characteristic bergamot odour, of specific gravity ·912, boiling at 105° at 11 mm. Linalol probably has the constitution :—

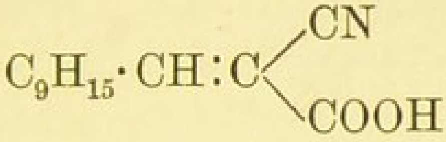
$$CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3)OH \cdot CH : CH_2$$

Citronellol $C_{10}H_{20}O$ is an alcohol closely related to geraniol. It was first obtained by the American chemist, Dodge, by reduction of the aldehyde citronellal $C_{10}H_{18}O$. The alcohol occurs in oil of roses and geranium, in both the *dextro-*

and the *laevo*-rotary forms. It is an odorous oil of specific gravity ·8565 and refractive index 1·4566. It boils at 117° under a pressure of 17 mm. Its optical rotation is about $+4°$ or $-4°$. The acetate is an oil of specific gravity ·894 and optical activity 2·4°. The probable constitution of citronellol is :—

$$C(CH_3)_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH_2OH.$$

Citral, $C_{10}H_{16}O$. This body is the aldehyde of the alcohol geraniol, and is found in numerous essential oils such as lemongrass, verbena, lemon, orange, etc., etc. It can be obtained as has been mentioned above, by the oxidation of geraniol or linalol, identical with the natural product. Citral is a fragrant oil, of specific gravity ·897, boiling at 229° at ordinary pressures or at 110° under a pressure of 12 mm. It is optically inactive, and has a refractive index 1·4931. It yields numerous crystalline derivatives, amongst which is the well-known compound with sodium bisulphite. By acting on it with pyruvic acid and β-naphthylamine it yields a well-defined crystalline acid—naphtocinchoninic acid $C_{23}H_{23}NO_2$, melting at 197°. It also yields a crystalline oxime and phenylhydrazone and two isomeric semicarbazones. One of the most important compounds, however, is citralidene cyanacetic acid, of the formula



$$C_9H_{15}\cdot CH:C\begin{cases}CN\\COOH\end{cases}$$

formed by the condensation of citral with cyanacetic acid. Citral is well known as the chief constituent of oil of lemongrass, but quite recently Stiehl has suggested that three isomeric aldehydes exist in this oil, and that citral is the one which occurs in smallest quantity. This assertion is quite unsupported by experimental evidence, however, and is probably incorrect. Tiemann has shown that two stereoisomeric forms of the aldehyde exist, which are practically identical in their physical properties, differing chiefly in the properties of some of their derivatives.

Citronellal $C_{10}H_{18}O$ is the aldehyde of citronellol; it is a liquid of characteristic odour of citronella, of specific gravity ·878 and refractive index 1·4481. It is dextrorotary, +8·2°. Under ordinary pressure it boils at 206°. Its probable constitution is

$$C(CH_3)_2:CH\cdot CH_2\cdot CH_2\cdot CH(CH_3)CH_2\cdot COH.$$

CHAPTER II.

ESSENTIAL OILS.

OIL OF ALMONDS (BITTER).

SOURCE. From the seeds of *Amygdalus communis var. amara.* (N. O. Rosaceæ). Much of the so-called almond oil of commerce is obtained from the kernels of the apricot or peach, which yield oils almost indistinguishable from that of the almond. The oil does not exist ready formed in the seeds, but results from the decomposition of the glucoside amygdalin in the presence of water by the natural ferment, emulsin.

PHYSICAL PROPERTIES. An oil of characteristic odour, white or faintly yellow, specific gravity 1·045 to 1·070, optically inactive. It contains hydrocyanic acid in the natural state, but this is frequently removed, when the oil is sold as "sine acid. prussic."

CONSTITUENTS. The chief constituent of this oil is benzoic aldehyde $C_6H_5 \cdot COH$, the other bodies present being of very small importance. Natural oil of almonds is often adulterated with, and sometimes entirely substituted by artificial benzaldehyde, which, however, usually contains chlorine compounds, and can thus be distinguished from the natural product.

METHODS OF ANALYSIS, &c. The specific gravity should vary between 1·045 and 1·070, but is seldom higher than 1·060. The oil is optically inactive. It should be examined for artificial benzaldehyde, and for the cheaper oil of mirbane (nitrobenzene, $C_6H_5 \cdot NO_2$). The presence of artificial benzaldehyde is indicated by the presence of traces of chlorine compounds, which, however, are sometimes removed by very careful purification, so that the test becomes inapplicable. A piece of fine blotting paper is soaked in the oil to be tested and placed on a small porcelain dish standing in a larger one. A large beaker with its sides moistened with distilled water is stood over the paper and smaller dish, and the paper is set alight. The gases formed during the combustion are partially absorbed by the water. A few drops of nitric acid are added to the liquid, and it is then tested in the usual way for chlorides. Nitrobenzene is detected by reduction to aniline by means of iron filings and acetic acid. The aniline, if present, is distilled off, and a few drops of chloride of lime solution are added. If aniline is present, a characteristic violet colour is produced. The pure oil should boil at 179°-180°, and should form a crystalline mass when shaken with solution of $NaHSO_3$.

Requirements. Specific gravity 1·045 to 1·070. The oil should be optically inactive, and should contain no traces of chlorine compounds.

OIL OF ANGELICA.

Source. The usual oil of commerce is distilled from the root of *Angelica officinalis* (N.O. Umbelliferae) but other parts of the plant also yield an essential oil.

Physical Properties. Oil of characteristic odour of the plant, of specific gravity ·865 to ·905, and optical activity + 15° to 30°.

Constituents. Dextrophellandrene is present in this oil, with, possibly, one or more other terpenes. One or more sesquiterpenes are also probably present. Methyl-ethyl-acetic and pentadecylic acids have been isolated, together with small quantities of oxy-acid anhydrides. There are also esters presents, the nature of which require elucidation.

Methods of Analysis and Requirements. In the present state of our knowledgo of this oil the physical characteristics are almost the only guides in the analysis of the oil. These are as given above.

OIL OF ANISEED.

Source. From the fruit of *Pimpinella Anisum* [N.O. Umbelliferae] which yields the so-called "ordinary" anise oil, and that of *Ilicium anisatum*, [N.O. Magnoliaceæ] which yields the Chinese star anise oil. The fruit of *Seseli Harveyanum* is known in parts of Australia under the name of anise, but in appearance and flavour it resembles fennel rather than this plant.

Physical Properties. Oil of characteristic odour, solidifying at about 15°. Specific gravity varies from ·975 to ·990. Squire (Ph. Jl. 3rd series, XXIV. 104) quotes an old sample as having a specific gravity of 1·10, but even if this sample were genuine, it must have been almost completely oxidized. Slightly laevorotary, usually about $-1°$ [Duyk (J. Pharm. Chim. 1896, 4, 38 and 206), states that it is dextro-rotary, $+ 2·25°$. This is, however, quite incorrect].

Constituents. The chief constituent of aniseed oil is anethol, upon which body the value of the oil depends almost entirely. This body, $C_{10}H_{12}O$, is the methyl ether of *para*-propenyl phenol. It forms white shining scales melting at 21° and boiling at 232°. There is also present in small quantity, the isomeric methyl-chavicol, which is the analogous allyl compound, and which yields anethol by a molecular rearrangement when heated with alcoholic potash. Oxidation products of anethol are usually present in minute quantity, increasing with the age of the oil. The chief of these are anise aldehyde $C_6H_4(O{\cdot}CH_3)CHO$ and anisic acid $C_6H_4(O{\cdot}CH_3)COOH$. According to Bouchardat and Tardy (*Comptes rendus*, 122, 198) a ketone, either $C_{10}H_{10}O_2$ or $C_{10}H_{12}O_2$, appears to exist in small quantities in Russian oil; also hydrocarbons of high molecular weight, and fenchone. It is, however, not certain that the oil which these chemists used in their investigations, was free from fennel oil, hence their results require confirmation. According to Tilden, both oils contain a dextro-rotary terpene.

METHODS OF ANALYSIS, &c. The specific gravity of aniseed oil should lie between ·975 and ·990. Oils which have become well oxidized have a higher specific gravity; but when this is so, a quantity of anise aldehyde can be found by shaking with strong solution of sodium bisulphite, and collecting the resulting crystalline compound. The fresh oil should yield no such compound.

The optical activity of both varieties of aniseed oil is very low; it is, however, negative in sign, from −1° to −3°. Dextro-rotation indicates adulteration with oil of fennel. Squire states (loc. cit.) that the rotations observed by him vary from + 1·25° to − 2·25° Most probably all these samples were not pure. The melting point is the most useful criterion of the purity of the oil. The following method of determining this is the most satisfactory:—Reduce the temperature of a small quantity of the oil contained in a very narrow test-tube, into which a thermometer is inserted, by immersing it in a freezing mixture, until the mass is quite solid. Then raise the temperature slowly. The mass should not become liquid again below 15°. Constant results cannot be obtained by determining the solidifying point, consequently the melting point should invariably be taken. (See J. C. Umney, Ph. Jl. 3rd Series, 1889, 648.) Oils with an abnormally low melting point have probably had much of the anethol removed. It has been stated that spermaceti has been used as an adulterant of the oil, possibly after some of the anethol has been removed. I have never met with such a case, however. In any appreciable quantity it would lower the specific gravity, raise the melting point, and reduce the solubility in alcohol. According to Squire anethol requires for solution, three parts of rectified spirit and two hundred of proof spirit. As oxidation proceeds, the solubility in alcohol increases, till the oil mixes with rectified spirit in all proportions. Schimmel (*Report*, October, 1895) gives the following table of solubilities for anethol in alcohol of various strengths. The solubility is expressed in grammes per litre of alcohol. Strength of alcohol 20 per cent., 25 per cent., 30 per cent., 40 per cent., 50 per cent. Quantity dissolved 0·12 gr., 0·20 gr., 0·32 gr., 0·86 gr., 2·3 gr. To distinguish between the oils of Pimpinella and Ilicium, the oil may be mixed with a saturated solution of hydrochloric acid gas in absolute alcohol. The former oil yields a blue colouration, whilst the star anise oil does not.

J. C. Umney (Essential oils and essences from the government flower farm, Dunolly, Victoria, Imperial Institute Journal, 1896, 302) has made a preliminary report on the so-called anise oil of Australian growth. He found it had a specific gravity of ·914, and an optical activity of + 19°, and was not solid at 4°. This oil appeared to resemble fennel oil much more than anise oil.

Requirements. Specific gravity ·975 to ·990. Optically active, laevorotary, not higher than –3°. When solidified should not melt below 15° (usually 15°–18°). Soluble in three volumes of rectified spirit. On shaking 5 cc. of the oil, with 20 cc. of 25 per cent. solution of sodium bisulphite, and keeping the temperature at 20° to prevent solidification of anethol, no crystals should separate.

OIL OF BAY.

Source. Distilled from the leaves of *Myrcia Acris* [N.O. Myrtaceæ.]

Physical Properties. Possesses a characteristic odour of the bruised leaves, specific gravity ·965 to ·985. Laevorotary, 0 to—3°.

Constituents. Mittmann found the terpenes pinene and dipentene in this oil, a hydrocarbon of the formula $C_{20}H_{32}$, eugenol and methyl-eugenol. Power and Kleber claim that a hydrocarbon which they term myrcene is also present, isomeric with the terpenes. Citral is also present, and chavicol and methyl-chavicol. Power and Kleber deny the presence of pinene and dipentene, but state that laevophellandrene exists in small quantity.

Methods of Analysis, &c. With rare exceptions the gravity of the oil varies from ·965 to ·985, usually about ·975. Fractionated oils, of course, have a lower or higher gravity as the case may be. The percentage of phenols in the pure oil is high, and, estimated in the same manner as eugenol in oil of cloves, should vary from 55 to 65 per cent. To detect adulteration with turpentine a small quantity should be distilled and the first 10 per cent retained. This is tested for pinene, the chief constituent of oil of turpentine, by adding to 1 cc. an equal volume of amyl nitrite and 2 cc. of glacial acetic acid. The tube in which the liquids are, is then cooled in ice and salt and a mixture of equal parts of glacial acetic and strong hydrochloric acids is added, drop by drop, so long as the liquid acquires a blue colouration. If pinene is present a white crystalline precipitate of pinene nitroso-chloride is produced. The presence of turpentine in oil of bay can be detected with certainty by this method. The United States pharmacopœia gives the following test to guard against the addition of oils of cloves or pimento. "If to three drops of the oil contained in a small test tube, five drops of concentrated sulphuric acid be added, and, after the tube has been corked, the mixture be allowed to stand for half an hour, a resinous mass will be obtained. On adding to this mass 4 cc. of diluted alcohol, vigorously shaking the mixture, and gradually heating to the boiling point, the liquid should remain nearly colourless, and should not acquire a red or purplish red colour (distinction from oil of pimento and oil of cloves)."

REQUIREMENTS. Specific gravity ·960 to ·990; should contain at least 55 per cent. of phenols estimated by potash absorbtion, should be laevo-rotary, not exceeding -3°, and should not give the reaction above described for oil of cloves or pimento.

OIL OF BERGAMOT.

SOURCE. From the fresh peel of the fruit of *Citrus Bergamia*, by mechanical means, [N.O. Rutaceæ, sub-order Aurantieæ].

PHYSICAL PROPERTIES. An aromatic oil, with characteristic odour of the fruit, generally of a green colour, due to the presence of chlorophyll. Specific gravity ·882 to ·885 at 15°. Rotary power about $+15^\circ$.

CONSTITUENTS. Limonene $C_{10}H_{16}$ and dipentene $C_{10}H_{16}$ appear to be the only terpenes existing in oil of bergamot. In addition to these the alcohol linalol $C_{10}H_{17}OH$ and linalyl acetate $C_{10}H_{17}O \cdot (C_2H_3O)$ occur in large amount, and to the latter body the greater part of the value of the oil is due. Bergaptene $C_{12}H_8O_4$, a body whose chemical relationships are scarcely understood yet, but which is probably a di-oxycumarin derivative, is present in greater or less quantity according to the age of the oil. On keeping the oil, this is gradually deposited as a crystalline magma. Crismer also claims to have isolated a second solid substance from the oil, which is not identical with bergaptene.

METHODS OF ANALYSIS, &c. The specific gravity of oil of bergamot is fairly constant. It should not vary outside the limits ·881 and ·886. The usual adulterants, turpentine, lemon, orange, or *distilled* bergamot oil (of far less value than the oil obtained by pressure) will lower the specific gravity, whilst fatty oils of course raise it. The rotary power of oil of Bergamot is low, and whilst any one of the usual adulterants present in any appreciable quantity would alter this value materially, judicious mixtures of laevorotary turpentine and lemon oil, would not do so. The oil is frequently too dark for its rotary power to be taken in 100 mm. tube, so that it may either be (as Umney suggests) decolourized or partly so, by filtration through animal charcoal, or preferably, the rotary power may be taken in a 50 or 20 mm. tube, and calculated for 100 mm. The rotary power should lie between +10° and +16°. (Schimmel allows rather wider limits, +8° to +20°.) As the oil contains a small quantity of solid constituents not volatile at 100°, the amount should always be estimated. Five grammes of the oil are evaporated to constant weight in a porcelain dish, on the water bath. The residue should be from 5 to 6 per cent. More than 6 per cent. will indicate adulteration with a fatty oil, less than 5 per cent. will suggest the presence of turpentine, orange, &c. The solubility of the oil in alcohol is also a useful feature. All bergamot oils should yield a clear solution with half their volume of 90 per cent. alcohol, remaining clear on further addition of the alcohol. Nearly all samples are soluble in twice their volume of 80 per cent. alcohol. If a sample is not completely dissolved (neglecting a slight turbidity due to the stearoptene present) the residue on evaporation should be carefully examined for fatty oils. The residue over 6 per cent. will probably be an adulteration of this character.

The estimation of the linalyl acetate, however, is the chief means of valuing the oil. The best method for estimating this is the simple saponification method, first applied to this oil by Schimmel. About two grammes of the oil are weighed into a flask and dissolved in 10 cc. of alcohol. A few drops of phenol-phthalein solution are added and alcoholic solution of potash of known strength (about half normal), is dropped in from a burette. If the first two or three drops colour the phenol-phthalein red, it may be taken that the amount of free acids present is negligible. Otherwise the quantity of potash solution used must be noted. The solution is then run in till 20 cc. have been added. The mixture is then boiled under a reflux condenser, on the water bath for an hour. It is then diluted with water and the excess of potash is estimated by titration with half normal acid. The amount of potash used in saponification (minus the quantity, if any, required to neutralize free acids) multiplied by 3·5 gives approximately the percentage of linalyl acetate. This is calculated easily from the equation

$$C_{10}H_{17}O \cdot CH_3CO + KOH = C_{10}H_{17}OH + CH_3CO_2K.$$

The results will, however, be from 1 to 2 per cent. too high, as the solid, more or less resinous, constituents of the oil are partially decomposed and retain a small quantity of potash. This can be allowed for by heating the residue left on evaporation, in the same way, and deducting the amount of potash used from that found necessary for saponifying the original oil. The normal amount of linalyl acetate present varies according to the ripeness of the fruits used, and the locality, soil, &c. Schimmel gives 30 per cent. as the minimum. This figure frequently exceeds 40 per cent., and assuming the oil is genuine, its value largely depends on its ester content. It would not be safe to accept oils yielding under 25 per cent. of ester. Rectification partially decomposes the linalyl acetate, so that the ester content is invariably low in distilled oils. Schimmel (Report, April, 1893) notes a case where a distilled oil contained only 12 per cent. of linalyl acetate, but which contained a correspondingly high quantity of free linalol. On acetylating, the oil gave an ester value of 61·5 per cent. The free linalol may be estimated in the oil by this means. It usually amounts to about 7 or 8 per cent. I believe it has been suggested to raise the ester value of poor oils by acetylation of the linalol present. Whether this would give satisfactory results, is uncertain, but Bouchardat states that acetylization of linalol at 100°-120° does not give linalyl acetate, but an isomeric acetate, probably geranyl acetate. How far this observation has been confirmed is not clear.

REQUIREMENTS. Specific gravity ·881-·886. Rotary power +10° to +16°. Residue on evaporation 5-6 per cent. Should be entirely soluble in half its volume of 90 per cent. alcohol, and in twice its volume of 80 per cent. alcohol (*see above*). Should contain at least 30 per cent. of linalyl acetate.

OIL OF BUCHU.

SOURCE. Distilled from the leaves of several species of *Barosma*, chiefly *B. serratifolia*, *betulina*, and *crenulata* [N.O. Rutaceæ.]

Physical Properties. The oil is a pale liquid of peculiar camphoraceous odour, of specific gravity ·935 to ·945.

Constituents. According to Kondakoff and Bialobrzeski, who are the most recent workers on this oil, there are at least three well defined constituents present in it. These are as follows. Diosphenol, $C_{10}H_{16}O_2$, a body of phenolic nature, forming crystals melting at 81° and boiling at 232°. This body occurs to only a small extent in the oil from *B. serratifolia* but to so great an extent in that from *B. betulina*, that the oil becomes semi-solid at ordinary temperatures. The other constituents are, a hydrocarbon $C_{10}H_{18}$ boiling at 176° and a ketone $C_{10}H_{18}O$.

Methods of Analysis and Requirements. With the exception of the physical characters of the oil, the only other test of general application is that for turpentine, which is the most frequent adulterant of the oil. This can be detected by distilling the oil and examining the earlier fractions, when the low specific gravity and other characters of turpentine will become apparent.

OIL OF CAJUPUT

Source. The oil of Cajuput official in the British Pharmacopœia is distilled from the leaves of *Melaleuca Leucadendron,* but several species of this plant furnish almost identical oils, so that the exact source can scarcely be recognised. Amongst them are *Melaleuca minor, M. uncinata, M. acuminata* and *M. viridiflora* [N. O. Myrtaceæ].

PHYSICAL PROPERTIES. Usually pale greenish colour, (due chiefly to the presence of copper) with a strong camphoraceous odour and a warm aromatic taste. Specific gravity about ·925, either slightly dextro-rotary or slightly laevorotary, according to the source.

CONSTITUENTS. The chief constituent of this oil is cineol (eucalyptol). Terpineol is also present. In some varieties traces of pinene and esters of butyric and valerianic acids occur. According to Bertrand (Bull. Soc. Chim. 1893, 432), the oil from *M. viridifolia,* known as essence of Niaouly contains in addition to cineol and terpineol, valeric and benzoic aldehydes, valerianic acid and its terpineol ester, pinene (*dextro*), limonene (*laevo*), methyl salicylate, and a sulphur compound.

METHODS OF ANALYSIS, &c. The specific gravity of this oil should lie between ·920 and ·930. At least 60 per cent. of the oil should distil between 175° and 185°. The cineol (eucalyptol) can be estimated as described under eucalyptus oil. No definite standard for this substance can yet be fixed, but good oils will yield from 50 to 70 per cent. of cineol.

Requirements. Specific gravity ·920 to ·930; optical rotation, usually not more than +3° or −3° (oil from *M. acuminata* rotates +15° however); at least 60 per cent. should distil between 175° and 185°, and the oil should contain not less than 50 (usually much higher) per cent. of cineol.

OIL OF CALAMUS.

Source. Distilled from the rhizome of *Acorus Calamus*, the sweet flag [N. O. Aroidae].

Physical Properties. A fragrant oil of specific gravity ·960 to ·970 and optical rotation +12° to +35°.

Constituents. A considerable quantity of a terpene, which is probably pinene, is present, together with a small quantity of a sesquiterpene. The more important constituents are not well understood. They are certainly oxygenated bodies.

Methods of Analysis, &c. The specific gravity and optical rotation should fall within the above-mentioned limits and the oil should be soluble in all proportions in 90 per cent. alcohol.

OIL OF CARAWAY.

SOURCE. Distilled from the fruits of *Carum Carui* (N. O. Umbelliferæ).

PHYSICAL PROPERTIES. Colourless or pale yellow oil, darkening with age, and with a spicy taste. Specific gravity about ·910, optical rotation about +80°.

CONSTITUENTS. The only constituents of this oil that can be said to be known with certainty are, limonene (chiefly, if not entirely, dextro-limonene) and carvone $C_{10}H_{14}O$. It is upon this latter body that the value of the oil chiefly depends.

METHODS OF ANALYSIS, &c. The value of this oil varies very greatly in commercial samples, and attention must chiefly be turned to the percentage of carvone contained in the oil. The specific gravity of genuine oils, from which no carvone has been extracted, seldom passes the limits ·905-·920. A lower specific gravity than ·905 indicates the removal of part of the carvone. J. C. Umney considers ·910 to be the lowest limit allowable. The optical rotation is usually close to +80°, but may vary from +75° to +85°. Fractional distillation is a useful indication of the composition of the oil, as carvone boils at 225°, whereas limonene boils at 175°. The fractions 170°-180°, and 220°-230° will give some indication of the proportion of the principal ingredients present, but no exact inferences can be drawn from these results. Various methods have been proposed to estimate the carvone, but as none of these are at all exact, we shall only briefly mention one of them. The oil is mixed with phenyl-hydrazine (equal volumes) and the mixture heated to 100° for an hour. Excess of glacial acetic acid is added, and the whole well shaken. From two to three times the volume of water is then added, and the whole mass thrown on a suction pump, and the crystalline carvone phenyl-hydrazone $C_{10}H_{14}{:}N{\cdot}NH{\cdot}C_6H_5$ is washed with water until of a pale yellowish colour. The mass can be re-crystallized from rectified spirit, but it is impossible to dry it without decomposition, so that only an approximate idea of its weight can be obtained. The crystalline oxime and the hydrogen sulphide compound have also been proposed as bases for estimation of the carvone, but in none of these cases can results be obtained that can be depended on to within 5 or 10 per cent.

REQUIREMENTS. Specific gravity ·905 to ·920. Optical activity + 75° to + 85°. Equal volumes of oil and phenyl-hydrazine, heated in a test-tube to 100° for a few minutes, give a light yellow mass of crystals on cooling (presence of carvone). At least 40 per cent. of the oil should distil at above 200°.

OIL OF CARDAMOMS.

Source. There are numerous varieties of cardamom oil, but that found in commerce is derived from the seeds of *Elletaria Cardamomum* [N. O. Zingiberaceæ].

Physical Properties. A golden yellow oil of camphoraceum odour and burning taste, of specific gravity about ·940 and optical rotation +40°.

Constituents. According to Weber, oil of cardamoms contains terpinene, and another terpene which according to Parry is limonene. Terpineol and eineal are also present, together with a high proportion of esters, chiefly of acetic acid.

Methods of Analysis, etc. According to Schimmel, oil of Malabar cardamoms has a specific gravity of ·943 and an optical rotation of +34° 52′, whilst that from Ceylon cardamoms has a specific gravity ·895 to ·910 and optical rotation +12° to +13°. There appears to be little doubt that Schimmels have been confusing the oil from the wild Ceylon cardamom, which is a variety of the ordinary cardamom, with the oil from the cultivated fruit. E. J. Parry has examined this oil and finds no difference between those from the Malabar and the Mysore varieties as cultivated in Ceylon, but finds that they in no way resemble that described as Ceylon oil by Schimmel. Parry's figures are probably the most reliable published, as they were distilled by himself from samples of seeds specially chosen by MacEwan for the purpose. The specific gravity should lie between ·936 and ·946 and the optical activity between + 34° and + 47°. The oil should dissolve in 3 to 6 parts of 70 per cent., and in 45 parts of 60 per cent. alcohol, with only a faint opacity. It should require at least 9 per cent. of potash to saponify the esters present.

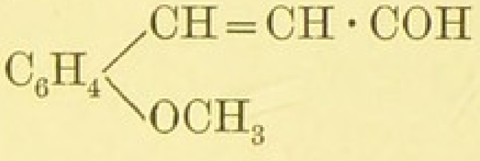
REQUIREMENTS. Specific gravity not exceeding the limits ·936-·946; optical activity +34°-+47°. Should require from 9-14 per cent. of potash for saponification.

OIL OF CASSIA.

SOURCE. By distillation from various parts of the plant, *Cinnamomum Cassia* [N.O. Lauraceæ].

PHYSICAL PROPERTIES. Pale yellow oil with characteristic odour of Cinnamon. Specific gravity about 1·055. Optically it is practically inactive, at most faintly laevorotary.

CONSTITUENTS. The chief constituent of oil of cassia, is, as in the case of oil of cinnamon, cinnamic aldehyde C_9H_8O. Small quantities of a terpene exist, and a compound of cinnamic and acetic acids has also been isolated. Oxidation products of cinnamic aldehyde occur in small quantity according to the age and exposure of the oil. Schimmels (Report, October, 1894), have recently isolated a solid cystalline body from the oil. It forms yellowish hexagonal tables with oblique sides, melting at 46°-47° and boiling at 160°-161° at 12 mm. pressure. The crystals are soluble in most organic solvents. This body appears to be an unsaturated aldehyde. Its formula is $C_{10}H_{10}O_2$ and its constitution is probably :—



$$C_6H_4\left\langle\begin{array}{l}CH=CH\cdot COH\\ OCH_3\end{array}\right.$$

which makes it the aldehyde of *p*-methyl coumaric acid. Bertram and Kürsten have investigated the body (Jour. prak. Chem. 1895, 51, 316).

METHODS OF ANALYSIS, &c. The specific gravity should lie between 1·050 and 1·065. The optical activity should be practically nil. Petroleum oil will be indicated by a low specific gravity. Hirschsohn recommends that the oil should be shaken in a graduated tube with three times its volume of light petroleum ether of specific gravity ·650. A diminution in its volume indicates the presence of petroleum, resin (which also leaves a hard, brittle residue on distillation), or fatty oils; an increase in volume indicates castor oil. The petroleum extract is shaken with copper hydroxide. A blue solution indicates copaiba or resin. One volume of the pure oil should give a clear or faintly opalescent solution with three volumes of 70 per cent. alcohol at 15°. The most important determination, however, is that of the cinnamic aldehyde. This will be found described under cinnamon oil. Carried out in this method, it should be at least 75-80 per cent.

Schimmel gives the following details for oils from various parts of the plant:—

(1.) Cassia bark, yield 1·5 per cent. Specific gravity 1·035; 88·9 per cent. aldehyde.

(2.) Cassia buds, yield 1·55 per cent. Specific gravity 1·026; 8·04 per cent. aldehyde.

(3.) Cassia budsticks, yield 1·64 per cent. Specific gravity 1·046; 92 per cent. aldehyde.

(4.) Cassia leaves, stalks and twigs, mixed, yield ·77 per cent. Specific gravity 1·055; 93 per cent. aldehyde.

From this it appears that cassia oil of commerce must be distilled from some less valuable portion of the plants, with the leaves and twigs.

Requirements. Specific gravity, 1·050-1·065. Optical activity, nil. Cinnamic aldehyde not less than 75 per cent.

OIL OF CEDAR WOOD.

Source. Distilled from the wood of several varieties of cedar. The chief oil, known as cedar oil is that from *Juniperus Virginiana.* [N.O. Coniferae: family, Cupressineæ].

Physical Properties. Oil with characteristic odour of the wood, varying in colour from red to yellow or nearly colourless, specific gravity from ·940 to ·960, optically active, laevorotary, about -20° to -40°.

Constituents. The chemistry of cedar oil is still imperfectly understood. It is known to contain at least one, and probably two, sesquiterpenes $C_{15}H_{24}$. Cedrene is the characteristic hydrocarbon, but possibly cadinene also occurs. Confusion seems to exist as to the exact nature of the hydrocarbons of this oil, as Chapoteaut (see Santal Wood Oil) held that a hydrocarbon $C_{15}H_{22}$ obtained by the action of P_2O_5 on santalal, was identical with the hydrocarbon of cedar oil. Chapman has lately compared these two and states they are not identical. But as the hydrocarbon from santalal is $C_{15}H_{22}$ and that from cedar oil admittedly $C_{15}H_{24}$, their identity is impossible. Whether that prepared from *santalol* may be identical with cedrene yet remains to be proved. Rousset has recently examined cedar oil chemically and states that cedrene obtained from it has a rotation of $+47{\cdot}9°$ and boils at 131°-132° under a pressure of 10 mm. When oxidized it yields a ketone which can be reduced to an alcohol, $C_{15}H_{26}O$ isocedrol, isomeric with cedar camphor or cedrol, the solid constituent of the oil. It is to the presence of this body, cedrol, that the absorption of acetic acid to form an ester is due (see under Santal Wood Oil) and it probably occurs to the extent of 10 per cent. or thereabouts in the oil. It forms a crystalline mass, which when purified by re-crystallization from alcohol, melts at 86°. Apparently it occurs in greater proportion in the oil, the longer the wood has been kept after cutting, before distillation.

METHODS OF ANALYSIS, &c. In view of the fact that this oil is largely used as an adulterant of Santal Wood Oil, it will be found mentioned under that oil, in so far as its detection in santal oil is concerned. Its specific gravity varies much, and closer limits than ·935 to ·960 can scarcely be laid down with safety. Its optical activity, too, varies very much, from − 20° to − 40°, usually about −30° to −35° According to Schimmel (Report, October, 1893), 80 per cent. distils (at a pressure of about 14 mm.) between 125° and 155°, and 14 per cent. between 155° and 170°. The refractive index is very high, which fact explains its use for oil-immersion lenses. It is about 1·505 to 1·510. It should not require more than traces of potash for saponification, and on acetylization and saponification it should not yield a higher result than 10 per cent of sesquiterpene alcohol ($C_{15}H_{26}O$), nor less than 5 per cent.

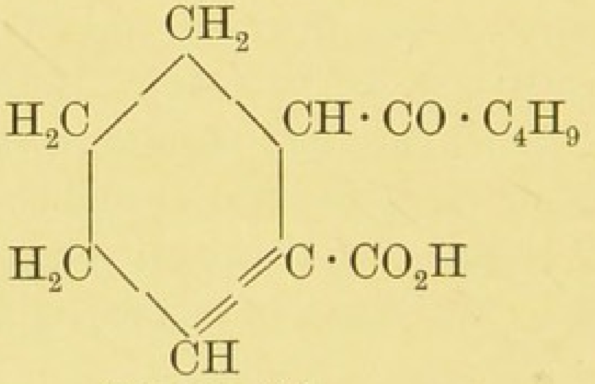
Requirements. Specific gravity ·935-·960. Optical activity −20° to −40°. Refractive index above 1·500. Should not require more than ·5 per cent. of KOH for saponification and should contain from 5 to 10 per cent. of sesquiterpene alcohol, as estimated by acetylization and saponification.

OIL OF CELERY.

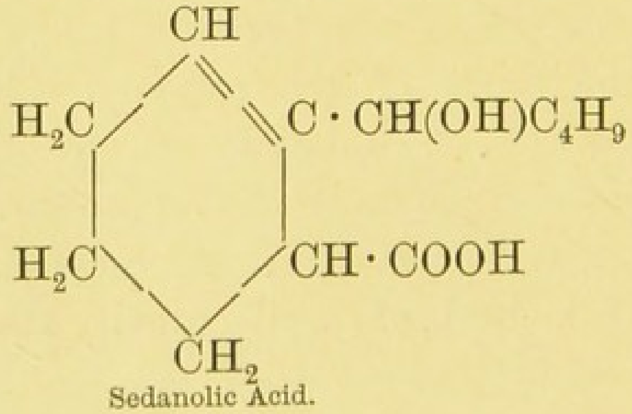
Source. The ordinary oil of celery is obtained from the seeds of the common celery, *Apium Graveolens* (N. O. Umbelliferae), but other parts of the plant also yield oils of fine flavour.

Physical Properties. An oil of characteristic odour of the herb, of specific gravity about ·880 and optical rotation about +70°.

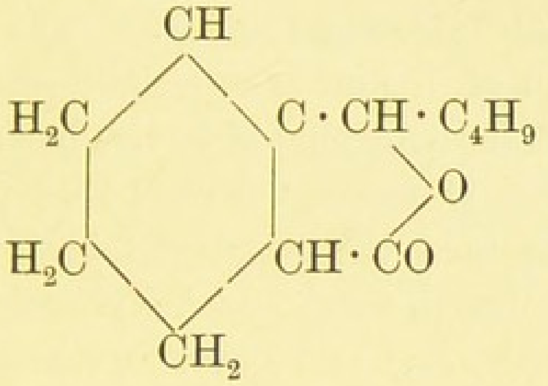
CONSTITUENTS. The preponderating constituent of this oil is the terpene dextrolimonene. Ciamician and Silber have recently investigated the oil and in it have found the following constituents; palmitic acid, guaiacol, a sesquiterpene, a crystalline body of the formula $C_{16}H_{20}O_3$ melting at 66°, and two other oxygenated bodies, together with the anhydride of one of them. These bodies are sedanolic acid and sedanonic acid, and the anhydride of the former—sedanolide. Sedanolic acid is a crystalline body of the formula $C_{12}H_{20}O_3$ melting at 88°, Sedanonic acid $C_{12}H_{18}O_3$, melts at 113°. The constitutions of these three bodies are expressed by the following formulae.



Sadanonic Acid



Sedanolic Acid.



METHODS OF ANALYSIS, AND REQUIREMENTS. In the present state of our knowledge of this oil the physical characters are the only reliable guides in its analysis. The specific gravity should be between ·870 and ·895 and the optical rotation between +65° and +80°. The first 10 per cent. distilled from the oil should possess a higher rotation than the original oil. A lower rotation indicates the presence of turpentine, &c.

OIL OF CHAMOMILE.

SOURCE. Distilled from flowers of *Anthemis Nobilis* [N.O. Compositæ], or from those of *Matricaria chamomilla* [N.O. Compositæ]. The former, which is official in the British Pharmacopœia, is Roman chamomile oil, the latter being known as German chamomile oil.

PHYSICAL PROPERTIES. Pale oil of characteristic odour, often of a bluish or greenish colour. Specific gravity about ·910, and slightly optically active.

CHEMICAL CONSTITUENTS. The chemical composition of this oil is especially interesting, in that it contains a number of bodies belonging to the fatty series. Demarcay showed that pure Anthemis oil contained the isobutyl ester of isobutyric acid, the isobutyl, amyl, and hexyl esters of angelic acid, and the amyl and hexyl esters of tiglic acid. Naudin also isolated a hydrocarbon which he termed anthemene, apparently of the olefine series. The only well ascertained constituent of Matricaria oil is a hydrocarbon, probably of the paraffin group.

METHODS OF ANALYSIS, &c. Apart from a tedious separation of the compounds contained therein, there are no characteristic methods of analysis of this oil. The specific gravity should vary within the limits ·904 and ·916 for Anthemis oil, and ·930 to ·940 for German oil. The oil should be only slightly optically active. German oil becomes semi-solid when cooled to 0°.

REQUIREMENTS. Specific gravity ·904-·916 for Anthemis oil, and ·930 to ·940 for Matricaria oil. Rotation +1° to +4°.

OIL OF CINNAMON.

SOURCE. Distilled from the bark of *Cinnamomum Zeylanicum* (N. O. Lauraceæ). An inferior oil, of quite different composition, is distilled from the leaves of the same plant, and is known as cinnamon leaf oil.

PHYSICAL PROPERTIES. Pale yellowish oil, of fragrant, characteristic odour. Specific gravity about 1·025. Optically, almost inactive; usually very slightly laevorotary.

CONSTITUENTS. The chief constituent of oil of cinnamon bark, and to which its value is in the greater part due, is cinnamic aldehyde C_9H_8O. Small quantities of eugenol $C_{10}H_{12}O_2$ are also present. Oxidation products of cinnamic aldehyde are invariably present, in proportion to the age of the oil. These are chiefly cinnamic acid and its esters. According to Tilden, a laevorotary terpene is present in very small quantity. Phellandrene has been found in the mixture of terpenes present. Cinnamon leaf oil, on the contrary, appears to contain only traces of cinnamic aldehyde, but large quantities of eugenol with some safrol and benzoic aldehyde. Stenhouse stated that benzoic acid was present in the leaf oil. Oil from cinnamon roots has been stated to contain eugenol as its chief constituent, and safrol and benzaldehyde in small quantities. It is said, however, that the ordinary "root" oil is, in reality, a leaf oil, and that the chief constituent of true root oil is camphor.

Methods of Analysis, &c. Cinnamon bark oil should have a specific gravity of from 1·023 to 1·035. Anything outside these limits may be regarded as very suspicious. The oil is practically optically inactive (never more than laevorotary to the extent of under ·5°). Cinnamon leaf oil, which is commonly used as an adulterant, has a specific gravity of from 1·045 to 1·065, and, consequently, causes an increased specific gravity when added to the bark oil. The leaf oil is also slightly dextrorotary, but to such a small extent that this feature is not of much practical value. The estimation of the cinnamic aldehyde and the eugenol is the most important criterion for determining the value of the oil. To determine the cinnamic aldehyde, the most useful method of procedure is as follows :—Twenty-five grammes of the oil are weighed into a flask holding about 400 cc. and well shaken with 100 cc. of a hot solution of sodium bisulphite (30 per cent.). It is well shaken for several minutes, and then allowed to stand for three hours. An equal volume of hot water is added, and the whole is allowed to stand on the water bath until the crystalline compound of the aldehyde and bisulphite is completely dissolved. The non-aldehyde constituents are now floating as a layer on the surface of the aqueous liquid. After cooling, the oily layer is separated carefully, and the aqueous solution well washed once with ether.

The ethereal liquid containing almost the last traces of non-aldehyde constituents is separated and added to the oil in a weighed flask. The ether is recovered at a low temperature, and the oil dried at 100°. It should be weighed every ten minutes, and when the loss is not more than ·050 grammes, it is taken as dry. A simpler method, and one yielding fairly accurate results, is to shake in a flask with a long graduated neck. When the crystalline compound is dissolved by heating on the water bath, the non-aldehyde constituents are driven up into the neck by the cautious addition of more bisulphite solution and read off when cold. These methods give of course the non-aldehyde constituents of the oil. The cinnamic aldehyde is calculated as the difference. It should not be less than 55 per cent. To determine the eugenol, Umney recommends treating the oil from which the cinnamic aldehyde has been removed with 10 per cent. solution of potash, and measuring the portion not absorbed in the graduated neck of the flask. The eugenol is reckoned as that part absorbed by the potash. This yields fairly accurate results, but probably the solution of potash and eugenol dissolves small quantities of non-phenolic constituents. Thoms' method may be well used here. Five grammes of the oil freed from aldehyde are treated with 20 cc. of 15 p.-c. soda solution and 6 grammes of benzoyl chloride. The resulting benzoyl-eugenol is then purified and weighed exactly as described under oil of cloves (p. 108). The percentage of eugenol in the original oil can then easily be calculated. This should not be more than from 3 to 7 per cent.

The German pharmacopœia Commission, 1893, recommended that as a test for pure cinnamon oil, one part of the oil should dissolve in one part of 50 per cent. aqueous solution of salicylate of sodium. The alcoholic solution of the oil should be nearly neutral (absence of appreciable amount of cinnamic acid), and should yield only a light bluish green colour with solution of ferric chloride.

REQUIREMENTS. Specific gravity 1·023-1·035; optical activity, practically nil. Should not exceed −0·5°. Should contain at least 55 per cent. of cinnamic aldehyde and not more than 8 per cent. of eugenol. Should only yield a pale green or greenish blue colour with solution of ferric chloride.

OIL OF CITRON.

SOURCE. Expressed from the fresh peel of the fruit of *Citrus medica*, the common citron [N. O. Rutaceæ].

Physical Properties. A greenish yellow oil of characteristic odour somewhat resembling lemon oil; specific gravity about ·865 and strongly dextrorotary.

Constituents. The only known constituents of this oil are the terpene, limonene, and the aldehyde citral.

Methods of Analysis, &c. The specific gravity should fall between the limits ·860 and ·870, and the optical rotation between + 65° and + 75°. Terpentine may be detected by distilling off the first 10 per cent., which should have a rotation not materially differing from that of the original oil. Additions of small quantities of lemon oil are almost impossible to detect.

OIL OF CITRONELLA.

Source. Distilled from an Indian grass, *Andropogon Nardus* [N. O. Gramineæ].

Physical Properties. Pale yellow oil (sometimes slightly green, due to traces of copper).

Constituents. This oil contains a notable quantity of citronellic aldehyde, $C_{10}H_{18}O$, and also of geraniol, one of the alcohols isomeric with this. Borneol; a ketone, methyl-heptenone, allied to citral; and the terpenes, camphene and dipentene, are also present in the oil. Schimmels have suggested that linalol also occurs, but this has not yet been confirmed. Possibly, also, a sesquiterpene exists in the oil.

METHODS OF ANALYSIS, &c. The usual adulterant of this oil is kerosene, although a kind of gurjun balsam is sometimes added fraudulently. The specific gravity, whilst only varying within certain fairly well defined limits, is not sufficient to indicate purity, but taken in conjunction with the solubility in alcohol, yields valuable information. The specific gravity usually lies between ·895 and ·910, although Umney and Schimmel are agreed that this may fall as low as ·886 in the case of steam distilled oils, without the addition of kerosene, which, in the case of oils distilled over the fire, would be indicated by so low a gravity. The solubility in 80 per cent. alcohol (specific gravity =·8645 at 15° C.) is a most useful test for indicating the presence of either kerosene or a fatty oil. One volume of citronella oil should yield a clear, or, at most, faintly opalescent solution with 10 volumes of 80 per cent. alcohol. Certain adulterants, however, will escape this test. It has been suggested that the amount of alcoholic bodies should be estimated by the acetylization process, but general experience goes to prove that this process is not applicable in the case of this oil, on account of the amount of aldehyde present, which is acted upon by acetic anhydride. The oil should be laevorotary from −1° to about −12°.

REQUIREMENTS. Specific gravity ·885-·910. Should be soluble in 10 volumes of 80 per cent. alcohol, with no separation of oily drops, either at the surface, or at the bottom of the liquid.

OIL OF CLOVES.

SOURCE. From the buds and stems, by distillation, of *Caryophyllus aromaticus* [N. O. Myrtaceæ].

PHYSICAL PROPERTIES. Colourless or pale yellow oil, which darkens on keeping, with a characteristic odour of cloves. Soluble about 1 in 60 of proof spirit, in all proportions of rectified spirit and glacial acetic acid. Specific gravity at 15°, 1·050 to 1·068 (various pharmacopœias give figures as low as 1·041, but any figure much below 1·050 should be regarded with suspicion). Rotary power about −1°.

CONSTITUENTS. The principal constituent of clove oil is the phenol, eugenol, $C_{10}H_{12}O_2$, which occurs to the extent of from 80 to 95 per cent. It also contains the sesquiterpene, caryophyllene

$C_{15}H_{24}$. These two bodies have long been looked upon as the only constituents of the oil, but lately Jorissen (*Pharm. Journal,* 1893, 261) has isolated traces of a body which he believes to be vanillin. Schimmels have also claimed (Report, October 1896) to have discovered methyl alcohol, CH_3OH, and furfurol, $C_5H_4O_2$, an aldehyde of the furfurane group. It is suggested that this body is responsible for the gradual darkening of oil of cloves. Schimmels have also announced (Report, April 1897) that they have discovered in clove oil a body of the formula $C_7H_{14}O$, occurring in minute quantity, and to this body they believe the fruity odour of clove oil is due. It boils at 151°-152°, and appears to be amyl-methyl-ketone $CH_3(CH_2)_4 \cdot CO \cdot CH_3$. Erdmann (Journ. prakt. Chem. 1897, 56, 143) states that he has found acetyl-eugenol and salicylic acid (probably combined with eugenol). He also confirms the presence of furfurol.

METHODS OF ANALYSIS, &c. The high specific gravity of oil of cloves is characteristic, and anything below 1·050 should be regarded with suspicion. Although alcohol is occasionally used as an adulterant, I have never found it myself, and when present is easily detected by the lowering of the specific gravity. Further, pure oil of cloves should yield no distillate below 245°-250°;

any alcohol present will distil over far below 100°. The main constituent, eugenol, being optically inactive, the oil itself is only slightly laevorotary, this being due to the sesquiterpene present. The rotary power should never exceed −1°, and frequently it is almost inactive. The estimation of the eugenol is however the most important matter, and this, combined with the specific gravity, rotary power, and boiling point will detect any ordinary sophistication. The simplest method of estimating the eugenol is to treat a definite quantity of the oil in a flask with a narrow graduated neck, with 10 per cent. solution of potash. The uncombined portion is allowed to rise and is measured at a temperature of 15°. The portion absorbed by the alkali is reckoned as eugenol. It is probable, however, that small quantities of non-phenolic constituents are held in solution by the potassium-eugenol in the aqueous solution. It must be remembered that the specific gravities of eugenol and caryophyllene are very different (eugenol 1·07, caryophyllene ·91), so that allowance must be made for this. Thus, if 25 grammes have been treated, and the unabsorbed portion measures 2·5 cc., this will represent 2·27 grammes approximately, which means a eugenol content of 90·9 per cent. It is found that the specific gravity of oil of cloves does not always agree with that calculated from the specific gravities of the constituents, eugenol and caryophyllene, when these are estimated, so that possibly a third body (other than those mentioned above, which only occur in very small quantities) is present, which is as yet unknown. This is especially probable, in view of the fact that eugenol and caryophyllene mixed do not possess the aroma of oil of cloves. Umney (Ph. Jour. XXV. 946, 977, 1039) finds that the gravity, however, of the oil agrees well with that of the constituents, but his results are based on the assumption that the specific gravity of eugenol is 1·069 and that of caryophyllene ·9031. Whilst the former is undoubtedly correct, the latter cannot be relied on, as according to Wallach and Walker (Ann. Chem. 271, 285) it is doubtful whether the sesquiterpene has been obtained pure (*vide* p. 16). They give the gravity of the purest they could obtain as ·9085. Erdmann gives the specific gravity of caryophyllene as ·9038 at 24°, which would be very nearly identical with Wallach's figures. A method has been devised by Thoms (Analyst, 1892, 11) which is apparently very accurate, but perhaps hardly necessary considering the simplicity of absorbing the phenol with alkali. The method is based on the conversion of eugenol into benzoyl-eugenol $C_{10}H_{11}O_2 \cdot C_7H_5O$. A preliminary experiment on pure eugenol gave a result of 99·25 per cent. The details of the process are as follows: five grammes of the oil are treated with 20 grammes of 15 per cent. caustic soda solution, and 6 grammes of benzoyl chloride are added. The mixture is vigorously shaken, during which operation much heat is evolved. It is allowed to cool, 50 cc. of water are added, and the mixture is again heated until the crystalline ester has become liquid, when it is again cooled. The aqueous liquid is then filtered off, and the residue repeatedly washed with water, heating and cooling at each washing. The removal of the sesquiterpene is effected by treating the crystalline mass with 25 cc. of 90 per cent. alcohol, heating on the water bath, shaking well to break up the cake, cooling, filtering, and collecting the filtrate in a graduated cylinder. This filtrate with the washings with 90 per cent. alcohol should measure 25 cc. The benzoyl-eugenol is then dried to constant weight at 100°, and weighed. It is best not to let the temperature rise to more than about 70°-80° at first, so as to get rid of most of the alcohol at as low a temperature as possible. A correction of ·55 grammes must be allowed for the ester dissolved in the alcohol. The weight of benzoyl-eugenol found + ·55 gramme, multiplied by ·612 gives the amount of eugenol. The chief objection to this method is the large correction required, which represents over ·3 gramme of eugenol.

Requirements. Specific gravity not less than 1·050 nor more than 1·068. Rotary power, between 0° and −1°, boiling point not below 245°. Percentage of eugenol, not less than 80.

OIL OF COPAIBA.

Source. From balsam of copaiba, obtained from copaiba species [N. O. Cesalpiniaceæ].

Physical Properties. Pale yellow oil, with odour of the balsam, laevorotary about −30°, specific gravity about ·900.

Chemical Constituents. Although this oil contains several different compounds, only one can be said to have been definitely separated and identified. This is the sesquiterpene caryophyllene, identical with that obtained from oil of cloves. An enquiry into the chemistry of this oil is greatly needed.

Methods of Analysis, &c. The oils from the South American varieties appear to differ from those of African origin, the latter being probably less valuable therapeutically. Umney has examined the latter kind, and states that it is dextrorotary, and whilst similar to the American oil, is not identical with it. A genuine American oil should be laevorotary—the limits of variation are, however, wide—and should have a specific gravity of ·900 to ·910. The oil is soluble in its own volume of absolute alcohol.

OIL OF CORIANDER.

Source. Distilled from the fruit of *Coriandrum sativum* [N. O. Umbelliferæ].

Physical Properties. Pale oil of characterstic odour of the fruits, specific gravity about ·880, slightly dextrorotary.

Chemical Constituents. The only well-established constituents of this oil are the terpene pinene, and the alcohol linalol. Coriandrol, which was formerly quoted as the main constituent, has been shown to be chiefly linalol. The body or bodies to which the characteristic odour is partly due are not yet known.

Methods of Analysis, &c. The physical characters of this oil are at present the most reliable criterion of its purity. The chemistry of the oil is hardly sufficiently definitely known to admit of purely chemical methods being used. The figures are given below.

Requirements. Specific gravity ·870 to ·885, rotation between +5° and +15°. It should dissolve in three times its volume of 70 per cent.

alcohol. Not less than 45 per cent. should distil between 190° and 200°.

OIL OF CUBEBS.

SOURCE. Distilled from the fruit of *Piper Cubeba* [N. O. Piperaceæ].

PHYSICAL PROPERTIES. Pale green or bluish green oil, with characteristic odour. Specific gravity about ·920, laevorotary about −30°.

CHEMICAL CONSTITUENTS. This oil consists chiefly of hydrocarbons. The only well-established constituents appear to be the terpene dipentene, the sesquiterpene cadinene, and an oxygenated body—the so-called cubeb camphor. This body $C_{15}H_{25}OH$ is a sesquiterpene alcohol and forms crystals melting at 65°, and boiling at 248°, with partial decomposition. It is laevorotary. Probably there are other terpenes or sesquiterpenes present, but so far they have not received positive identification.

METHODS OF ANALYSIS, &c. The specific gravity of the oil lies between ·910 and ·930 at 15°, and the rotation for 100 mm. between −30° and −40°. Fractional distillation appears to be the only other useful method of analysis, as this oil is now so cheap that it is seldom adulterated.

Not more than 10 per cent. should distil below 250°, and at least 75 per cent. should distil between 250° and 280°. Further investigation of this oil is much needed.

REQUIREMENTS. Specific gravity ·910-·930, laevorotation $-30°$ to $-40°$. At least 75 per cent. should distil between 250° and 280°.

CUMIN OIL.

SOURCE. Distilled from the fruit of *Cuminum cyminum* [N. O. Umbelliferæ].

PHYSICAL PROPERTIES. A light yellow oil of specific gravity about ·900 and slightly dextrorotary.

CONSTITUENTS. The only well-identified constituents of this oil are the hydrocarbon cymene and cumic aldehyde. A terpene also possibly exists.

METHODS OF ANALYSIS, &c. The physical characters are the only ones upon which much reliance can be placed, as the relative proportions of aldehyde and hydrocarbon are not constant enough to maintain very close limits. The specific gravity should be from ·890 to ·930, and the optical rotation from $+4°$ to $+6°$. Turpentine may be detected with certainty by the identification of pinene, which also causes the early fractions distilled to be of higher optical rotation.

OIL OF DILL.

Source. From the fruit of *Anethum graveolens* [N. O. Umbelliferæ].

Physical Properties. Pale oil of characteristic odour, dextrorotary about +75°, specific gravity about ·915.

Constituents. The well-defined constituents of this oil are carvone, $C_{10}H_{14}O$, the terpenes limonene and phellandrene, and a hydrocarbon of the paraffin series.

Methods of Analysis, &c. Physical methods are the most trustworthy in the case of this oil. The specific gravity should lie between ·905 and ·925. The optical rotation should not be less than +70°, nor greater than +85°. An approximate separation of terpenes and carvone, by means of fractional distillation, should give the following results. Not more than 20 per cent. should distil over below 185°, and at least 35 to 40 per cent. between 185° and 225°.

OIL OF DILL (INDIAN).

Source. This oil is distilled from the seeds of *Anethum Sowa,* which may be a different species from that just mentioned, or may be only a variety of it.

Physical Properties. An oil of odour much resembling ordinary dill oil, but possessing a much higher specific gravity—usually about ·960.

Constituents. Indian dill oil contains much less carvone than the ordinary oil. The terpene limonene is also present as well as a body of the composition $C_{12}H_{14}O$, isomeric with ordinary apiol, and therefore termed dill apiol.

Methods of Analysis, &c. The specific gravity lies between ·945 and ·970, and the optical rotation between +40° and +50°.

OIL OF EUCALYPTUS.

Source. Distilled from the leaves of various species of *Eucalyptus* [N. O. Myrtaceæ]. Many different trees afford essential oils of very different character, and commercial samples cannot be relied on as being derived from a single source. Hence much of the information given here and elsewhere on this oil must be, at present, accepted with some caution. The principal trees used for preparing the oils, with the specific gravities, &c., of the oils, are given below in brief.

PHYSICAL PROPERTIES. Slightly yellow, red, or white mobile oil with, in most cases, a characteristic odour, recalling camphor or menthol. In some cases however, that of *Eucalyptus Citriodora* especially, the oil is sweet scented, and recalls that of lemon-grass. The specific gravity varies with the source, from about ·860 to ·930. The optical rotation is equally variable, from strongly laevorotary to dextrorotary.

CONSTITUENTS. The chief constituent of the medicinal varieties of this oil appears to be cineol (formerly known as eucalyptol), although it has been suggested that the oil owed its value to other constituents. Various other bodies are found in the oils from different trees. These include the terpenes phellandrene, pinene, and possibly dipentene; valeric, butyric, and caproic aldehydes; cymene, cumic aldehyde, citronellol, geraniol, cumic alcohol, citral, citronellal, possibly menthone, ethyl and amyl alcohols.

METHODS OF ANALYSIS, &c. The various oils possessing as they do so widely different characteristics, it is impossible to lay down any standards for all genuine oils at present. The British

Pharmacopœia does not limit the oil to any one species, although it refers especially to *E. Globulus* as the chief species. The characters as far as known are given for the various oils in the table. The oil may be examined for phellandrene by dissolving 1 cc. of the sample in 2 cc. of glacial acetic acid, and adding 2 cc. of a saturated solution of sodium nitrite, when the oil separates and rises to the surface. If phellandrene is present in appreciable quantities the oily mass will become more or less solid, while in its absence it will remain quite liquid. The presence of phellandrene is an indication of the origin of the oil. The estimation of the amount of cineol or eucalyptol, however, is probably the criterion of the value of the oil, except in the case of the sweet scented oils. The eucalyptol—for it is usually so termed when referring to this oil—can only be approximately estimated, and, perhaps, Scammell's process yields the best results. This consists of mixing a known weight of the oil with about one and a half times its weight of syrupy phosphoric acid. The acid should be added drop by drop to the oil kept cold, with continual stirring, until a deep colouration appears. A crystalline compound of eucalyptol and phosphoric acid is formed and is collected on filter paper and drained, and finally pressed to remove adhering terpenes and phosphoric acid. The crystalline compound is then decomposed by hot water, and the separated eucalyptol is measured in a graduated tube. Its specific gravity is ·930, from which the weight can be calculated. The crystalline compound has the composition $C_{10}H_{18}O\cdot H_3PO_4$. The eucalyptol so separated should become solid at $-3°$, otherwise it must be regarded as impure and the operation repeated. Lower results are obtained by the simple freezing out method, which consists in fractionating the oil, and submitting the fractions to low temperatures, by which means the greater part of the eucalyptol crystallizes out, and is separated and measured. The phosphoric acid method, however, gives more satisfactory results. No definite limits can be laid down in the figures for this oil in the present state of our knowledge, but good oils, such as those of Eucalyptus Globulus, &c., should yield *over* 50 per cent. of eucalyptol. Further, the oils high in eucalyptol have a specific gravity of ·905 to ·930, the low gravity oils being, generally, rich in phellandrene. Oils rich in eucalyptol distil chiefly between 170° and 190°.

The following are the chief species of eucalyptus of which the oils have been examined (for this table the author is indebted to Parry's "Chemistry of Essential Oils"):—

EUCALYPTUS OILS.

Oil.	Sp. Gr.	Rotation.	Constituents.
E. Amygdalina	·855–·890	−25° to −89°	Phellandrene, eucalyptol
E. Backhousia	·895–·902	—	Citral, phellandrene
E. Baileyana	·890–·920	—	Eucalyptol, citral, phellandrene
E. Capitellata	·915	—	Eucalyptol, eudesmol
E. Cneorifolia	·915–·925	−5° to +5°	Eucalyptol, cumic aldehyde
E. Corymbosa	·880	—	Citral, geraniol, eucalyptol
E. Crebra	—	—	Eucalyptol
E. Dealbata	·885–·900	—	Citronellal, citronellol, geraniol, citral
E. Dextropinea	·873–·876	Dextrorotary	Dextropinene, aldehydes
E. Dumosa	·900–·912	—	Eucalyptol
E. Eugenoides	·905–·910	+4° to +6°	Eucalyptol, phellandrene
E. Globulus	·910–·930	+1° to +10°	Eucalyptol, pinene, ethyl alcohol, amyl alcohol, and various aldehydes
E. Goniocalyx	·915–·920	—	Eucalyptol
E. Gracilis	—	—	Eucalyptol
E. Haemostoma	·880–·890	—	Cymene, cumic aldehyde
E. Incrassata	—	—	Eucalyptol

EUCALYPTUS OILS—*continued.*

OIL.	SP. GR.	ROTATION.	CONSTITUENTS.
E. Laevopinea	·873	Laevorotary	Laevopinene
E. Leucoxylon	·920–·925	—	Eucalyptol
E. Loxopheba	·883	+5°	Eucalyptol, phellandrene, aldehydes
E. Macrorhyncha	·927	—	Eucalyptol, phellandrene, eudesmol, esters
E. Maculata var. citriodora	·870–·905	0° to +2°	Citronellal, geraniol
E. Microcorys	·895–·930	—	Eucalyptol
E. Obliqua	·895–·915	-70	Eucalyptol, phellandrene
E. Odorata	·900–·925	—	Eucalyptol, phellandrene, cumic aldehyde
E. Oleosa	·905–·930	-5° to +5°	Eucalyptol
E. Populifolia	—	—	Eucalyptol, cumic aldehyde
E. Punctata	·912–·921	-3° to +5°	Eucalyptol
E. Planchoniana	·915	—	Citronellal
E. Resinifera	·900	-15° to -20°	Eucalyptol
E. Rostrata	·915–·930	-2° to +13°	Eucalyptol, valeric aldehyde
E. Risdonia	·910–·925	-2° to -6°	Eucalyptol, phellandrene
E. Staigeriana	·880	—	Citral

FENNEL OIL.

Source. From the fruit of several varieties of Foeniculum [N. O. Umbelliferæ].

Physical Properties. Pale oil of characteristic odour; specific gravity very variable with the country in which the plant is grown.

Constituents. The terpenes, pinene, phellandrene, dipentene, and limonene; fenchone; and anethol, have all been detected in this oil, but all of these bodies are not found in each variety.

Methods of Analysis, &c. The physical characters of this oil form the best criteria of its purity. They are given below.

Requirements. Specific gravity ·960 to ·980; optical rotation +5° to +25°. Not more than 3 per cent. should distil below 220° C.

OIL OF GERANIUM.

Source. The true Geranium oil is obtained from Pelargonium species [N. O. Geraniaceæ]. Indian geranium oil or Palmarosa oil is obtained from *Andropogon Schœnanthus*, one of the Gramineæ.

Physical Properties. An oil of varying colour, often somewhat dark when kept, of pleasant odour, of specific gravity about ·890, slightly optically active.

Constituents. In ordinary geranium oil there exist the alcohols geraniol and citronellol, and certain of their esters, chiefly of tiglic acid. Doubtless other bodies are also present, but they cannot be said to be definitely known, except those occurring in traces. Réunion oil, for example, has been found to contain two ketones $C_{10}H_{18}O$ (possibly menthone) and $C_{10}H_{16}O$, and possibly linalol. Palmarosa oil—the so-called Indian geranium oil—contains traces of dipentene, methyl-heptenone, geranyl acetate, geranyl caproate and free geraniol.

METHODS OF ANALYSIS. True geranium oil should be soluble in three volumes of 70 per cent. alcohol. The specific gravity should lie between ·888 and ·905, usually about ·892. According to Dietze, the acid and ester numbers yield some useful information. He gives the following figures for seven typical samples:—

	Per cent. of KOH.		
	Acid.	Ester.	Saponification.
French	·68	4·79	5·47
French	·50	5·41	5·91
African	·75	4·56	5·31
Spanish	·98	7·19	8·17
Spanish	·34	7·19	7·53
Indian	·15	3·10	3·25
Indian	·18	2·60	2·78

An estimation of the free and combined geraniol or other alcohols present, calculated as geraniol, by means of a preliminary saponification, and saponification after acetylization, gives most valuable information. The following table, published by Schimmel & Co., gives the constants obtained for a number of pure samples. All the samples were soluble in three volumes of 70 per cent. alcohol:—

Oil.	Sp. gr. at 15°	Rotation.	Ester as geranyl tiglate.	Total geraniol.
Palmarosa	·894	−1·9°	15·0	90·5
Réunion	·890	−9·3°	31·3	84·3
,,	·891	−9°	31·1	84·6
,,	·893	−8·5°	33·3	84·9
,,	·891	−8·1°	32·5	80·0
,,	·891	−9°	34·1	79·3
African	·898	−8·8°	29·1	82·1
Spanish	·898	−8·2°	23·7	85·5
German	·906	−16°	27·9	74·1

REQUIREMENTS. The oil should be soluble in three volumes of 70 per cent. alcohol; specific gravity ·888 to ·905; laevorotary from − 6° to − 18° (except in the case of palmarosa oil); the percentage of ester, calculated from a saponification, as geranyl tiglate, should be from 25 to 35 per cent., and the total amount of alcohols, calculated as geraniol, should not be less than 75 per cent.

OIL OF GINGER.

Source. This oil is distilled from the rhizome of *Zingiber officinale* [N. O. Zingiberaceæ].

Physical Properties. A yellow to brownish oil, of characteristic odour, varying somewhat according to the variety of ginger from which it is distilled. Specific gravity about ·880, optical activity about – 30°.

Constituents. The terpenes phellandrene and camphene have been found in this oil in small quantity, together with one or more sesquiterpenes. The constitution of the oxygenated bodies present in the oil is quite unknown. If, however, the terpenes be distilled off, a high gravity residue is left of a deep brown colour, in which the oxygenated bodies are left. This is practically the "terpeneless oil of ginger," although sesquiterpenes are present in most samples. One sample of this product examined in the author's laboratory, which was sold at an exceedingly high price, was quite pale yellow, and found to be nothing but ordinary oil of ginger.

Methods of Analysis, &c. The specific gravity of the pure oil should be between ·870 and ·885, and the optical rotation between −25° and −45°. According to Thresh the following represents the behaviour on fractional distillation :—

	Per cent.
Below 150°	5
150°—200°	10
200°—240°	8
240°—265°	60
265°—300°	7
Residue	10

OIL OF HOPS.

SOURCE. Distilled from the flowers of the common hop, *Humulus lupulus*. [N. O. Urticeæ.]

PHYSICAL PROPERTIES. A pale yellow to greenish yellow oil with an odour of hops. Specific gravity about ·890 and nearly inactive, or at most faintly dextrorotary.

CONSTITUENTS. A small quantity of a terpene is, possibly, present, but this is not yet settled. Chapman has found tetrahydro-cymene and possibly another hydrocarbon. A considerable proportion of the sesquiterpene, humulene is present, and small quantities of oxygenated bodies, probably including the alcohol, geraniol.

Requirements. The specific gravity should be from ·855 to ·882, and the optical rotation from 0° to +1°.

JASMIN OIL.

Source. Extracted by solvents from the pomade of the jasmin flowers, *Jasminum grandiflorum* [N. O. Jasmineæ].

Physical Properties. A sweet-smelling oil of specific gravity about 1·01 and optical activity about +3°.

Constituents. According to Verley the principal constituent of this oil is the body phenyl-glycol-methylene-acetal, $C_9H_{10}O_2$. This appears however to be incorrect, and the recent work of Hesse and Müller tends to show that this body is entirely absent from the oil, and that the chief odorous bodies are benzyl acetate, linalyl acetate, and the ketone, jasmone. In addition to these bodies, the free alcohols, linalol and benzyl alcohol, are present, and small quantities of methyl anthranilate and indol, both of which are nitrogenous bodies.

Methods of Analysis and Requirements. The specific gravity, optical rotation and ester content are the most important features to be noted. The genuine samples examined by Hesse gave the specific gravity as between 1·006 and 1·018, the optical rotation from +2°30′ to +3°30′, and the esters, calculated as benzyl acetate, as 69·1 per cent. to 73 per cent., or as linalyl acetate, between 90·3 per cent. and 95·4 per cent.

OIL OF JUNIPER.

Source. Distilled from the berries of *Juniperus communis* [Coniferæ].

Physical Properties. Pale oil with characteristic odour, of specific gravity about ·875, laevorotary about – 10°.

Constituents. So far the only well defined bodies which have been detected in this oil are the terpene pinene, the sesquiterpene cadinene, and a camphor termed juniper camphor.

Methods of Analysis, &c. The physical properties of the oil are the only tests upon which much reliance can be placed, in our present state of knowledge of this oil. These are the specific gravity, fractional distillation, optical activity and solubility, These are as given below.

Requirements. Specific gravity ·865 to ·885; optical activity between –3° and –18°; should be soluble in four volumes of 95 per cent. alcohol.

OIL OF LAVENDER.

Source. By distillation, from the flowers of *Lavandula vera* [N. O. Labiatæ]. If the stalks also are used an inferior oil is obtained.

Physical Properties. Pale yellow or nearly colourless oil with a fragrant odour of the flowers. Specific gravity about ·885. Laevorotary from $-4°$ to $-8°$. Soluble in three volumes of 70 per cent. alcohol.

Chemical Constituents. Lavender oil varies much in its composition, according to the soil and locality in which the plant is grown. A very marked difference exists between English oil and that from other countries, France in particular. Tiemann and Semmler (Berichte, 25, 1180) published the results of their examination of lavender oil and stated that it contained lavendol (an alcohol) and its acetic ester, as well as limonene, a sesquiterpene and some unknown oxygenated bodies which had great influence on the odour. Bertram and Walbaum (J. prakt. chem. 45, 590) showed that lavendol was in reality linalol $C_{10}H_{18}O$. It is largely in the percentage of linalyl acetate that Mitcham oil differs from the French oil. The former contains only about 7 per cent., whereas the latter contains from 30 to 40 per cent. Pinene $C_{10}H_{16}$ occurs in traces only. Cineol $C_{10}H_{18}O$ also occurs, but not in any great quantity, except in the English oil. Duyk (J. pharm. chim. 1896, 453) states that both borneol and linalol occur free and as esters (acetic, butyric and valeric) also cineol and a sesquiterpene. Bouchardat (Bull. Soc. Chim. 1804, 147) found small quantities of dextro-camphene $C_{10}H_{16}$. Small quantities of geraniol esters also occur, and a variable amount of an oxygenated stearoptene, the constitution of which is not known. Charabot (Bull. Soc. Chim. 17, 378) records an examination of a sample of Spanish lavender oil, but does not quote the plant from which it was obtained. Only 3 per cent. of esters, but large quantities of the free alcohols were found. Borneol was found in the higher fractions. It may be taken that the oil contains a free alcohol, chiefly linalol, esters, including the acetate, butyrate and valerate, terpenes, cineol and some odoriferous bodies not yet detected.

METHODS OF ANALYSIS, &c. Messrs. Schimmel and Co. have made vigorous attempts to cause the ester content to be adopted as the basis of valuing lavender oils. When it is stated that French oil of lavender contains about five times as much ester as Mitcham oil, it is seen how fallacious such a comparison is. The determination of the ester content is, however, very useful in comparing oils grown in similar localities, especially as spike lavender oil, the common adulterant of French oils, contains practically no esters. The determination is carried out in exactly the same way as described under oil of bergamot (*quod vide*). In the case of English oil, it is advisable to use about 5 grammes of the oil, whilst with foreign oil 2 grammes is sufficient, on account of the higher ester content. English oil should contain about 7 per cent. of esters, calculated as linalyl acetate $C_{10}H_{17}.O.OC.CH_3$, whilst French oil contains from 30 to 40 per cent. J. C. Umney has found up to 9·3 per cent. in English oil, and 41 to 42 per cent. has been found in fine French oils. The free alcohols do not admit of exact determination, as they are so unstable as to be decomposed by almost any re-agent. The specific gravity of English oil usually lies between ·884 and ·890, but oils that have been kept for any length of time often have a specific gravity approaching ·900. Adulteration with alcohol or turpentine lowers this figure considerably, whilst cedar oil and spike lavender oil raise it. The gravity of French oil is about the same, usually from ·883–·895. The optical rotation of both varieties lies between -4° and -10°. Spike oil is dextrorotary to a very small extent, so that adulteration with this oil lowers the rotation. French turpentine and cedar wood oil increase it largely.

The oil should be quite soluble in three volumes (or less) of 70 per cent. alcohol. Turpentine diminishes the solubility greatly. This adulterant is also easily detected on account of the fact that only traces of pinene exist in lavender oil. The greater part of the turpentine will distil under 170°, and yield a strongly rotary fraction, in which pinene can, if necessary, be identified by preparing its characteristic nitrosochloride or dihydrochloride. Messrs. Schimmel and Co. state that the presence of any appreciable quantity of cineol may be taken as indicative of adulteration with oil of spike, but this does not apply to English oil, which contains much cineol. The aroma must at present entirely guide one in judging of the quality of lavender oil, unless gross adulteration has been practised; for judicious admixtures of English with small quantities of French lavender oil and spike oil will give a specific gravity, rotation and ester content, which do not fall outside the limits for pure Mitcham oil. Some exceedingly anomalous results have been obtained by early workers on lavender oil, and it is certain that much of the oil used in their examinations must have been adulterated very grossly. Even so late as 1895, the following impossible figures have been published by Massol (Jour. de Pharmacie et de Chimie, 1895, 49). They embrace his own and other chemists' figures:—

	Massol.	Buignet.	Bruylants.
Lavender Oil, sp. gr.	·930	·886	·876
„ „ rotation	−3·7°	−21·2°	−2·3°
Spike oil, sp. gr.	·935	·886	·908
„ rotation	+9·6°	+3·3°	−0·3°

The following figures are quoted by Umney (Ph. Jl. 3rd Series xxv. 946, &c.) :—

	Sp. gr.	Rotation.	Solubility in 70 p. ct. alcohol.	Esters as linalyl acetate.
Mitcham Oil	·8937	−8°	1 in 2·5	9·3 p. ct.
French Oil 1	·8896	−7·5°	1 in 2	37·1 „
„ „ 2	·8879	−6·75°	1 in 2·25	32·5 „

Requirements. Specific gravity ·882–·900. Optical activity −4° to −10°. The oil should dissolve in three volumes, at most, of 70 per cent. alcohol. When tested by the saponification method, English oil should contain at least 7 per cent. of esters, calculated as linalyl acetate, and French oil should contain at least 32 per cent. A lower ester number than this renders the presence of spike oil very probable; but as defective distillation may cause the esters to decompose, this may in some cases be responsible for a rather lower ester number.

OIL OF LEMON.

SOURCE. From the fresh peel of lemons by mechanical means. (*Citrus limonum*, N. O. Rutaceæ, sub-order Aurantieæ.)

PHYSICAL PROPERTIES. Pale yellow oil, with a fragrant odour and a sharp, somewhat bitter taste. Soluble in all proportions of glacial acetic acid and absolute alcohol. Specific gravity at 15°, ·857 to ·867. Rotary power + 57° to + 67°.

CONSTITUENTS. The well-defined constituents of oil of lemons are the terpenes dextro and laevo-limonene $C_{10}H_{16}$, citral (geranaldehyde) $C_{10}H_{16}O$ and citronellal $C_{10}H_{18}O$. Probably cymene is present in traces (Tilden, Bouchardat, and Lafont), and also pseudocymene. Pinene has also been stated by several observers to be present, but recently Schimmel has examined 50 kilogrammes, and is unable to confirm its presence (*Schimmel's Report*, October, 1897). Traces of phellandrene, however, are present. An alcohol $C_{10}H_{17}{\cdot}OH$ and its acetate $C_{10}H_{17}O$ (C_2H_3O) have been stated to be present, and Ladell (*Chemical News*, 69, 20-21) states that a body $C_{10}H_{18}O$ of specific gravity ·962, has been isolated by fractional distillation. These statements are in accord with the later publication of Umney and Swinton, who state that esters of geraniol and linalol, chiefly the acetate, are present in lemon oil. The earlier communication of these chemists (Ph. Journ. 1898, 196) describes the preliminary experiments which led to these results. They distilled 2 kilogrammes of lemon oil under a very low pressure, and obtained 300 cc. of the higher boiling fraction. This was acetylated in the usual manner by boiling for 2 hours under a reflux condenser with acetic anhydride, and found the resulting oil contained 68 per cent. of saponifiable constituents. They decomposed the aldehydes present by means of alcoholic potash solution, and subsequently distilled the oil under reduced pressure, obtaining a fraction between 230° and 250°, which had the characteristic odour of geraniol. They found geranyl acetate was a normal constituent of both the Messina and the Palermo oils, and that linalyl acetate was present in very small quantities in the Palermo variety. These results were very severely, but apparently without any valid reason, criticised by Messrs Schimmel; Umney and Swinton therefore repeated their work in a somewhat different manner, and have (Ph. Journ. 1898, 370) proved the presence of these bodies in the oil beyond dispute.

In working with very large quantities of oil of lemon in the author's laboratories, the presence of a high boiling constituent had long been noticed, but no attempt was at first made to identify it. The main portion of the oxygenated bodies other than citral appear to be esters of geraniol, but it is clear that some one or more bodies other than these esters are present. A series of experiments have been undertaken, and are now in progress, with the object of isolating this body. Twenty kilogrammes of Messina oil and 20 kilogrammes of Palermo oil were concentrated under a pressure of 10 to 15 mm. until 17·5 kilogrammes of terpenes were obtained. The residual oil, about 2500 cc., was allowed to stand for several weeks, and the separated stearoptene was filtered off. A portion of this concentrated oil was then further concentrated, until every trace of terpene was removed. This was repeated with a fresh 20 kilogrammes of each variety of oil, and the terpeneless residue was found to be optically active between − 7° and − 10° in every case. No trace of terpene was found in this oil after very careful fractionation, hence the optical activity cannot be due to this source. Citral, geraniol and geranyl acetate are all optically inactive, hence the presence of some highly active high boiling constituent must be assumed. The aldehydes present in the concentrated oil were removed in two methods: (1) by shaking several times with hot 25 per cent. solution of sodium bisulphite; (2) by shaking with cyanacetic acid and potash, with the formation of citralidene cyanacetic acid. The latter method, although it entails the use of the very expensive reagent cyanacetic acid, yields very good results, and the unabsorbed residues consisting of the high boiling non-aldehydic constituents, are obtained in a state of purity with great ease. In both cases they have a very pleasant aromatic odour, which, in the case of the Palermo oil, is exceedingly fine and recalls faintly the odour of bergamot. By saponification and distillation of the resulting oil, geraniol can be isolated with great ease from both these oils. Although linalol was not isolated in a state of purity sufficient for its identification from the Palermo oil, the odour of one fraction, especially after acetylization, is so characteristic as to leave no doubt as to its presence. Attempts are now being made to isolate the remaining constituents of the oil. A very careful fractionation of the terpenes from the oil fails to reveal the smallest traces of pinene.

Tilden and Beck (Chem. Soc. Jour., 1890, Trans. 326–327) have isolated a yellow crystalline body from the greasy deposit formed in oil of lemons. It possesses the formula $C_{14}H_{14}O_6$, and melts at 115°–116°. They assigned no name to it. Crismer (*Bull. Soc. Chim.* [3] 6, 30) isolated a second crystalline body from the residue of the distillation of oil of lemons at 10 mm. pressure. It forms a white crystalline powder, melting at 144°, of the formula $C_{10}H_{10}O_4$. A variable amount of stearoptene occurs, the chemistry of which is not further understood at present. A sesquiterpene is also said to exist in minute quantity.

METHODS OF ANALYSIS, &c. The specific gravity of genuine oil of lemons is fairly constant. The best varieties, according to J. C. Umney, have a gravity at 15° of ·858-·859. The limits allowed by Schimmel, and which my experience entirely confirms, are ·857-·862. (The variation in specific gravity, with alteration of temperature, is about ·008 per degree.) The optical activity is usually from +62° to +64°, but occasionally is a little lower or higher, so that +58° to +67° may be regarded as the extreme limits. The variation in optical activity appears to be due to the district in which the lemons are grown. Schimmel (*Report*, April, 1896, p. 30) gives the following table :—

(1) Oils from Messina and Nizza di Sicilia	+59°	to	+61°
(2) Oils from Acireale, Santa Teresa di Riva, Scaletta, S. Lucia, Patti, S. Agata, S. Stefano	+61°	to	+63°
(3) Oils from Catania, Giarre, Giardini, Acireale, Lentini	+63°	to	+64°
(4) Oils from Barcellona, Siracusa	+64°	to	+67°

Change in temperature within small limits scarcely affects the optical activity of the oil. According to Kauffmann (*Pharmaceutical Era*, 1894, 420) exposure to air and light causes a great diminution in rotary power, but this is denied by Schimmel. The determination of the optical activity is of the highest importance, for the most common adulterant, oil of turpentine, is either laevorotary (French), or slightly dextrorotary (American), so that sophistication with either is easy to detect. But mixtures of turpentine and orange oil (which has a rotary power of about 95°) are often used, so that the rotary power is normal. But as turpentine contains as its chief constituent, pinene, boiling at about 156°, whereas lemon oil begins to boil at about 173°, the first fraction of about ten per cent. of the oil will contain pinene, according to the amount of turpentine present. This fraction can then be examined; the pinene can be converted into its characteristic monohydrochloride, or, more simply, the optical activity of the fraction can be taken. This should not vary much from that of the original oil. Schimmel gives 5° as the maximum variation in the optical activity of the first 10 per cent. distilled, but this limit is seldom attained. Indeed, 3° is as high as most oils will differ, and the B. P., 1898, allows only 2°. A blank experiment on pure oil should be made, under the same conditions, for the sake of comparison. Umney gives the following details of the fractionation of pure lemon oil, and gives 30 per cent. as the maximum quantity distilling under 172°:—

	Below 173°	173° to 175°	175° to 178°	178° to 185°	185° to 194°	Residue
(1) Messina	25 p.c.	21 p.c.	21 p.c.	18 p.c.	4 p.c.	11 p.c.
(2) Reggio	25 ,,	25·2 ,,	17·6 ,,	18 ,,	5·6 ,,	8·4 ,,
(3) Messina	18 ,,	32 ,,	26 ,,	16 ,,	2 ,,	6 ,,
(4) Messina	20 ,,	28 ,,	14 ,,	17 ,,	9 ,,	12 ,,

The aldehydes are the most important constituents of lemon oil, as upon them the odour largely depends. Doebner (*Berichte* 27, 352) has published a very useful method of detecting the aldehyde in oils, and by this method detected the aldehyde citronellal in lemon oil, in addition to citral (geranaldehyde). Pyruvic acid $CH_3 \cdot CO \cdot COOH$ and the oil containing the aldehyde are dissolved in alcohol; *b*-naphthylamine $C_{10}H_7 \cdot NH_2$ is also dissolved in alcohol and added to the mixture. The bodies should be in as nearly molecular proportions as can be estimated. The whole is heated on the water bath for three hours under a reflux condenser. The substituted cinchoninic acid formed crystallizes out on cooling, and is purified by washing with ether, and re-crystallizing.

In this way Doebner obtained from citral, citral-*b*-naphthocinchoninic acid $C_9H_{15} \cdot C_{14}H_8NO_2$, in yellow scales, melting at 197°, and citronellal-*b*-naphthocinchoninic acid, $C_9H_{17} \cdot C_{14}H_8NO_2$, in colourless needles, melting at 225°. Of these aldehydes, citral is the most important in lemon oil, as it forms more than half of the oxygenated constituents. Up to the present time, no reliable and accurate method for determining the amount of citral present is known. A fairly accurate method, however, and one which yields useful comparative results, is to shake a definite volume of the oil with hot nearly saturated solution of sodium bisulphite in a flask with a long graduated neck, and allow the non-aldehyde constituents, which are not absorbed by the bisulphite, to rise into the neck. After cooling, this portion is measured, and the difference taken as aldehyde. The amount of aldehydes in pure oil usually varies from 5·5 per cent. to 7·5 per cent. estimated in this method. Garnett proposes to estimate the citral by reducing with sodium, which converts the aldehyde into geraniol, acetylating this body and saponifying the geranyl acetate with alcoholic potash. The great instability of the bodies citral and geraniol, however, causes secondary re-actions to take place, and the process is not reliable to anything more than an approximate degree of accuracy.

The most reliable method of determining the citral in oil of lemons is certainly an absorption process. But the oil should first be concentrated under the lowest possible pressure to about 15 per cent. of its volume. It may then be absorbed by the sodium bisulphite solution, or according to Parry, more accurately by a solution of cyanacetate of potash (using 5 grammes of cyanacetic acid, 5 grammes of potash and 30 cc. of water for 10 cc. of oil of lemons). This latter method has been found to yield very concordant results in the author's laboratory, and if the estimation of citral is required, it certainly gives the most accurate results.

Citral in an impure condition is largely used as a substitute for oil of lemons, on account of its greater keeping powers, and its greater solubility in alcohol. For this purpose, however, in the author's opinion, it is practically useless. The importance of an accurate method of estimation is seen from the fact that there is a large amount of the more useless constituent of oil of lemon, known as citrene, resulting from the manufacture of "terpeneless" oil, which may possibly be used for adulterating the genuine oil.

REQUIREMENTS. Specific gravity between ·857 and ·862. Rotary power + 58° to + 67°. Rotary power of first 10 per cent. distilled off should not vary by more than 3° from that of the original oil. Should not yield more than 30 per cent. distillate under 172°. Should not give more than 95 per cent. of non-aldehyde constituents by the bisulphite method (usually less than this—and upon the citral content, the value, to a certain extent, depends).

LEMON OIL (CONCENTRATED).

Before leaving the subject of lemon oil, attention may be drawn to the so-called concentrated oil of lemons. The rapid deterioration, and the great insolubility of ordinary lemon oil in spirit, have resulted in the preparation of a concentrated oil which is free from both of these disadvantages. The concentrated oil is prepared by removing the greater portion of the terpenes, by distillation under reduced pressure. If about 85 to 90 per cent. be distilled over at a temperature not exceeding 100° C, the residual 10 to 15 per cent. contains practically the whole of the oxygenated odoriferous constituents of the oil. This can then be steam distilled, by which means the objectionable stearoptene and part of the colouring matter are left behind. The distillate collected, amounting to from 4 to 6 per cent. of the original oil used, possesses a high aroma value, and contains nearly the whole of the valuable constituent, of the oil, and practically none of the objectionable ones. It consists, as may be demonstrated by shaking with bisulphite solution, largely of aldehydes. When used for mineral water purposes, this concentrated oil is very soluble in spirit, and does not become "turpentiny."

The value of a genuine terpeneless oil of lemon, that is, an oil which consists entirely of lemon oil from which all the terpenes (and part of the high boiling valueless constituents) have been removed, has been so clearly demonstrated, that many impure substitutes are now on the market, which can be, in general, as the author has shown in a paper read before the British Pharmaceutical Conference in 1899, separated into two classes. These are: (1) Oils which are badly prepared, that is, are pure lemon oil from which a portion only of the terpenes have been removed. Sometimes citral from lemon grass oil is added to this to bring up the aldehyde value. These oils I have generally found to have a specific gravity ·855 to ·880, and an optical rotation of +10° to +50°. By fractional distillation the terpenes have been separated and identified, and the oils have no claim whatever to the name terpeneless. They are merely concentrated lemon oil. (2) Oils which consist almost entirely of purified lemon grass citral. These are usually nearly inactive optically, but have the same specific gravity, or nearly so, as genuine oils. The marked verbena odour, however, is apparent, especially when the oil is diluted. Genuine samples prepared in my own laboratory by distilling off the terpenes under reduced pressure, and then steam distilling the residue, have invariably possessed the following characteristics: specific gravity from ·892 to ·898; optical rotation, −7° to −10°; aldehydic constituents, about 60 per cent. The non-aldehydes have an appreciably higher specific gravity than the terpeneless oil and contain geraniol esters.

OIL OF LEMON GRASS.

Source. Distilled from the fresh Indian grass, from one or more species of *Andropogon* [N. O. Gramineæ].

Physical Properties. Brownish oil, of characteristic verbena odour, specific gravity about ·900.

Constituents. The chief constituent of lemon grass oil is the aldehyde citral $C_{10}H_{16}O$, which was first detected in this oil by Dodge (Amer. Chem. Jour., 12, 553). Later, Barbier and Bouveault found a ketone, methyl-heptenone $C_8H_{14}O$, which they considered was not identical, but isomeric with, the methyl-heptenone obtained by Wallach from cineolic anhydride, and by Tiemann and Semmler from citral. Schimmel and Co., however, have proved the identity of the ketone in lemon grass oil with the already known methyl-heptenone. It has been stated that the aldehyde citronellal $C_{10}H_{18}O$ occurs in this oil, but Barbier and Bouveault deny this (Comptes rendus, 121, 1159). A terpene, or a mixture of terpenes, also occurs in variable quantity, but the nature of these requires elucidation. A variable quantity of the alcohol geraniol $C_{10}H_{18}O$ also occurs in the oil, together with some other bodies as yet unknown.

Stiehl has recently stated that lemon grass oil contains three aldehydes, which he terms allo-lemonal, citriodor-aldehyde and the ordinary citral. He claims that these bodies are all isomeric and that citral occurs in the smallest proportion. The work of Doebner, Semmler, and Tiemann has, however, conclusively proved that there are no grounds for Stiehl's statements.

METHODS OF ANALYSIS, &c. But little has been published on the constants of this oil, but the most important factor in the valuation of the oil is certainly its citral content. In this respect, J. C. Umney writes in the *Chemist and Druggist* as follows :—" The samples of lemon grass oil which I have examined during the past few years, contained percentages of citral varying from 44 to 75 per cent., and even six samples sent to me recently as representing a shipment of thirty cases, have been found to vary from 44 to 69 per cent.... Certain slight modifications of the process adopted for the estimation of the aldehyde in the last named (cassia oil) are necessary, on account of the presence of methyl-heptenone (a ketone which forms a compound with acid sulphite of sodium)."

The specific gravity usually falls between ·895 and ·905. More reliable information about this oil is much needed.

OIL OF LIMES.

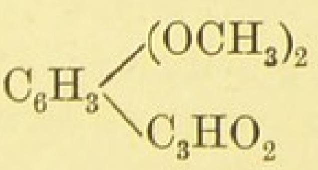
Source. Either expressed or distilled from the peel of *Citrus medica var. acida* [N. O. Rutaceæ].

Physical Properties. Pale yellow or white liquid of characteristic odour varying according to the process by which it is prepared. The expressed oil has a far more pleasant odour, somewhat resembling lemon oil, whilst the less valuable distilled oil has a sharper and more terpene-like odour. Specific gravity about ·870; optical rotation about +40°.

Constituents. The hitherto recognised constituents of this oil are the terpene limonene, which exists in considerable quantity in both the expressed and the distilled oils, and, in the case of the former, citral. E. J. Parry has examined these two oils quite recently, and shows that they differ very materially. After distilling off the first 95 per cent., the residual 5 per cent. possessed the following characteristics in the two cases:—

	Sp. gr.	Rotation.
Expressed oil .	0·8959	−8° 38′
Distilled oil. .	0·9202	−2° 12′

The residue from the expressed oil was found to contain a large quantity of citral (about 65 per cent.) and a considerable quantity of esters, which appeared to be chiefly geranyl acetate. No citral was detected in the distilled oil, and only a very small quantity of esters. A considerable quantity of a body with a high specific gravity and low optical rotation was found to be present. This is in all probability a sesquiterpene. Tilden has found an odourless stearoptene in this oil, which he terms limettine. This has the formula:—



$$C_6H_3\left\langle\begin{matrix}(OCH_3)_2\\C_3HO_2\end{matrix}\right.$$

METHODS OF ANALYSIS, &c. The physical properties are the only criteria of the purity of this oil at present, in addition, of course, to the characteristic odour, which can be fairly well judged by an experienced nose. The following are the limits of specific gravity and rotation for pure oils. Distilled oil: sp. gravity ·855 to ·870, optical rotation +35° to +40°. Expressed oil: sp. gravity ·873 to ·885, optical rotation about +38° to +45°.

OIL OF LIMETTA.

Source. Expressed from the peel of the fruit of *Citrus Limetta* [N. O. Rutaceæ].

Physical Properties. A brownish yellow to greenish yellow oil, of characteristic odour with a secondary odour of bergamot. Specific gravity about ·870 and optical activity about +60°.

Constituents. The greater portion of this oil consists of the terpene limonene, but there is also about 25 per cent. of linalyl acetate present which is responsible for the bergamot odour. There is also about 5 per cent. of free linalol in the oil.

Methods of Analysis, &c. This oil should have a specific gravity of ·870 to ·876 and an optical rotation varying between +55° and +60°. On saponification it should yield an ester percentage equivalent to at least 20 per cent. of linalyl acetate.

OIL OF LINALOE.

Source. Distilled from the wood of various species of *Bursera* [N. O. Buseraceæ], chiefly from that of *Bursera Delpechiana* and *Bursera aloexylon*.

Physical Properties. An oil of fragrant odour, with a faint secondary odour of bergamot. Specific gravity about ·880, and optical rotation about −10°.

Constituents. The most recent work done on this oil is that of Barker and Bouveault. They have confirmed the original statement of Semmler, that the principal constituent of the oil was the alcohol, linalol, $C_{10}H_{18}O$. This occurs to the extent of about 90 per cent., and is the body chiefly responsible for the characteristic odour of the oil. In addition to this, the following bodies have been isolated : geraniol, $C_{10}H_{18}O$ (2 per cent.) ; a sesquiterpene $C_{15}H_{24}$ (3 per cent.) ; methyl-heptenone $C_8H_{14}O$ (·1 per cent.); and two terpenes $C_{10}H_{16}$ (·2 per cent.).

Methods of Analysis, &c. The specific gravity should lie between ·875 and ·900, and the optical rotation between −5° and −15°. By the acetylation and saponification process the linalol content should be at least 80 per cent.

OIL OF LOVAGE.

Source. Distilled from the roots of *Levisticum officinale.* [N. O. Umbelliferæ].

Physical Properties. A dark and somewhat viscous oil of characteristic odour of the root, of specific gravity about 1·020, and slightly dextro-rotary.

Constituents. The only well defined body which has, so far, been isolated from this oil is the alcohol terpineol; several other bodies are undoubtedly present and await identification.

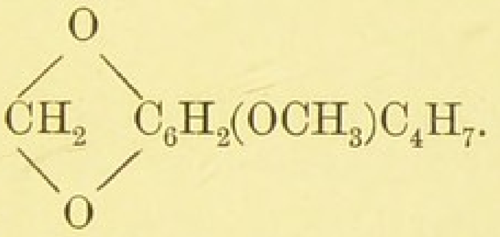
Requirements. The specific gravity of this oil should lie between 1·005 and 1·045, and the optical rotation between +2° and +10°.

OIL OF MACE.

Source. Distilled from the arillus of the nutmeg, usually known as mace [N.O. Myristiceæ]. Much of the commercial oil of mace is merely nutmeg oil, frequently of an inferior quality.

Physical Properties. A pale oil with strong odour of the spice, of specific gravity about ·920, and optical rotation about +10°.

Constituents. Both *dextro*-pinene and *laevo*-pinene are present, together with the terpene limonene. In all, the terpenes represent about 50 per cent. of the oil. Myristicol, $C_{10}H_{16}O$, is present to the extent of about 15 per cent. Two other bodies have been detected by Semmler, of which one is a phenol and the other a crystalline compound of the formula $C_{12}H_{14}O_3$, melting at 30°, to which he gave the name myristicin. This body is probably oxymethylene-methoxy-butenyl-benzene, of the constitution :—



Requirements. The specific gravity should lie between ·910 and ·935. Low gravity oils are to be guarded against, as they usually consist chiefly of oil of nutmeg. The optical rotation varies from +7° to +12°.

OIL OF MUSTARD.

Source. This oil is obtained by the distillation with water of the seeds of the black mustard, *Sinapis nigra* [N. O. Cruciferæ]. White mustard oil, from the seeds of *Sinapis alba*, has also been examined.

Physical Properties. A yellow oil of pungent and disagreeable odour and taste. Specific gravity about 1·020, optically inactive or at most slightly dextrorotary.

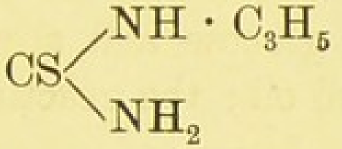
Constituents. The seeds do not contain this essential oil ready formed; there exists in mustard seed a glucoside, potassium myronate, which, under the influence of the ferment myrosin, which is present in the seeds, in the presence of water breaks up into glucose and allyl isothiocyanate, which is mustard oil; the reaction takes place as follows:—

$$\underset{\text{potassium myronate.}}{C_{10}H_{18}KNO_{10}S_2} = \underset{\text{mustard oil.}}{CSN \cdot C_3H_5} + \underset{\text{glucose.}}{C_6H_{12}O_6} + KHSO_4.$$

Traces of allyl thiocyanate, cyanallyl and carbon disulphide are also formed and are therefore present in the oil. Pure artificial allyl isothiocyanate is an article of commerce, and is sold as "artificial oil of mustard." It is formed by the action of potassium thiocyanate on allyl iodide:—

$$CNSK + C_3H_5I = CSN \cdot C_3H_5 + KI.$$

Methods of Analysis. The specific gravity of the oil should vary from 1·015 to 1·030 (the B.P. limits are 1·018 to 1·030) and be optically inactive, or at most dextrorotary to the extent of $-1°$. The allyl isothiocyanate should be present to the extent of at least 95 per cent. It can be estimated in the following manner, which is that of the United States Pharmacopœia. Three grammes of the oil and three grammes of alcohol are shaken in a flask with six grammes of 10 per cent. ammonia. The mixture should become clear after standing for a few hours, or after a few minutes when warmed to 50°, and deposit crystals of thiosinamine (allyl thio-urea), a body of the constitution :—



$$CS\begin{cases} NH \cdot C_3H_5 \\ NH_2 \end{cases}$$

The supernatant liquid is then poured off and evaporated slowly on a water bath in a weighed capsule, fresh portions of the liquid being added as the odour of ammonia disappears. The crystals from the flask used in the first instance are then added, the flask being rinsed out with alcohol, and the capsule is heated on the bath to a constant weight. Three grammes of oil should yield between 3·25 and 3·5 grammes of thiosinamine. The resulting crystals should be examined as to their melting point. The United States Pharmacopœia gives this as 70°, but, according to Parry, from 70° to 74° is admissible, the latter being the melting point of the pure compound.

Requirements. Specific gravity, 1·015 to 1·030. Optical activity, 0° to $+1°$. Allyl isothiocyanate, 95 to 99 per cent.

OIL OF NEROLI.

Source. The true neroli oil (bitter) is obtained by distillation from the flowers of *Citrus bigaradia* (Aurantieæ). Sweet neroli oil is obtained from the flowers of *Citrus Aurantium.*

Physical Properties. Pale yellow oil of sweet odour. Specific gravity from ·870 to ·890. Dextrorotary.

Constituents. Several hydrocarbons have been detected in this oil, of which the best defined is limonene. A paraffin hydrocarbon is also present. In addition to these, the alcohols, geraniol and linalol, together with the acetate of the latter are present. Quite recently the ester, methyl anthranilate which is intensely odorous has been discovered in this oil.

Methods of Analysis, &c. The bitter oil should have a specific gravity of ·870 to ·885, and should be dextrorotary, about +10°. Frequently, however, it is practically inactive. The percentage of potash requisite for saponification yields some information—but too much reliance cannot be placed on it. It usually varies between 2·0 per cent. and 5 per cent. The sweet oil has a slightly higher gravity, usually about ·880, and may be dextrorotary to the extent of +20° or thereabouts. More definite information on this oil is much wanted.

Requirements. Specific gravity ·870 to ·890. Dextrorotation from 0° to + 25°.

OIL OF NUTMEG.

Source. Distilled from the fruit of *Myristica Fragrans* [Myristicaceæ].

Physical Properties. Pale yellowish or nearly colourless oil, often containing small quantities of the so-called fixed oil, which passes over during distillation; with characteristic nutmeg odour, specific gravity near ·900 (very variable, however). Dextrorotary, about 20°.

Constituents. The terpenes pinene and limonene appear to exist in tolerably large quantity, the former especially, in this oil. An oxygenated body myristicol, and some others not yet identified also exist.

Methods of Analysis, &c. Physical methods of analysis are, so far, the most reliable criteria of the purity of this oil. The specific gravity, solubility, rotation and behaviour on fractionation should be determined. The absence of fixed oil may be determined by evaporation on a water bath, when no crystalline residue will be left.

Requirements. Specific gravity ·865 to ·912; dextrorotation +10° to +25°; should be soluble in an equal volume of 95 per cent. alcohol;

about 50 per cent. of the oil distils between 160° and 185°.

OIL OF ONION.

Source. Distilled from the bulbous stem and fresh herb of *Allium Cepa.* [N. O. Liliaceæ.]

Physical Properties. An objectionably smelling oil, slightly heavier than water and laevorotary to the extent of $-5°$.

Constituents. According to Semmler, who is the chief authority on this and the related oils, it contains no oxygenated constituent at all. It is frequently stated that allyl sulphide is normally present in this oil, but according to Semmler this is not correct. The main portion of the oil consists of a sulphur compound of the formula $C_6H_{12}S_2$, an oily liquid of specific gravity 1·023, which boils at about 80° under a pressure of 10 mm. The remaining constituents have, so far, not been identified.

Requirements. The specific gravity should vary from 1·035 to 1·045, and the optical rotation from 0° to $-5°$.

OIL OF ORANGE.

Source. Oil of sweet orange, expressed from fresh peel of the fruit of *Citrus Aurantium* ; oil of bitter orange from that of *Citrus bigaradia* ; [N. O. Rutaceæ, sub-order Aurantieæ.]

Physical Properties. Orange-coloured oil of characteristic odour of the fruit. Specific gravity about ·850. Rotary power, about +96° for the sweet oil, and from +92° to +96° for the bitter oil.

Constituents. The main constituent of this oil is the terpene dextro-limonene $C_{10}H_{16}$. Laevo-limonene occurs to a very small extent, and possibly traces of pinene.

Völckel states (*Annalen* 39, 120) that orange oil contains no oxygen at all. Semmler however (Berichte 24, 201) contradicts this, and ascribes the odour of oil of oranges to an aldehyde or ketone. He states that if the oil be allowed to stand for several weeks after being shaken with a saturated solution of acid sodium sulphite, crystals will separate. On decomposing these with soda and distilling with steam, an oil is obtained having an odour of oranges. Fractional distillation separates from this oil a portion boiling between 225° and 230°. This was found to be citral (geranaldehyde).

The percentage of oxygenated bodies is exceedingly small. Citral is present to the extent of up to about 1 per cent., and traces of citronellal have, according to Flatau and Labbé, been found. Samples carefully examined in the author's laboratory, gave a total aldehyde content, estimated by distilling off most of the terpenes and then absorbing with sodium bisulphite, of from 1 to 1½ per cent. Flatau and Labbé also state that myristicol and myristinic acid, an aldehyde not yet identified, and a crystalline ester are also present. This last named body melts at 65°. The difference between the oils from the bitter and the sweet oils is not yet understood. The most recent contribution to the chemistry of this oil is that by E. J. Parry who has shown that it contains traces of nitrogen in the form of methyl anthranilate, one of the characteristic odour bearers of neroli oil.

METHODS OF ANALYSIS, &c. Owing to the scanty knowledge which we possess about the chemical constituents of this oil, the only available methods of analysis are the determination of the physical constants. Consisting as it does mainly of dextrorotary limonene, this oil presents fairly constant properties, and it is not easy to adulterate it without altering some of these. The only adulterants commonly occurring are oil of lemon, turpentine, the residuum of the manufacture of the so-called terpeneless oil of orange, and alcohol. With regard to the latter, the specific gravity and the optical rotation will be lowered, and a distillate can be obtained at quite a low temperature. The specific gravity may be taken as varying from ·847 to ·856, and the optical rotation as from +95° to +98° in the case of tho sweet oil, and from +92° to +98° in the bitter oil. The admixture of oil of lemon or turpentine tends to raise the specific gravity, but an orange oil of specific gravity ·850 can be mixed with considerable quantities of either lemon oil or turpentine, without its gravity exceeding that of many normal pure oils. Distillation affords useful information. The pure oil commences to boil at about 173°-174°.

Umney gives the following figures for the fractional distillation of a pure sample :—

Fractions.			
173°—175°	175°—178°	178°—188°	Residue.
20 p. c.	61 p. c.	14 p. c.	5 p. c.

Admixture with much turpentine lowers the boiling point of the oil, and the first fraction will possess a very much lower rotary power than the oil itself. In the case where French turpentine has been used, the fraction may be laevorotary, whereas with American turpentine it will be dextrorotary. The optical rotation of the original oil should lie between +92° and +98°. Adulteration with turpentine or much lemon oil will lower this considerably.

The first 10 per cent. distilled from the oil should give a rotary power not far different from that of the original oil. A number of samples examined in the author's laboratory, all of authentic origin, gave a difference not exceeding 5°, some higher and some lower than that of the original oil. An examination of a much larger number of samples, however, is necessary.

It is hardly possible at present to detect with certainty adulteration with the oil *distilled* from pressed or worthless fruit, or with the residuum of the preparation of "terpeneless" oil. The colour is lightened and the odour impaired, but until we know more of the chemistry of the oil, it will be difficult to discriminate chemically between the pure oil and that mixed with the less valuable product.

REQUIREMENTS. (For both the bitter and sweet varieties.) Specific gravity ·847 to ·857. Optical rotation +92° to +98°. Oil commences to distil at about 173° and at least 80 per cent. should distil under 180°. The first 10 per cent. distilling should possess a rotary power not materially different from that of the oil.

OIL OF ORRIS.

SOURCE. Distilled from the rhizome of species of *Iris*, chiefly, if not entirely, from *Iris germanica*, *Iris pallida*, and *Iris florentina*.

Physical Properties. A semi-solid oil of the consistence of butter, with a beautiful odour of violets.

Constituents. According to Flückiger oil of orris contains a quantity of myristic acid, which is not in reality part of the true volatile oil, but is carried over mechanically by the steam during distillation. The liquid oil of orris of commerce, which is exceedingly expensive, has been deprived of this body. Our present knowledge of this oil is due to the late Dr. Tiemann who confirmed Flückiger's observation that myristic acid constituted the bulk of the solid portion of the oil. He further observed, in conjunction with Krüger, that methyl myristicate, oleic acid, oleic aldehyde and an oxygenated body of intensely fragrant odour were present. This body they termed irone. It is a liquid of the formula $C_{13}H_{20}O$, possessing all the well marked properties of a ketone. Its specific gravity is ·942, and it boils at 144° under a pressure of 16 mm. It is slightly dextrorotary. Its odour is somewhat nondescript, but when diluted, it has a characteristic violet odour. The discovery of this body led to the artificial formation of the isomeric ketone ionone, the basis of the well known artificial violet oil.

OIL OF PATCHOULI.

Source. Distilled from the dried leaves of *Pogostemon Patchouli* [N.O. Labiatæ.]

Physical Properties. A brown (sometimes green) oil of fragrant odour, of specific gravity about ·980 and optical rotation about $-60°$. In Penang the two varieties, brown and green are known, and it has been suggested that the former is distilled from the old, and the latter from the young leaves, but this is doubtful.

Constituents. Gladstone in 1864, was the earliest investigator of this oil, and he stated that it contained a sesquiterpene. Later, the so-called patchouli camphor was discovered by Gal and Montgolfier, which Wallach has shown to be a sesquiterpene alcohol, of the formula $C_{15}H_{26}O$. When pure it melts at 56°. The sesquiterpene in the oil is cadinene, but as neither this nor patchouli camphor have any odour resembling the oil, it is clear that the active constituent of the oil still awaits discovery.

Requirements. The oil should have a specific gravity ·975 to ·995 and an optical rotation $-50°$ $-65°$. It should dissolve to a clear solution in an equal volume of 90 per cent. alcohol.

OIL OF PENNYROYAL.

Source. Distilled from the herb, *Mentha pulegium* [N.O. Labiatæ.]

Physical Properties. An oil of yellow or greenish yellow colour, with a powerful odour of the plant. Specific gravity about ·950 and optical rotation about +20°.

Constituents. The only well defined constituent of this oil is the ketone pulegone. Several other compounds appear to be present but have not, so far, been identified.

Requirements. The specific gravity should lie between ·910 and ·960, and the optical rotation between + 15° and +25°. The oil is soluble in twice its volume of 70 per cent alcohol, a characteristic which is destroyed by the addition of turpentine.

OIL OF PEPPERMINT.

Source. Distilled from the fresh or dried herb, *Mentha Piperita* [N.O. Labiatæ]. The British Pharmacopœia requires it to be distilled from the *fresh* herb only. Japanese oil is distilled from *Mentha Arvensis.*

Physical Properties. Pale yellow or yellowish green oil, with an odour of the plant and a sharp pungent taste. Specific gravity about ·900. Optical activity about $-30°$.

Constituents. Peppermint oil is one which is largely influenced in odour and value by changes of soil, climate, &c. The composition of the various oils, however, is, in the main, very similar, and the bodies which modify the odour of the oil so much as to produce the characteristic difference between English and American oils, for example, are not yet known with certainty.

Menthol $C_{10}H_{20}O$ and some of its esters occur to the largest extent in the oil. Power and Kleber (*Zeit. Anal. Chem.* 1894, 33, 762) have made a thorough investigation of the constituents of American oil, and claim to have identified the following bodies :—

Acetic Aldehyde	CH_3COH
Acetic Acid	$CH_3 \cdot COOH$
Pinene	$C_{10}H_{16}$
Limonene	$C_{10}H_{16}$
Menthone	$C_{10}H_{18}O$
Menthyl acetate	$C_{10}H_{19} \cdot C_2H_3O_2$
A Lactone	$C_{10}H_{16}O_2$
Valeric Aldehyde	C_4H_9COH
Isovaleric acid	$C_4H_9 \cdot COOH$
Phellandrene	$C_{10}H_{16}$

Cineol - - - $C_{10}H_{18}O$
Menthol - - - $C_{10}H_{19}\cdot OH$
Methyl isovalerate - $C_{10}H_{19}\cdot CH_9O$
Cadinene - - - $C_{15}H_{24}$
The menthyl ester of an acid $C_8H_{12}O_2$

Traces of amyl alcohol $C_5H_{11}OH$, and of dimethyl sulphide $S(CH_3)_2$ have also been found in the oil. According to Andres and Andreef (*Berichte* 25, 609), Russian oil of peppermint contains, in addition to terpenes a hydrocarbon $C_{10}H_{18}$.

METHODS OF ANALYSIS, &c. The specific gravity of the various oils differs somewhat, that of Japanese oil usually lying between ·895 and ·905. English grown oil varies from ·900 to ·910, and American between ·910 and ·920. All the oils are laevorotary, the Japanese oil being the highest in this respect. Menthol from peppermint being strongly laevorotary (about −60°), it follows that dementholised oil has a lower rotation than natural oil. English oil usually rotates about −25° to −30°, but sometimes exceeds these limits, and 22° to −32° may be taken as covering all pure oils. American oils vary rather more than this, rising to −35° or more, and Japanese oils sometimes exceed −40°; so that somewhat gross adulterations would not be detected by the optical rotation. In any case, much of the Japanese oil on the market is merely the residue of menthol manufacture, and is thus of a very inconstant character. Apart from the specific gravity and optical rotation, the only really useful methods of analysis in the present state of our knowledge, are the quantitative determination of the menthol, both free and as esters, and of the menthone.

To determine the menthol in the form of esters, a known weight, about 5 to 10 grammes, is boiled on a water bath under a reflux condenser with 25 cc. of seminormal alcoholic potash, and the excess of potash titrated with seminormal acid. Every cc. of normal alkali (*i.e.* 2 cc. of seminormal solution) corresponds to ·156 grammes of menthol combined as esters. The total menthol is estimated by boiling an arbitrary quantity of the saponified oil with acetic anhydride and a little sodium acetate in the usual way, washing the acetylated oil and saponifying this with alcoholic potash. From 3 to 5 grammes of the acetylated oil is a convenient quantity to use. To calculate the quantity of menthol it must be remembered that the saponified oil has increased in weight by acetylization, so that to refer the percentage of menthol found to the saponified oil a correction must be used. The formula

$$P = \frac{A \times 15{\cdot}6}{S - (a \times {\cdot}042)}$$

where P is the percentage, A the number of cc. of *normal* alkali used for saponification of the acetylated oil, and S the weight of the acetylated oil used, will give the total percentage of menthol in the oil which has been previously saponified. From this the percentage of total menthol in the oil can easily be calculated, as the saponification of the original oil has decreased its weight approximately in the proportion of ·042 grammes for every cc. of normal alkali used. The difference between the combined and total menthol of course gives the free menthol.

As a matter of fact, these determinations are only approximate, as part of the esters consists of menthyl isovalerate, but the error is quite small and need not be taken into account. The menthone can be readily determined by reducing it to menthol by means of sodium acting on a hot solution of the oil in alcohol. The total menthol now found will represent that originally present in the oil and that formed by the reduction of the menthone. (Menthone, $C_{10}\ H_{18}\ O$ and menthol $C_{10}\ H_{20}\ O$ having almost identical molecular weights, the difference may be neglected).

Umney suggests that not less than 50 per cent. of the oil should distil between 210° and 220°.

The figures on the next page show the chief characteristics of a number of typical samples of known sources :—

Requirements. These must necessarily depend on the variety of the oil. Japanese may vary in specific gravity from ·895 to ·910, American from ·905 to ·925, and English from ·900 to 910. The optical activity varies in the same way. The menthol as esters should lie between 4 and 15 per cent. for American, 4 to 10 per cent. for English (white mint often as high as 14 per cent.), and for Japanese , 3 to 7 per cent. The total menthol should be from 40 to 60 per cent. (American), 50 to 70 per cent. (English), 60 to 90 per cent. (Japanese).

	Specific Gravity.	Rotation.	Menthol as esters.	Free Menthol.	Total Menthol.	Observer.
Wayne County	·914	−32°	14·12	45·5	59·62	Power & Kleber
Michigan	·9007	−29·3°	6·39	43·6	49·99	Power & Kleber
Mississippi	·925	−13·7°	11·47	24·2	35·67	Power & Kleber
Japanese	·910	−34·7°	3·45	72·7	76·15	Power & Kleber
Japanese (dementholised)...	·903	−31·3°	5·71	55·1	60·81	Power & Kleber
Mitcham	·907	−27·9°	4·92	53·9	58·82	Power & Kleber
Saxon	·910	−26°	6·38	61·2	67·58	Power & Kleber
Japanese	·898 (at 24°)	−41·3	3·6	87·3	90·9	Schimmel
English	·906	−24·5°	5·5	53·2	58·7	Schimmel
English	·905	−26·8°	4·6	54·4	59·0	Schimmel
English	·907	−25·6°	5·7	52·5	58·2	Schimmel
English (black mint) ...	·9036	−25·5°	3·7	59·4	63·1	Umney
English (white mint) ...	·9058	−33°	13·6	51·9	65·5	Umney
Australian (Victoria) ...	·912	−27°	8·3	45·6	53·9	Umney

OIL OF PETITGRAIN.

Source. Distilled from the young shoots and leaves of the bitter or sweet orange. *Citrus bigaradia* and *C. aurantium*. [N.O. Rutaceæ.]

Physical Properties. A sweet smelling oil of pale yellow colour, of specific gravity about ·890, and either slightly laevorotary (European) or dextrorotary (South American).

Constituents. The terpene limonene and a sesquiterpene have been identified among the hydrocarbons present in the oil, together with the alcohols geraniol and linalol and their acetic esters.

Methods of Analysis, &c. The specific gravity of the oil should lie between the limits ·885 and ·900. The European oil, distilled exclusively from the leaves, shoots and buds is invariably of laevorotary form, from 0 to $-2°$. The American oil, which possibly is distilled from a mixture of the above with a few immature fruits, is always dextrorotary, owing probably to an excess of limonene. The oil should dissolve easily in twice its volume of 80 per cent. alcohol and should yield on saponification an ester value equivalent to at least 50 per cent. of linalyl acetate. This figure often reaches as high a value as 75 to 80 per cent. The oil from the bitter orange is by far the most valued, on account of its superior odour, but the differences in the two oils are not sufficiently well understood to allow of standards being laid down.

Requirements. Specific gravity ·885 to ·900. Rotation −2° to +4°, soluble in two volumes of 80 per cent. alcohol. Ester value (calculated as linalyl acetate) at least 50 per cent.

OIL OF PIMENTO.

Source. Distilled from the fruit of the allspice tree, *Pimenta officinalis.* [N.O. Myrtaceæ.]

Physical Properties. A brownish oil of characteristic aromatic odour of the spice, in which eugenol predominates. Specific gravity about 1·050, slightly laevorotary.

Constituents. The characteristic principle of this oil is the phenol, eugenol, which is found in large quantities in the oils of cloves and bay. The only other well acertained constituent is a sesquiterpene whose properties are not accurately known. Other bodies are undoubtedly present, which are responsible for the secondary odour of the oil.

METHODS OF ANALYSIS. The estimation of the eugenol content is one of the most effective methods of controlling the purity of this oil, but it must be remembered that oil of cloves contains about 80 to 85 per cent. of this phenol, hence adulteration with this oil would not be indicated unless the amount of eugenol found were higher than the maximum present in genuine pimento oils. The methods adopted for the estimation of the eugenol are identical with those described under oil of cloves. By Thom's method the minimum should be 65 per cent. and not more than 25 per cent. should remain unabsorbed by caustic potash solution. The specific gravity varies from 1·040 and 1·055, the lower limit being prescribed by the British Pharmacopœia. The oil is laevorotary—from $-2°$ to $-4°$. It is soluble in all proportions in 90 per cent., and in two volumes of 70° alcohol.

REQUIREMENTS. Specific gravity not below 1·040 ; optical rotation $0°$ to $-4°$; eugenol content (Thom's method) at least 65 per cent.

PINE-NEEDLE OILS.

Source. There are, of course, many Conifers whose leaves yield essential oils, and many oils of commerce are merely mixtures of several of these bodies. The most important, however, of the fine oils, are those of *Pinus pumilio,* and *Pinus sylvestris* (Coniferæ).

Physical Properties. Pleasant smelling, light coloured oils, of specific gravity about ·865 to ·885; optically active. The oil from *Pinus pumilio* is laevorotary; that from *Pinus sylvestris* is variable.

Constituents. Both oils appear to contain nearly identical constituents, although not always in the same quantity. These, as far as recognised; are the terpenes, pinene, sylvestrene, dipentene; the sesquiterpene cadinene, and bornyl acetate. Possibly phellandrene is also present in *Pinus pumilio* oil. Abietic acid or its anhydride may also be present in traces.

Methods of Analysis, &c. According to Umney, true oil of *Pinus sylvestris* is not usually met with. The following characteristics were found for this oil, distilled from leaves at different parts of the year :—

	1	2	3
Specific gravity	·886	·885	·889
Rotation	+ 10°	− 19°	− 7·75°
Bornyl acetate	3·5 p.c.	3·5 p. c.	2·9 p.c.

Pinus pumilio oil contains more bornyl acetate than the oil of *Pinus sylvestris,* and the characters of this oil are given by Umney as follows:—

	1	2
Specific gravity	·8667	·8682
Rotation	− 7·75°	− 8·5°
Bornyl acetate	5·6 p.c.	6·3 p.c.

On fractionation, a process chiefly useful in guarding against adulteration with turpentine, not more than 10 per cent. should distil below 165° and considerable fractions from 165° to 200° should be obtained.

Requirements. The requirements for a genuine oil of *Pinus pumilio,* which is now official, are as follows:—specific gravity ·865–·870, optical activity − 5° to − 10°. Not more than 10 per cent. should distil below 165° C.

TABLE OF PINE NEEDLE OILS (SCHIMMEL).

Oil.	Specific Gravity.	Rotation.	Constituents.
Abies excelsa ...	·865—·875	– 20° to – 60°	Pinene, limonene, cadinene, bornyl acetate.
Pinus sylvestris ...	·880—·885	+ 20° to – 20°	Pinene, sylvestrene, dipentene, cadinene, bornyl acetate.
Pinus pumilio ...	·865—·875	– 5° to – 10°	Pinene, phellandrene, sylvestrene, cadinene, bornyl acetate.
Abies sibirica ...	·910—·920	– 40° to – 45°	Bornyl acetate.
Picea vulgaris ..	·888	– 21° 40′	Pinene, phellandrene, dipentene, cadinene, bornyl acetate,
Pinus nigra ...	·925	– 40°	Bornyl acetate.
Abies canadensis ..	·907	– 20° to – 26°	Pinene, camphene, cadinene, bornyl acetate.
Picea nigra	·913	– 24°	Bornyl acetate.

OIL OF ROSEMARY

Source. Distilled from the flowering tops of *Rosmarinus officinalis* [N.O. Labiatæ].

Physical Properties. Pale yellow or colourless oil, with characteristic odour and sharp taste. Specific gravity about ·900–920; slightly dextrorotary.

Constituents. Pinene was originally found in this oil, and reported as *laevo*pinene. There is no doubt, however, that the oil examined was adulterated with French turpentine oil. A more recent examination of oil of unquestionable purity has shown that a little pinene is present, but it is always *dextro*pinene. Camphene also exists in small quantity. Besides these terpenes, the oil contains borneol, both free and as esters, chiefly as acetate, and also camphor and cineol.

Methods of Analysis, &c. Pure rosemary oil should not have a specific gravity below ·900, nor above ·920. It is dextrorotary, but not more than + 10°. Frequently it is not higher than + 2° or + 3°. The specific gravity and rotation are both materially altered by the addition of turpentine. Pure oil should be soluble in, at most, twice its volume of rectified spirit. The solubility is, of course, much lessened by adulteration with turpentine. The optical activity of the first 10 per cent. distilled will also be much different from that of the original oil, if turpentine has been added, laevorotary if French oil is used, and dextrorotary if American. Judicious mixtures of both of these, however, interferes with this test. Not more than 20 per cent. should distil over or below 170° in pure oils. The oil should be saponified in the usual way, and the esters calculated as bornyl acetate $C_{10}H_{17} \cdot O_2C \cdot CH_3$. This usually amounts to from 4 to 6 per cent. The free alcohols are estimated by acetylization and saponification. These are calculated as borneol $C_{10}H_{17}OH$, and vary from 10 to 20 per cent. Schimmel gives the following figures for five pure samples of their own distillation :—

No.	Yield of Oil.	Specific gravity.	Rotation.	Rotation of 1st 10 p.c. distilled.	Bornyl acetate.	Borneol.
1	1·4 %	·913	+4·3°	+1·5°	5·4 %	16·8 %
2	1·7	·909	+3·7°	+1·4°	5·8 %	18·8 %
3	1·5	·910	+5·9°	+6·4°	—	—
4	1·73	·904	+6·9°	+7·8°	—	—
5	1·75	·906	+8·9°	+8·4°	—	—

Umney gives the following for three samples :—

	Sp. gr.	Rotation.	Borneol.
Australian (Victoria)	·9060	+0·25°	15·1°/o
English	·9097	+7·5°	13·26°/o
French	·9079	+3·5°	11·07° o

Requirements. Specific gravity not below ·900. Optical rotation, dextrorotary, not more than +10°. Soluble in one or two volumes of rectified spirit. Should contain at least 4 per cent. of esters calculated as bornyl acetate, and 12 per cent. of free alcohols calculated as borneol.

OIL OF ROSES

Source. From the fresh flowers of *Rosa Damascena*, and other varieties of the rose [N.O. Rosaceæ], by distillation.

Physical Properties. A pale yellow oil at temperatures above about 20°, depositing a variable amount of crystalline stearoptene at ordinary temperatures, which causes some variation in the melting point of the semi-solid " otto " or " attar " of roses. Specific gravity about ·860 to ·870. Optical activity, small, usually about −3°.

Constituents. The chemistry of the constituents of rose oil has long been a matter of dispute, but recent work has succeeded in clearing up a good deal of what was till lately a matter of doubt. However, the perfume of this oil, as in the case of many oils in which the chief constituent is well defined, depends on several bodies, and is probably much modified by the presence of traces of some as yet unknown compound. Markovnikoff originally stated that the chief constituent of the liquid portion of the oil was roseol, an alcohol of the formula $C_{10}H_{20}O$. Poleck and C. Eckart on the other hand held the view that the alcohol was geraniol $C_{10}H_{18}O$. Eckart then proposed the name rhodinol for the alcohol, which he agreed was of the formula $C_{10}H_{18}O$, but which he considered different from geraniol. Bertram and Gildemeister then showed that rhodinol was geraniol, containing a small quantity of another alcohol. The word rhodinol then became quite indefinite and was used by several chemists for quite different substances, so that great confusion resulted. These differences were satisfactorily explained by Tiemann and Schmidt, who in 1896 proved that the alcoholic constituent of oil of roses consisted of two alcohols, geraniol $C_{10}H_{18}O$ and citronellol $C_{10}H_{20}O$. These chemists stated that Turkish rose oil contains 80 per cent. of alcohols boiling at 112° to 116° at 12 mm. pressure.

These alcohols consist of about 75 per cent. geraniol and 25 per cent. citronellol. The latter is laevorotary −4·3°. (*Berichte* 1896. *903*). Dupont and Guerlain suggested that a laevorotary ethereal salt, which is hydrolysed on prolonged boiling with water, exists in French oil, but that it has been probably almost entirely hydrolysed in the Turkish oil during its preparation. (*Comptes rendus* 1896. *700*). Charabot (*ibid.* 1896, *752*) stated that he always finds a small quantity of free acid in rose water distilled from the flowers, which supports Dupont's observation. Eckart states that ethyl alcohol is a normal constituent of oil of roses, occurring to the extent of 5 per cent. in the liquid portion. Poleck claims that no ethyl alcohol exists in oil prepared from the roses directly they are picked, and suggests that its presence is due to fermentation in the roses when kept before distilling—during transport to the factory, for example. More than the above cannot be said to be known with any certainty of the chemistry of the liquid portion of the oil. The stearoptene, according to Markovnikoff and Reformatzky (*Ph. zeit. fur Russland* 1893, *102*) consists of a single paraffin hydrocarbon. The solid body obtained by freezing the oil was recrystallized several times from 98 per cent. alcohol and dried over sulphuric acid. The purified body then melted at 36·5°—37° and appeared to possess the formula $C_{16}H_{34}$. They agreed that small quantities of other hydrocarbons were present.

Eckart separates it by dissolving the oil in 75 per cent. hot alcohol and then cooling to 0°, when the stearoptene separates. Schimmel & Co. however state that they have separated two hydrocarbons from the stearoptene, melting at 22° and 41° respectively. Other chemists have confirmed this result.

Further light on the chemistry of oil of roses is much needed, for the oils used so largely for adulterating it contain either the same or closely allied bodies, so that detection of adulteration is frequently a matter of great difficulty. This will necessarily remain so, until a body entirely characteristic of oil of roses is isolated.

METHODS OF ANALYSIS, &c. Few oils vary so much under different conditions of soil and climate, as does rose oil. The percentage of stearoptene varies from a comparatively small, to a very large amount. The quantity of the stearoptene present cannot therefore be used as any guide to the purity of the oil. As it is inodorous, however, it is an indication of the quality. In adulterated oils, the natural stearoptene is frequently imitated by paraffin wax, stearin, or spermaceti. The melting point of the separated stearoptene should lie between 32° and 37°, and it should be examined for spermaceti. This is effected by saponifying with alcoholic potash, evaporating the alcohol, adding water, and washing the aqueous liquid well with ether several times. From the aqueous solution fairly pure palmitic acid is separated by the addition of hydrochloric acid. This will possess a melting point of from 55° to 60°. Stearin will in the same way yield stearic acid. It is very difficult to lay down any limits for the specific gravity of oil of roses. Turkish oil usually has a gravity of ·855 to ·865 at 30° and ·860 to ·870 at 20°. French oil however according to Dupont (*Compt. rendus*, 1885, *700*) has a gravity of ·822 to ·865 according as there is more or less stearoptene present. Dietze also gives the gravity of French oil as ·828. These figures appear very dubious. A Persian oil, apparently perfectly pure, examined by Schimmel & Co. had a gravity of ·8326. It may be taken, that the optical rotation should not exceed − 4°. Markovinkoff gives − 3·3°, − 3·6° and − 3·9° for three pure Bulgarian oils. Dupont (*loc. cit.*) gives − 6·7°, − 8°, and − 3·5° for three French oils. The Persian oil above mentioned had a rotation of − 9·1°. But as geranium oil rotates from − 7° to − 17° (palmarosa oil even falls as low as − 1°) this figure does not yield much information. The melting point of the oil should not vary more than from 17° to 22°. Outside these limits the oil should be regarded with some suspicion. But this depends on the amount of stearoptene, which is the worthless constituent of the oil. An estimation of the amount of alcohols present is of little use on account of the similarity in this respect of geranium oils. Further, the instability of the alcohols renders them very liable to change by the action of most reagents, so that the results are little more than comparative. By acetylisation and saponification the percentage of alcohols calculated as $C_{10}H_{18}O$ is from 70 to 75, whereas in geranium oils this figure is usually 85 per cent. Dietze. (*Suddeutsche Apotheker Zeitung* xxxvii, 89, *835*) strongly recommends the acid and ester numbers (expressed in terms of KOH) as being of great value in determining the purity of the oil. A known quantity of the oil is titrated in alcoholic solution with seminormal alkali, and then saponified for an hour with excess of alcoholic potash, on a water bath, with a reflux condenser. The excess of potash is estimated in the usual way by means of semi-normal acid, using phenol-phthalein as an indicator. Dietze gives the following table of results for genuine and doubtful samples, and for some geranium oils. The acid and ester numbers are here expressed in percentage of potash.

	Acid.	Ester.	Saponification (Total)
Pure German Oil	·21	·65	·86
Pure Bulgarian Oil	·12	·80	·92
Pure Turkish Oil	·14	·75	·89

	Acid.	Ester.	Saponification (Total).
Doubtful Sample	·21	1·49	1·70
" "	·18	1·87	2·05
" "	·22	1·71	1·94
" "	·26	1·08	1·34
" "	·14	1·12	1·26
French Geranium Oil	·68	4·79	5·47
" "	·50	5·41	5·91
African Geranium Oil	·75	4·56	5·31
Spanish " "	·98	7·19	8·17
" " "	·34	7·19	7·53
Indian " "	·15	3·10	3·25
" " "	·18	2·60	2·78

A sample of French oil examined by Dietze, which he believed was pure—but which had the abnormal gravity of ·828, gave a saponification number of 1·81. These results show that the ester content of rose oil is decidedly lower than that of geranium oil, and this fact can render useful information in the analysis.

An Indian geranium oil largely used in Turkey for adulterating rose oil has been examined by Dietze, and the following figures are given.

Specific gravity	·8922 at 15°
Rotation	—·6°
Acid number	·13
Ester number	2·09

As has been mentioned above, the oil probably contains an ester which is in most cases hydrolysed more or less completely by the repeated distillations of the oil. Dupont claims that this ester occurs to a greater extent in oils which have been only once distilled, and oils of this character he has examined, possess a more fragrant odour than Turkish oils. No ester determinations are however recorded for these oils. In this connection it may be mentioned that Schimmel & Co. (*Report*, April 1893) state that they have examined a sample of green otto of roses, of exquisite odour. It was simply the first runnings of the distillate which separates mechanically before the oily water is redistilled. This, they urge, proves, if proof is necessary, how repeated distillation over an open fire injures the odour of oil of roses. This green otto melted at 25° and, in spite of its exquisite odour, contained 63·7 per cent. of stearoptene.

REQUIREMENTS. As far as our present knowledge of this oil goes, the requirements of a pure oil may be formulated as follows. Specific gravity should not exceed ·870 at 20°. The melting point should lie between 17° and 22°. The optical activity should not exceed $-3°$ to $-4°$.

OIL OF RUE.

SOURCE. Distilled from the herb, *Ruta Graveolens* [N.O. Rutaceæ].

PHYSICAL PROPERTIES. A pale yellow oil of characteristic sharp odour. Specific gravity very low, about ·840 ; slightly dextrorotary.

CONSTITUENTS. The predominating constituent of this oil is the ketone, methylnonyl ketone, $CH_3 \cdot CO \cdot C_9 H_{19}$, a liquid of low specific gravity, which constitutes at least 90 per cent. of the oil. No other constituent appears to have been isolated and definitely identified.

METHODS OF ANALYSIS, &c. The specific gravity, which is so low as to be very characteristic should fall between ·830 and ·842. The oil is always faintly dextrorotary, from 0° to +2°50. The whole of it should distill between 215° and 235° and it should be soluble in from two to three volumes of 70 per cent. alcohol. When cooled to about zero the oil solidifies and melts at +9° again. The oil is so characteristic in its properties that any adulteration is easily detected.

OIL OF SAGE.

SOURCE. Distilled from the leaves of *Salvia Officinalis* [N.O. Labiatae].

Physical Properties. A pale yellow or yellowish green oil of characteristic odour of the plant. Specific gravity about ·920 and optical rotation about +20°.

Constituents. The terpene, pinene, and a sesquiterpene have been identified amongst the constituents of this oil. In addition, the oxygenated bodies cineol, borneol and thujone have been isolated. The body named by Muir, salviol, has been shown by Semmler to be identical with the now well known ketone, thujone.

Requirements. The specific gravity should lie between ·915 and ·930 and the optical rotation between +10° and +25°.

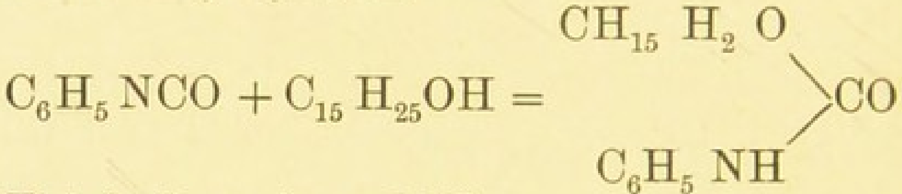
OIL OF SANTAL WOOD.

Source. Several plants of the natural order Santalaceæ yield essential oils which, although not identical, are very similar in odour. The ordinary oil, which is most prized for medicinal and perfumery purposes, is that distilled from the wood of *Santalum Album* (East India and Macassar). Western Australian oil is distilled from several different trees, the chief of which *Santalum cygnorum*, yields the Swan River oil. In addition to these, *S. Preisii*, *S. Lanceolatum*, *S. Acuminatum*, and *S. Persicarium* are occasionally used in Australia for distillation, and hence the difficulty of obtaining an oil from this source, whose origin can be relied upon. Other Santal trees are used elsewhere, but little is known of the exact properties of the oils they yield. The oil from *Santalum Album* is the only one official in the British Pharmacopœia. West Indian Santal oil is the product of one of the Rutaceæ, *Amyris balsamifera.*

PHYSICAL PROPERTIES. A pale yellow to almost colourless oil, of characteristic odour, of specific gravity about ·980 (East Indian oil), about ·945 to ·965 (Australian oil), and about ·960 (West Indian oil). East Indian oil is laevorotary about $-15°$ to $-20°$, whereas Australian oil is dextrorotary about $+5°$ to $+8°$. West Indian oil is also dextrorotary about $+25°$.

CONSTITUENTS. The chemistry of santal wood oil cannot be said to be in a very advanced state. But little is definitely known of its constituents, although our knowledge of this oil is now rapidly increasing, and still less is known of the difference between the different varieties of oil. The earliest work on this oil of a purely scientific nature is that of Chapoteaut (*Bull. Soc. Chim.* 37, 303). Chapman and Burgess have also examined some derivatives of the oil (*Proc. Chem. Soc.* 168, 140). Chapoteaut's work, although of great importance, is discounted by the fact that he must have been using either an adulterated or a Western Australian oil, as he quotes the gravity as ·945. He states that the oil consists almost entirely of two oxygenated bodies, santalol $C_{15}H_{26}O$, an alcohol, and santalal $C_{15}H_{24}O$ the corresponding aldehyde, the latter being the preponderating constituent. Phosphorus pentoxide withdraws water from these with the formation of the hydrocarbons $C_{15}H_{24}$ and $C_{15}H_{22}$ respectively. The latter is, according to Chapoteaut, identical with the hydrocarbon of cedar oil. Chapman, however, holds that they are not identical. Chapman has also prepared the aldehyde santalal from the oil, and states that he separated it by fractional distillation. But as the alcohol and the aldehyde boil at almost the same temperature, and a little decomposition takes place on boiling, the purity of this body is a matter of doubt. He gives the following figures for it, however. Specific gravity ·9793, and rotary power $-14·7°$. Parry has shown that small quantities of esters and free acid occur in the oil, and further, that the preponderating constituents are of an alcoholic nature. Berkenteim (*Jl. Russian Chem. Soc.* 24, 688) has examined a crystalline body which he found in the oil of Santalum Preisii. He found the melting point to be 101°–103°, and assigned to it the formula $C_{15}H_{24}O$. It appears to be a solid alcohol, as it yields an acetic ester, melting at 68°–69°. A chloride was also obtained of the formula $C_{15}H_{23}O \cdot Cl$, melting at 119°–120°.

The best defined crystalline compound of the alcoholic constituent (or one of them) yet obtained is the santalyl ester of phenyl-carbamic acid, discovered by E. J. Parry. This body is obtained by the interaction of phenyl isocyanate and the oil itself. The reaction is represented by the following equation.



$$C_6H_5\,NCO + C_{15}\,H_{25}OH = \left.\begin{matrix} CH_{15}\ H_2\ O \\ C_6H_5\ NH \end{matrix}\right\rangle CO$$

This body melts at 237°.

It is still uncertain as to whether "santalol" is a definite compound or a mixture of several bodies. According to Schimmel & Co., it can be separated by fractional distillation into fractions of very different optical rotation. They have also prepared a crystalline compound from the oil,—santalyl phthalate of silver, which crystallizes with great difficulty, and then melts at 50°. Soden and Müller have also recently examined this oil. They agree with Parry and Schimmel that santalol is not a homogeneous body, and furthermore they state that they have isolated from the oil a sesquiterpene which boils at 261°–262° of specific gravity ·898 and optical rotation about – 21°. They also state that there are present a number of other bodies, in traces, amongst which are a phenol, one or more lactones, an acid melting at 154° and possibly also borneol.

METHODS OF ANALYSIS, &c. The remarks in this paragraph apply to the oil of Santalum Album. The specific gravity of Santal Wood oil is sufficiently high to be very characteristic. Much too low figures have, until fairly recently, usually been quoted. The 1885 edition of the British Pharmacopœia gives it as about ·960, but this is far too low. The 1890 edition gives it as ·975 to ·980. The author has never (and this experience is amply confirmed by Parry, McEwan, Schimmel, and others) met with a genuine sample below ·974. The average is about ·979–·981, but ·974 to ·982 may be taken as safe limits. In this connection it may be mentioned that E. J. Parry (*Year Book of Pharmacy*, 1895, p. 317) examined the first, middle, and last two ounces of a batch of 20 pounds of the oil, specially distilled for him by the late Mr. M. Conroy. The specific gravities of these fractions were ·9649, ·9758, and ·9805, showing that gravity rose as distillation proceeded. An examination of these fractions showed that the earliest fraction contained much less santalol than the later, and that the proportion of saponifiable matter (esters) rose as distillation proceeded. Cedar oil, a common adulterant, and Australian oil, will lower the specific gravity. Castor oil does the same, but not to quite so great an extent.

Recent advances in regard to the analysis of this oil are due to E. J. Parry. He has shown that on saponification with alcoholic solution of potash, santal wood oil should not require more than 1 per cent. of potash. Castor oil—often added to the oil on account of its high specific gravity—requiring about 18 per cent., is easily detected if present in any quantity, in this way. The iodine absorption, by Hübl's method, is from 190 to 220 per cent., so that castor oil (about 85 per cent.) considerably reduces this number also.

Admixture with cedar wood oil is indicated by fractional distillation under reduced pressure. Under a pressure of from 15 to 22 mm., no distillate is obtained from pure oil under 150°, when at least 90° per cent. passes over between 150°–175°. With cedar oil 85 to 90 per cent. distils over, under these conditions, between 125°–155°. The oil should be soluble in 5 volumes of 70 per cent. alcohol at 20°.

The optical rotation is a very important factor in the analysis of the oil. East Indian oil has a rotation of from $-15°$ to $-20°$; Cedar Wood oil rotates the plane of polarised light much more strongly, from − 32° to − 40°. West Indian oil is dextro-rotary, about + 25°, and West Australian oil also dextro-rotary, but to a smaller extent, about + 5°. Castor oil is also slightly dextro-rotary + 3° to + 5°.

The valuation of santal wood oil is best carried out by the process devised by E. J. Parry (*loc. cit.*) depending on the estimation of the amount of santalol. This depends on the acetylisation of the oil, which converts the alcoholic constituents into acetic esters, and saponification of the acetylated oil.

In this way, santal wood oil should yield at least 90 per cent. of alcoholic constituents calculated as santalol. Cedar wood oil lowers this figure materially, as the percentage of alcoholic bodies (calculated as santalol) never exceeds 16 per cent. Copaiba oil, which is sometimes added to santal wood oil, gives a result equivalent to about 7 per cent. This process, combined with the determination of the specific gravity, optical rotation, and solubility in alcohol, will be found sufficient to detect any of the ordinary adulterants.

The following figures were obtained by Pearmain and Moor (*Analyst*, 1895, 174) for some samples of Indian and Australian oils :—

	Sp. gravity.	Rotation.
East Indian	·9815	– 13·8°
„ „	·9792	– 15·2°
„ „	·9798	– 15·5°
„ „	·9792	– 15·7°
„ „	·9840	– 19·5°
West Australian	·9496	+6·2°
„ „	·9495	+4·8°

Requirements. Specific gravity ·974–·982. Optical rotation –15° to –20°. Should be soluble in 5 volumes of 70 per cent. alcohol at 20°. C Should not require more than 1 per cent. of potash for saponification. Should contain at least 90 per cent. of santalol, estimated as described above.

OIL OF SASSAFRAS.

Source. Distilled from the root of *Sassafras Officinale* [N.O. Laurineæ].

Physical Properties. A pale, yellowish oil of characteristic aromatic odour, of specific gravity about 1·075 and slightly dextro-rotary.

Constituents. The chief constituent of this oil, to which it owes its characteristic odour, is safrol. In addition to this body the following have also been detected. The terpenes, pinene and phellandrene, dextro-rotary camphor, eugenol, and the sesquiterpene cadinene. According to Schimmel, the average composition of the oil is as follows:—

Safrol	80 p. c.
Pinene Phellandrene	10 ,,
Camphor	7 ,,
Eugenol	0·5 ,,
Cadinene	2·5 ,,

Requirements. The oil should possess a specific gravity between 1·065 and 1·095 and an optical rotation of +1° to +4°.

SAVIN OIL.

Source. Distilled from the leaves and twigs of *Juniperus sabina* [N.O. Coniferæ].

Physical Properties. A pale oil of strong and characteristic odour, of specific gravity about ·920 and optical rotation about +50°.

Constituents. A considerable proportion of terpenes is present, the chief of these being pinene. Cadinene has also been detected. Fromm has recently investigated this oil and found that it could be separated by fractional distillation into three chief portions. The earliest distillate (below 195°) consisted chiefly of terpenes, in which pinene predominated. The middle fraction (195° to 235°)

contained a considerable quantity of esters, and the highest boiling fraction (235° to 310°) consisted of cadinene and probably contained some decomposition products. The middle fraction on saponification yielded an alcohol of the formula $C_{10}H_{15}OH$ which Fromm terms sabinol. This is a colourless oil, boiling at 208°-209° and with only a faint odour. The pure acetate,—which occurs in the oil— is of more marked odour.

METHODS OF ANALYSIS, &c. The specific gravity lies beween ·910 and ·928 and the optical rotation between +40° and +60°. The oil should dissolve to a clear solution in an equal volume of 90 per cent. alcohol. On fractional distillation it should yield under 30 per cent. under 200°

OIL OF SPIKE LAVENDER.

SOURCE. Distilled from the flowering herb, *Lavandula Spica* [N. O. Labiatæ].

PHYSICAL PROPERTIES. Pale oil recalling the odour of lavender and rosemary. Specific gravity about ·905, slightly dextrorotary, below +10°. Soluble in three volumes of 70 per cent. alcohol.

CHEMICAL CONSTITUENTS. The most important difference in the constitution of this oil from that of the true lavender oil is its almost entire freedom from esters. It contains, however, a larger amount of bodies of an alcoholic nature. We are chiefly indebted to Bouchardat for our knowledge of the chemistry of this oil (*Comptes rendus*, 106, *551* and 107, *53*). It contains dextropinene, dextrocamphene, possibly a sesquiterpene, cineol (eucalyptol), linalol, geraniol, terpinene, camphor and borneol. Of these the principal constituents appear to be linalol, cineol and camphor. Traces of esters of the various alcohols occur, but never any large quantity.

METHODS OF ANALYSIS, &c. The specific gravity of spike oil varies from ·900 to ·920. Turpentine is frequently used as an adulterant, and this lowers the gravity greatly. The optical rotation, which should lie between +1° and 10°, is also entirely altered by the addition of turpentine. The following figures have been given by Massol and others (*J. de Pharm et de Chim.* 1895, *49*) but are not reliable. Three samples gave specific gravities ·935, ·886 and ·908, and rotations +9·66°, +3·30 and −0·34. The ester content is very low, often practically nil. But the amount of free alcohols is very high. It is doubtful whether exact determination of these is possible, as such bodies as geraniol and linalol are so unstable as to be partially decomposed by almost any reaction. But very useful comparative results may be obtained by acetylating, and saponifying the acetylated oil. Calculating the free alcohols as $C_{10}H_{18}O$ (geraniol, linalol, &c.) a good spike oil should yield by this process at least 30 per cent. Usually 35 to 38 per cent. is obtained. The oil should be easily soluble in three times its volume of 70 per cent. alcohol.

REQUIREMENTS. Specific gravity ·900—·920. Optical activity +1° to +10°. Soluble in three volumes of 70 per cent. alcohol. Ester content practically nil. Alcohol content, at least 30 per cent.

OIL OF TANSY.

SOURCE. The commercial oil of tansy is distilled from the herb *Tanacetum vulgare* [N.O. Compositae]. An oil is also obtained from *T. balsamita.*

PHYSICAL PROPERTIES. A pale oil of somewhat camphoraceous odour, specific gravity about ·930, optical activity about +40° or −40°, according to source.

CONSTITUENTS. Bruylants was one of the earliest workers on this oil, and he isolated a body of the formula $C_{10}H_{16}O$, which he said was an aldehyde and termed it tanacetylhydrine.

Semmler, who made a very close examination of the oil, showed that this body was in reality a ketone, and termed it tanacetone. Wallach, however, has proved that it is identical with the previously known ketone occurring in oil of Thuja, well known as Thujone. Schimmels have further examined the oil and have isolated traces of borneol and *laevo*-camphor.

Requirements. The oil should have a specific gravity between ·925 and ·950. Oil distilled from plants grown in England has an optical rotation of −25° to −35°, whilst oil distilled from the Continental or American plants is dextro-rotary, +30° to +40°. It is soluble in an equal volume of 90 per cent. alcohol.

OIL OF THUJA.

Source. This oil is distilled from the leaves and small twigs of *Thuja Occidentalis* [N.O. Coniferæ].

Physical Properties. The oil is a pale oil of characteristic odour, of specific gravity about ·920 and optical rotation −10°.

Constituents. A considerable quantity of the terpene pinene is present, but the characteristic constituent of the oil is the ketone, thujone

$C_{10}H_{16}O$. Traces of formic and acetic esters, and of carvone are also present. There are several other constituents present of high boiling point, but these have not yet been identified.

Requirements. Specific gravity between ·910 and ·925; optical rotation $-6°$ to $-15°$; soluble in three times its volume of 70 per cent. alcohol.

OIL OF THYME.

Source. Distilled from the herb, *Thymus vulgaris* [N.O. Labiatæ].

Physical Properties. An oil of marked camphoraceous odour, red or white in colour, according to whether it is crude or has been carefully rectified. Specific gravity about ·920 and optical rotation about $-3°$.

Constituents. This oil contains from 20 to 30 per cent. of phenols, of which the chief is thymol, with a little of the isomeric body carvacrol. There are present also the terpene pinene, cymene, borneol, linalol and bornyl acetate.

Methods of Analysis, &c. The oil is frequently adulterated with turpentine, and also with the oil of *Thymus serpyllum*. The specific gravity of the pure oil lies between ·905 and ·935. This is reduced by turpentine but not altered by the addition of the oil of *Thymus serpyllum.* The optical rotation is low, usually about −2° or −3°. This is altered by the addition of either of the above mentioned adulterants. The thymol—or rather the total phenols—may be approximately estimated by shaking the oil with an aqueous solution of potash (15 per cent.) and calculating the absorbed portion as thymol. This should not fall below 25 per cent.

OIL OF VETIVERT.

SOURCE. Distilled from the root of an Indian grass, *Andropogon muricatus* [N.O. Gramineæ].

PHYSICAL PROPERTIES. A sweet scented oil of brownish colour, of specific gravity about 1·02, and optical rotation +30°.

CONSTITUENTS. The compounds occurring in this oil do not appear to have been, in any single instance, separated and identified.

METHODS OF ANALYSIS, &c. The specific gravity varies from 1·010 to 1·030 unless the oil has been rectified, when the gravity varies considerably. The optical rotation lies between +25° and +40°. The oil should dissolve to a clear solution in 1½ to 2 volumes of 80 per cent. alcohol; Schimmel & Co. give the following figures for samples distilled by themselves:

Specific gravity 1·019—1·027
Optical rotation +25° to +26°
Ester No. (°/o KOH) 7 to 8

Solubility in 80 per cent. alcohol 1 in 1½ to 2.

A genuine sample was fractionated with the following results :

B.P. at 23 m.	Per cent.	Rotation.
144° – 164°	8	– 4° 10′
164° – 170°	10	– 3° 20′
170° – 180°	24	+ 2° 5′
180° – 185°	30	+31° 40′
185° – 200°	20	+47° 5′

OIL OF WINTERGREEN.

Source. The true wintergreen oil is obtained by distillation from the leaves of *Gaultheria procumbens* [N.O. Ericaceæ]. But most of the commercial " natural " oil is obtained from the bark of *Betula Alba,* the sweet birch, which is almost identical with the oil from Gaultheria. As the oil consists almost entirely of methyl salicylate, this ester prepared synthetically is largely sold under the name of artificial oil of wintergreen.

PHYSICAL PROPERTIES. A pale oil of characteristic odour, of specific gravity about 1·18, almost or entirely optically inactive.

CHEMICAL CONSTITUENTS. The chief constituent of this oil is methyl salicylate. Other bodies have been found, but only in very small proportions, so that artificial methyl salicylate largely replaces the natural oil.

METHODS OF ANALYSIS, &c. The specific gravity of the natural oil, whether from *Gaultheria* or from *Betula*, varies from 1·175 to 1·188, whilst the artificial oil is usually about 1·188 to 1·189. The oil should be optically inactive, or at most laevorotary to the extent of —·5°. The whole of the oil should distil between 216° and 224°. Further, the oil should yield but little unsaponifiable matter. The salicylic acid obtained by saponification and liberation from the resulting salt by means of hydrochloric acid, should melt at 156°–158° as extreme limits.

REQUIREMENTS. Specific gravity 1·175 to 1·188, and optically inactive (or at most —·5°). The salicylic acid yielded on decomposition with alkali should melt at 156°–158°.

APPENDIX.

TABLE OF CONSTANTS
OF THE
MORE IMPORTANT ESSENTIAL OILS.

Reproduced from "The Chemistry of Essential Oils and Artificial Perfumes," by E. J. PARRY, B.Sc., F.I.C., *by permission of* MESSRS. SCOTT, GREENWOOD, & CO.

APPEN-

TABLE OF CONSTANTS OF THE

Specific gravities are given for 15·5° C. and optical

Note.—The most important constituents

Oil.	Source.	Yield Per Cent.
Ajowan oil	Ptychotis ajowan ; fruit . .	3·0–4·0
Almond oil (bitter) . . .	Amygdalus communis ; fruit .	·5–1·0
Ammoniacum oil	Dorema ammoniacum ; resin .	0·3
Angelica oil	Angelica officinalis ; root . .	·25–1·0
Angostura oil	Galipea cusparia ; bark . . .	1·5
Aniseed oil	Pimpinella anisum ; fruit . .	1·5–6·0
Aniseed oil (star)	Illicium verum ; fruit	5·0
Arnica oil	Arnica montana ; root	1·0
Asafœtida oil	Ferula species ; resin	3·0–4·0
Asarum oil	Asarum Europæum ; root . .	1·0

DIX.

MORE IMPORTANT ESSENTIAL OILS.

rotations for a column of 100 mm., unless otherwise stated.

are printed in heavier type than the remainder.

Specific Gravity.	Optical Rotation.	Constituents.
·900–·930	dextro-rotary	**Thymol** $C_{10}H_{14}O$; cymene $C_{10}H_{14}$; terpene.
1·045–1·070	Inactive	**Benzaldehyde** C_6H_5COH ; prussic acid HCN.
·890	dextro-rotary	
·860–·905	+18° to +30°	Phellandrene $C_{10}H_{16}$; methyl-ethyl-acetic acid ; oxypentadecylic acid.
·930–·960	−36°	**Galipol** $C_{15}H_{26}O$; cadinene $C_{15}H_{24}$; galipene $C_{15}H_{24}$.
·980–·990	0° to −2°	**Anethol** $C_{10}H_{12}O$; methyl chavicol $C_{10}H_{22}O$; anisic aldehyde $C_8H_8O_2$; anisic acid ; anise ketone $C_{10}H_{12}O_2$ (?)
·980–·990	0° to −2°	**Anethol** $C_{10}H_{12}O$; methyl chavicol $C_{10}H_{12}O$; anise aldehyde : anisic acid ; ethyl hydroquinone ; safrol ; pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$.
·990–1·000	−1° to −2°	Phlorone isobutyric ether $C_{16}H_{26}O_2$; thymohydroquinone dimethyl ether $C_{12}H_{18}O_2$; phlorone dimethyl ether $C_{10}H_{14}O_2$; esters ; hydrocarbons.
·975–·990	−10°	$C_7H_{14}S_2$; $C_{10}H_{20}S_2$; $C_8H_{16}S_2$; $C_{10}H_{18}S_2$; $C_{10}H_{16}O$; terpenes ; sesquiterpene.
1·050–1·070	—	Asarone $C_{12}H_{16}O_3$; pinene $C_{10}H_{16}$; methyl eugenol $C_{11}H_{14}O_2$.

Oil.	Source.	Yield Per Cent.
Asarum oil	Asarum Canadense ; root . .	3·0–5·0
Bay oil	Pimenta acris ; leaves	2·0–3·0
Bay oil (Californian) . . .	Laurus Californica ; leaves . .	4·0
Bergamot oil	Citrus bergamia ; fruit . . .	—
Betel oil	Piper betle ; leaves	·5–1·0
Buchu oil	Barosma species	1·0–2·0
Cajuput oil	Melaleuca species ; leaves . .	—
Calamus oil	Acorus calamus ; rhizome . .	·8–5·0
Camphor oil	Camphora officinalis ; wood and root	4·0
Caparrapi oil	Nectandra caparrapi	—
Caraway oil	Carum carui ; seed	3·0–7·0
Cardamom oil	Elettaria cardamomum ; fruit	1·0–3·0
Cardamom oil (Bengal) . .	Amomum aromaticum ; fruit.	1·12
Cardamom oil (Kameroon)	Amomum Danielli ; fruit . .	2·3
Cardamom oil (Siam) . . .	Amomum cardamomum ; fruit	2·4
Carrot oil	Daucus carota ; seed	1·0–1·5
Cascarilla oil	Croton eleutheria ; bark . . .	1·0–3·0
Cassia oil	Cinnamomum cassia	·5–2·0
Cedar oil	Juniperus virginiana ; wood .	2·5–5·0
Cedar leaf oil	Juniperus virginiana ; leaves.	—

Specific Gravity.	Optical Rotation.	Constituents.
·930–·960	—	Terpene; asarone $C_{12}H_{16}O_3$; esters; methyl eugenol $C_{11}H_{14}O_2$.
·965–·995	− 0° 30′ to − 2°	**Eugenol** $C_{10}H_{12}O_2$; pinene $C_{10}H_{16}$(?); dipentene $C_{10}H_{16}$; methyl eugenol $C_{11}H_{14}O_2$; phellandrene $C_{10}H_{16}$; hydrocarbon $C_{10}H_{16}$; chavicol $C_9H_{10}O$; methyl chavicol $C_{10}H_{12}O$; citral $C_{10}H_{16}O$.
·930–·950	—	Cineol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$ (?)
·882–·886	+ 8° to + 20°	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; **linalyl acetate** $C_{12}H_{20}O_2$; bergaptene $C_{12}H_8O_4$.
·958–1·045	+ 2° 50′	**Methoxy-chavicol** $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$; chavicol $C_9H_{10}O_2$.
·940–·945	—	Diosphenol $C_{10}H_{16}O_2$: ketone $C_{10}H_{18}O$; hydrocarbon $C_{10}H_{18}$.
·920–·930	0° to − 2°	**Cineol** $C_{10}H_{18}O$: terpineol $C_{10}H_{18}O$; terpinyl esters; butyric, valeric and benzoic aldehydes; pinene $C_{10}H_{16}$ (?).
·960–1·000	+ 12° to + 35°	Terpenes; sesquiterpene; oxygenated bodies not identified.
—	—	**Camphor** $C_{10}H_{16}O$; **safrol** $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; eugenol $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$.
·915–·935	− 3°	Caparrapiol $C_{15}H_{26}O$; an acid $C_{15}H_{26}O_3$.
·905–·920	+ 70° to + 85°	**Carvone** $C_{10}H_{14}O$; limonene $C_{10}H_{16}$.
·936–·946	+ 34° to + 47°	Cineol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$; acetic esters; limonene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
·920	− 12° 41′	
·907	− 20° 34′	
·905	+ 38° 4′	Borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$; **bornyl esters.**
·870–·930	− 13° to − 40°	Pinene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; cineol $C_{10}H_{18}O$.
·890–·930	+ 5°	Terpenes.
1·050–1·065	+ 1° to − 1°	**Cinnamic aldehyde** C_9H_8O; terpenes; cinnamic esters; *o*-methyl-coumaric aldehyde $C_{10}H_{10}O_2$.
·940–·960	− 25° to − 40°	**Cedrene** $C_{15}H_{24}$; cedrol $C_{15}H_{26}O$.
·883–·888	+ 55° to + 65°	Limonene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$; borneol $C_{10}H_{18}O$, and bornyl esters.

Oil.	Source.	Yield Per Cent.
Celery oil	Apium graveolens ; seed . . .	3·0
Chamomile oil (Roman). .	Anthemis nobilis ; flowers . .	·5–1·0
Chamomile oil (German) .	Matricaria chamomilla ; flowers	·1–·3
Cheken-leaf oil	—	1·0
Chenopodium oil	Artemisia absinthium ; fruit .	1·0
Cherry-bark oil (wild) . .	Prunus virginiana ; bark .	·2
Cherry-laurel oil.	Prunus laurocerasus ; leaves .	·5
Cinnamon oil	Cinnamomum zeylanicum ; bark	·5–1·0
Cinnamon-leaf oil	Cinnamomum zeylanicum ; leaves	1·5–2·0
Citronella oil	Andropogon nardus ; grass. .	—
Citron oil.	Citrus medica ; peel of fruit .	—
Clove oil	Eugenia caryophyllata ; buds.	14·0–19·0
Coriander oil	Coriandrum sativum ; seed. .	·2–1·0
Costus oil.	Aplotaxis lappa ; root	1
Cubeb oil.	Piper cubeba ; fruit.	10·0–18·0
Culilaban oil	Cinnamomum culilavan ; fruit	3·0–4·0
Cumin oil.	Cuminum cyminum ; fruit . .	2·5–4·0
Dill oil	Anethum graveolens ; fruit. .	3·0–4·0
Dill oil (East Indian). . .	Anethum Sowa ; fruit. . . .	2·0–3·0

Specific Gravity.	Optical Rotation.	Constituents.
·870–·895	+65° to +80°	Limonene $C_{10}H_{16}$; sedanolic acid $C_{12}H_{20}O_3$; **sedanolide** $C_{12}H_{18}O_2$; sedanonic acid $C_{12}H_{18}O$; sesquiterpene; guaiacol; palmitic acid.
·905–·915	—	Esters of tiglic and angelic acids $C_5H_8O_2$ (chiefly amyl and hexyl); isobutyl isobutyrate $C_8H_{16}O_2$, esters of an alcohol, anthemol $C_{10}H_{16}O$.
·930–·940	—	Esters of caproic acid $C_6H_{12}O_2$; hydrocarbons.
·880	+20°	Pinene $C_{10}H_{16}$; **cineol** $C_{10}H_{18}O$.
·900–·975	−5° to −18°	
1·050	Inactive.	**Benzaldehyde** C_6H_5COH; prussic acid HCN.
1·050–1·065	Inactive.	**Benzaldehyde** C_6H_5COH; prussic acid HCN.
1·025–1·035	0° to −1°	**Cinnamic aldehyde** C_9H_8O; phellandrene $C_{10}H_{16}$; eugenol $C_{10}H_{12}O_2$.
1·045–1·060	−1° to +1°	**Eugenol** $C_{10}H_{12}O_2$; cinnamic aldehyde, C_9H_8O; safrol $C_{10}H_{10}O_2$.
·885–·920	−4° to −16°	**Citronellal** $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; methyl-heptenone $C_8H_{14}O$; camphene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
·860–·870	+66° to +76°	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$.
1·049–1·065	0° to −1° 30′	**Eugenol** $C_{10}H_{12}O_2$; caryophyllene $C_{15}H_{24}$; amyl methyl ketone $C_7H_{14}O$; methyl alcohol, CH_4O; furfurol $C_5H_4O_2$; aceteugenol (?).
·870–·885	+7° to +14°	**Linalol** $C_{10}H_{18}O$; pinene $C_{10}H_{16}$.
·980–·987	+15° to +16°	
·910–·930	−30° to −40°	Cadinene $C_{15}H_{24}$; dipentene $C_{10}H_{16}$; cubeb camphor $C_{15}H_{26}O$.
1·050	—	Eugenol $C_{10}H_{12}O_2$; methyl-eugenol, $C_{11}H_{14}O_2$.
·890–·930	+4° to +6°	Cymene $C_{10}H_{14}$; **cumic aldehyde** $C_{10}H_{12}O$.
·900–·920	+70° to +80°	**Carvone** $C_{10}H_{14}O$; limonene $C_{10}H_{16}$; a paraffin hydrocarbon.
·970	+40°	Carvone $C_{10}H_{14}O$; limonene $C_{10}H_{16}$; dill apiol $C_{12}H_{14}O_4$.

Oil	Source.	Yield Per Cent.
Dog-fennel oil	Eupatorium foeniculaceum; herb	—
Elecampene oil	Inula helenium ; root	1·0–2·0
Eucalyptus oils ; leaves—		
,, Amygdalina .	—	To 4·0
,, Backhousia. .	—	To 4·0
,, Baileyana . .	—	1·0
,, Capitellata . .	—	—
,, Cneorifolia . .	—	—
,, Corymbosa . .	—	4·0
,, Crebra	—	—
,, Dealbata . . .	—	3·0
,, Dextro-pinea .	—	0·8
,, Dumosa . . .	—	—
,, Eugenoides. .	—	0·7
,, Globulus . . .	—	0·8–1·5
,, Goniocalyx . .	—	—
,, Gracilis . . .	—	—
,, Hæmostoma .	—	2·0
,, Incrassata . .	—	—
,, Laevo-pinea	—	0·7
,, Leucoxylon .	—	1·1
,, Loxophleba .	—	—
,, Macrorhyncha	—	0·3
,, Maculata var. Citriodora .	—	1·0–4·0
,, Microcorys . .	—	1·0–2·0
,, Obliqua . . .	—	—
,, Odorata . . .	—	1·5
,, Oleosa	—	1·3
,, Populifolia . .	—	—

Specific Gravity.	Optical Rotation.	Constituents.
·935	+18°	Phellandrene $C_{10}H_{16}$.
—	—	Alantic acid $(C_6H_8O)_x$; alanto-lactone, alantol.
·855–·890	−25° to −89°	**Phellandrene** $C_{10}H_{16}$; cineol $C_{10}H_{18}O$.
·895–·902	—	**Citral** $C_{10}H_{16}O$; phellandrene $C_{10}H_{16}$.
·890–·920	—	**Cineol** $C_{10}H_{18}O$; citral $C_{10}H_{16}O$; phellandrene $C_{10}H_{16}$.
·915	—	**Cineol** $C_{10}H_{18}O$; eudesmol.
·915–·925	−5° to +5°	**Cineol** $C_{10}H_{18}O$; cumic aldehyde $C_{10}H_{12}O$.
·880	—	Citral $C_{10}H_{16}O$ (?); geraniol $C_{10}H_{18}O$ (?); cineol $C_{10}H_{18}O$.
—	—	**Cineol** $C_{10}H_{18}O$.
·885–·900	—	**Citronellal** $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$; geraniol $C_{10}H_{18}O$ (?); citral $C_{10}H_{16}O$ (?);
·873–·876	dextro-rotary	**Dextro-pinene** $C_{10}H_{16}$; aldehydes.
·900–·912	—	**Cineol** $C_{10}H_{18}O$.
·905–·910	+4° to +6°	**Cineol** $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
·910–·930	+1° to +10°	**Cineol** $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; ethyl alcohol C_2H_6O; amyl alcohol $C_5H_{12}O$; butyric, caproic and valeric aldehydes.
·915–·920	—	Cineol $C_{10}H_{18}O$.
—	—	Cineol $C_{10}H_{18}O$.
·880–·890	—	Cymene $C_{10}H_{14}$; **cumic aldehyde** $C_{10}H_{12}O$.
—	—	Cineol $C_{10}H_{18}O$.
·873	laevo-rotary	**Laevo-pinene** $C_{10}H_{16}$.
·920–·925	—	**Cineol** $C_{10}H_{18}O$.
·883	+5°	Cineol $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$; aldehydes.
·927	—	**Cineol** $C_{10}H_{18}O$; phellandrene, $C_{10}H_{16}$; esters; eudesmol.
·870–·905	·0° to +2°	**Citronellal** $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$.
·895–·930	—	**Cineol** $C_{10}H_{18}O$.
·895–·915	−7°	**Cineol** $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
·900–·925	—	**Cineol** $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$; cumic aldehyde $C_{10}H_{12}O$.
·905–·930	−5° to +5°	**Cineol** $C_{10}H_{18}O$.
—	—	**Cineol** $C_{10}H_{18}O$; cumic aldehyde $C_{10}H_{12}O$.

Oil.	Source.	Yield Per Cent.
Eucalyptus oils ; leaves—		
,, Punctata	—	0·6–1·2
,, Planchoniana	—	—
,, Resinifera	—	—
,, Rostrata	—	—
,, Risdonia	—	—
,, Staigeriana	—	—
Fennel oil	Foeniculum vulgare ; fruit	1·0–6·0
Feverfew oil	Pyrethrum parthenium ; flowers	·1–·4
Fir cone oil	Abies excelsa ; cones	—
Fleabane oil	Erigeron canadensis ; herb	·5
Galangal oil	Alpinia galanga ; rhizome	·5–1·5
Galbanum oil	Peucedanum galbanifluum ; resin	12·0–24·0
Garlic oil	Allium Sativum ; herb	0·1
Geranium oil	Pelargonium species ; herb	—
Geranium oil (Indian)	Andropogon schoenanthus ; grass	·3–·4
Ginger oil	Zingiber officinale ; rhizome	2·0–3·0
Golden-rod oil	Solidago canadensis, and other species	—
Grains of Paradise oil	Amomum Melegueta ; seeds	·75
Hedychium oil	Hedychium coronarium ; flowers	—
Helichrysum oil	Helichrysum stoechas ; herb	—
Hemp oil	Cannabis Sativa ; herb	·1
Hemp oil (Indian)	Cannabis Indica ; herb	—
Heracleum oil	Heracleum sphondylium ; fruit	1·0–3·0
Hop oil	Humulus lupulus ; flowers	·3–1·0

Specific Gravity.	Optical Rotation.	Constituents.
·912–·921	− 3° to + 5°	**Cineol** $C_{10}H_{18}O$.
·915	—	Citronellal $C_{10}H_{18}O$.
·900	− 15° to − 20°	**Cineol** $C_{10}H_{18}O$.
·915–·930	− 2° to + 13°	**Cineol** $C_{10}H_{18}O$; valeric aldehyde $C_5H_{10}O$.
·910–·925	− 2° to − 6°	**Cineol** $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
·880	—	**Citral** $C_{10}H_{16}O$.
·960–·980	+ 6° to + 20°	Pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; fenchone $C_{10}H_{16}O$; **anethol** $C_{10}H_{12}O$.
·900–·960	—	Borneol $C_{10}H_{18}O$ and its esters.
·855–·870	to − 80°	Pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; **bornyl acetate** $C_{12}H_{20}O_2$ (1 to 2 %).
·850–·890	+ 50°	Limonene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$.
·915–·925	− 1° to − 4°	Cineol $C_{10}H_{18}O$.
·910–·940	− 5° to + 20°	Pinene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$.
1·052	Inactive	Allyl-propyl-disulphide $C_6H_{12}S_2$; **diallyl disulphide** $C_6H_{10}S_2$; $C_6H_{10}S_3$; $C_6H_{10}S_4$.
·888–·905	− 6° to − 16°	**Geraniol** $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$ and tiglic acid esters.
·885–·896	+ 2° to − 2°	**Geraniol** $C_{10}H_{18}O$; geranyl esters ; dipentene $C_{10}H_{16}$; methyl-heptenone $C_8H_{14}O$ (?).
·872–·885	− 25° to − 45°	Phellandrene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; sesquiterpene.
·859	− 11° 10′	Terpenes ; **borneol** $C_{10}H_{18}O$; **bornyl acetate** $C_{12}H_{20}O_2$; cadinene $C_{15}H_{24}$.
·894	− 4°	
·869	− 0° 28′	
·873	—	Pinene $C_{10}H_{16}$.
·930	− 10° to − 12°	Terpenes and sesquiterpenes.
·930	—	Cannibene $C_{15}H_{24}$.
·860–·880	dextro-rotary	Octyl alcohol $C_8H_{18}O$; octyl acetate $C_{10}H_{20}O_2$; octyl caproate $C_{14}H_{28}O_2$; ethyl butyrate $C_6H_{12}O_2$.
·855–·882	to + 1°	Humulene $C_{15}H_{24}$; geraniol $C_{10}H_{18}O$; tetrahydrocymene $C_{10}H_{18}$ (?) ; terpenes.

Oil.	Source.	Yield Per Cent.
Jasmin oil	Jasminum grandiflorum; flowers	traces only.
Juniper-berry oil	Juniperus communis; berries.	·5–1·5
Kaempferia oil	Kaempferia rotunda; root	·2
Kiku oil	Pyrethrum Indicum; leaves	—
Kuromoji oil	Lindera sericea; leaves and twigs	—
Laurel oil	Laurus nobilis; leaves	1·0–3·0
Lavender oil	Lavandula vera; flowers	—
Lemon oil	Citrus limonum; peel	—
Lemon-grass oil	Andropogon citratus; grass	—
Lime oil	Citrus limetta; fruit	—
Lime oil	Citrus medica var. acida (expressed)	—
Lime oil	Citrus medica var. acida (disdilled)	—
Linaloe oil	Bursera species	7·0–12·0
Lovage oil	Levisticum officinale; roots	1·0
Mace oil	Myristica fragrans; arillus	4·0–15·0
Marjoram oil	Origanum majorana; herb	·3–1·0
Marjoram oil (Cretic)	Origanum Smyrnaeum	—
Marsh tea oil	Ledum palustre; leaves	·5–1·0
Massoi bark oil	Massoia aromatica; bark	6·0–8·0
Masterwort oil	Imperatoria ostruthium; root	1·0
Matico oil	Piper angustifolium; leaves	·5–3·5

Specific Gravity.	Optical Rotation.	Constituents.
1·009–1·018	+2° 30′ to +3° 30′	**Benzyl acetate** $C_9H_{10}O_2$; linalyl acetate $C_{12}H_{20}O_2$; benzyl alcohol C_7H_8O; linalol $C_{10}H_{18}O$.
·865–·890	–4° to –7°	Cadinene $C_{15}H_{24}$; pinene $C_{10}H_{16}$; an alcohol, m. p. 165°, and its acetic ester.
·945–·950	+12°	Cineol $C_{10}H_{18}O$.
·880–·890	—	
·890–·915	laevo-rotary	Limonene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; carvone $C_{10}H_{14}O$.
·920–·930	–15° to –18°	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$.
·885–·900	–5° to –10°	Linalyl acetate $C_{12}H_{20}O_2$ (English 7-10%; French 25-40%); pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; geraniol $C_{10}H_{18}O$; sesquiterpene; cineol $C_{10}H_{18}O$ (in English oil).
·857–·862	+59° to +65°	**Citral** $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; limonene $C_{10}H_{16}$; geranyl and linalyl acetates $C_{12}H_{20}O_2$; phellandrene $C_{10}H_{16}$; stearoptene.
·895–·905	+3° to –3°	**Citral** $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; methyl heptenone $C_8H_{14}O$; esters and terpenes.
·870–·875	+56° to +60°	**Linalyl acetate** $C_{12}H_{20}O_2$; limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$.
·873–·885	+35° to +40°	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$; limettin $C_{11}H_{10}O_4$.
·856–·868	+40°	
·872–·895	–4° to –13°	**Linalol** $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; methyl heptenone $C_8H_{14}O$.
1·005–1·045	+2° to +7°	Terpineol $C_{10}H_{18}O$.
·910–·932	+10°	Pinene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; myristicol $C_{10}H_{16}O$; myristicin $C_{12}H_{14}O_3$; a phenol.
·890–·910	+15° to +20°	
·915–·945	–3° to –15°	**Carvacrol** $C_{10}H_{14}O$; linalol $C_{10}H_{18}O$; cymene $C_{10}H_{14}$.
·925–·935	—	**Ledum camphor** $C_{15}H_{26}O$.
1·040–1·060	—	**Eugenol** $C_{10}H_{12}O_2$; safrol $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$.
·875	—	Angelic aldehyde (?) C_5H_8O.
·930–1·070	+5°	Asarone $C_{12}H_{16}O_3$; matico camphor $C_{12}H_{20}O$.

Oil.	Source.	Yield Per Cent.
Meadowsweet oil	Spiræa ulmaria; herb	—
Melissa oil	Melissa officinalis; herb . . .	traces only
Mew oil.	Meum anthamanticum; root .	0·75
Mountain mint oil	Pycnanthemum incanum; herb	1·0
Musk root oil (sumbul) . .	Ferula sumbul; root	0·2–0·4
Mustard oil	Sinapis nigra; seeds	—
Myrtle oil	Myrtus communis; leaves . .	—
Myrtle oil (bog)	Myrica gale; leaves	1·0
Myrtle oil (wax)	Myrica cerifera; leaves . . .	·02–·05
Neroli oil	Orange flowers	·05–·1
Nutmeg oil	Myristica fragrans; fruit . .	8·0–15·0
Onion oil	Allium cepa; herb and bulb .	·005
Orange oil	Citrus bigaradia (bitter) and citrus aurantium (sweet) . .	—
Orange oil (tangerine) . .	—	—
Origanum oil		(See
Orris oil	Iris species; rhizome	·1 to ·2
Paracoto oil		1·0–2·0
Parsley oil	Petroselinum sativum; seeds.	2·0–6·0
Pastinac oil	Pastinaca sativa; fruit . . .	1·5–2·5
Patchouli oil	Pogostemon patchouli; leaves	2·0–4·0
Peucedanum oil	Peucedanum grande; root . .	traces.
Pennyroyal oil.	Mentha puelegium; herb . .	—
Pepper oil.	Piper nigrum; fruit	1·0–2·5
Peppermint oil	Mentha piperita; herb . . .	·1–1·5
Peppermint oil (Japanese)	Mentha arvensis; herb . . .	—
Persea oil	Persia gratissima; leaves . .	·5

Specific Gravity.	Optical Rotation.	Constituents.
—	—	Salicylic aldehyde $C_7H_6O_2$; terpene.
·890–·925	0° 30′ to −6° 30′	**Citral** $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; linalol $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$.
1·001	—	
·910–·940	+3° to +5°	Carvacrol $C_{10}H_{14}O$; pulegone $C_{10}H_{16}O$.
·950–·965	—	
1·014–1·032	0° to +1°	**Allyl thiocyanate** $C_3H_5.CNS$; carbon disulphide CS_2; cyanallyl.
·895–·920	+10° to +20°	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; dipentene $C_{10}H_{16}$ (?).
·870	—	
·885	−5°	
·870–·880	dextro-rotary	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; linalyl acetate $C_{12}H_{20}O_2$; geraniol $C_{10}H_{18}O$; methyl anthranilate $C_6H_4(NH_2)(CO_2CH_3)$.
·868–·915	+14° to +30°	Terpenes; myristicol $C_{10}H_{16}O$ (?).
1·037	−5°	**Allyl-propyl sulphide** $C_6H_{12}O_2$.
·848–·856	+92° to +98°	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; a crystalline ester melting at 65°.
·859	+70°	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$.
Marjoram	Oil.)	
—	—	**Irone** $C_{13}H_{20}O$; myristic acid $C_{14}H_{28}O_2$ and its methyl ester; oleic acid $C_{18}H_{34}O_2$; an oleic ester; oleic aldehyde $C_{18}H_{34}O$.
·925–1·020	0° to +5°	Cadinene $C_{15}H_{24}$; methyl eugenol $C_{11}H_{14}O_2$.
1·050–1·100	−5° to −10°	**Apiol** $C_{12}H_{14}O_4$; pinene $C_{10}H_{16}$.
·870–·890	laevo-rotary	Ethyl alcohol C_2H_6O; octyl propionate C_8H_{17},C_3H_5O; octyl butyrate $C_8H_{17}.C_4H_7O$.
·975–·995	−50° to −65°	Cadinene $C_{15}H_{24}$; patchouli camphor $C_{15}H_{26}O$.
·900	+30° to +35°	
·930–·960	+16° to +25°	**Pulegone** $C_{10}H_{16}O$.
·873–·905	−3° to −5°	Terpenes; sesquiterpenes.
·900–·920	−18° to −33°	**Menthol** $C_{10}H_{20}O$; **menthyl acetate** $C_{12}H_{22}O_2$; and numerous other bodies for which see text.
·895–·905	−25° to −43°	
·960	+2°	Methyl-chavicol $C_{10}H_{12}O$.

Oil.	Source.	Yield Per Cent.
Petit-grain oil	Orange twigs and shoots	—
Pichurim oil	Nectandra puchury	·5 to 1·0
Pimento oil (allspice)	Pimenta officinalis; fruit	3·0–4·5
Pimpinella oil	Pimpinella saxifraga; root	—
Pine needle oils	—	
Poplar oil	Populus nigra; buds	·3–·6
Ragweed oil	Ambrosia artemisifolia; herb.	·1
Rose oil	Rosa damascena; flowers	·02
Rosemary oil	Rosmarinus officinalis; flowering tops	—
Rosewood oil	Convolvulus species; wood	—
Rue oil	Ruta graveolens; herb	—
Sage oil	Salvia officinalis; leaves	1·0–3·0
Santal-wood oil (East Indian).	Santalum album; wood	1·5–6·0
Santal-wood oil (West Indian).	Amyris balsamifera; wood	—
Santal-wood oil (West Australian).	Santalum cygnorum; wood	—
Sassafras oil	Sassafras officinale; wood	3·0–8·0
Savin oil	Juniperus sabina; twigs	3·0–5·0
Savory oil	Satureja montana; herb	—
Shaddock oil	Citrus decumanum; fruit	—
Silaus oil	Silaus pratensis; fruit	1·0–1·5
Snakeroot oil		
Spearmint oil	Mentha viridis; herb	·3–·5
Spicewood oil	Laurus benzoin; bark	·43
Spike oil	Lavandula spica; flowers	—

Specific Gravity.	Optical Rotation.	Constituents.
·885–·900	−2° to +4°	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; linalyl acetate $C_{12}H_{20}O_2$; geraniol $C_{10}H_{18}O$; geranyl acetate $C_{12}H_{20}O_2$; sesquiterpene.
—	—	Esters of lauric and valerianic acids (?).
1·040–1·055	−1° to −4°	**Eugenol** $C_{10}H_{12}O_2$; sesquiterpene.
·960	—	
·900–·905	—	
·870	−26°	
·855–·865 at 30°	+1° to −8°	**Geraniol** $C_{10}H_{16}O$; **citronellol** $C_{10}H_{18}O$; esters; paraffins.
·900–·918	+1° to +12°	Borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$; bornyl acetate $C_{12}H_{20}O_2$; cineol $C_{10}H_{18}O$; camphene $C_{10}H_{16}$; pinene $C_{10}H_{16}$.
·900–·910	laevo-rotary	Terpenes.
·832–·841	0° to +3°	**Methyl-nonyl-ketone** $C_{11}H_{22}O$; lauric aldehyde $C_{12}H_{24}O$.
·915–·930	+10° to +25°	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; thujone $C_{10}H_{16}O$; sesquiterpene.
·973–·981	−15° to −20″	**Santalol** $C_{15}H_{26}O$; an isomeric alcohol; santalal $C_{15}H_{24}O$; esters.
·950–·964	+10° to +30°	Santalol $C_{15}H_{26}O$ (?)
·945–·965	+5°	Santalol $C_{15}H_{26}O$ (?); esters.
1·065–1·095	+1° to +4°	**Safrol** $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$: phellandrene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; eugenol $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$.
·910–·928	+40° to +60°	Pinene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$; sabinol $C_{10}H_{16}O$; **sabinol actetate** $C_{12}H_{18}O_2$.
·935–·940	−3°	**Carvacrol** $C_{10}H_{14}O$; pinene $C_{10}H_{16}$ (?); cymene $C_{10}H_{14}$ (?).
·860	+90° to +95°	Limonene $C_{10}H_{16}$.
·980–·990 (See Asarum	dextro-rotary Oil.)	
·920–.940	−30° to −50°	**Carvone** $C_{10}H_{14}O$.
·923	—	**Methyl salicylate** $C_8H_8O_3$; terpenes.
·905–·918	+1° to +7°	Linalol $C_{10}H_{18}O$; cineol $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; borneol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$.

Oil.	Source.	Yield Per Cent.
Sweet basil oil	Ocymum basilicum ; herb . .	—
Tansy oil	Tanacetum vulgare ; herb . .	·1–·2
Tetranthera oil	Tetranthera citrata ; fruit . .	5·0
Thuja oil	Thuja occidentalis ; leaves . .	·5–1·0
Thyme oil	Thymus vulgaris ; herb . . .	·3–2·5
Turmeric oil	Curcuma longa ; root	5·0
Turpentine oil (American)	Pinus Australis ; wood . . .	—
Turpentine oil (French) .	Pinus pinaster ; wood	—
Turpentine oil (German) .	Pinus sylvestris ; wood . . .	—
Turpentine oil (Russian and Swedish)	Pinus ledebourdii ; wood . .	—
Valerian oil	Valeriana officinalis ; root . .	1·0
Valerian oil (Japanese) . .	Valeriana angustifolia	6·0–7·0
Verbena oil	Verbena officinalis	—
Veti-vert oil.	Andropogon muricatus ; grass	about 1
Wintergreen oil	Gaultheria procumbens ; leaves	·5–1·0
Wintergreen oil	Betula alba ; bark	·5–1·0
Wormseed oil	Artemisia maritima	2·0
Wermwood oil	Artemisia absinthum ; herb .	·2–·9
Zedoary oil	Curcuma zedoaria ; roots . .	1·02–·0

Specific Gravity.	Optical Rotation.	Constituents.
909–·990	+15° to −20°	**Methyl-chavicol** $C_{10}H_{12}O$; linalol $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; cineol $C_{10}H_{18}O$.
925–·950	−25° to −35° (English) +30° to +45° (American)	**Thujone** $C_{10}H_{16}O$; borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$.
·920	—	Citral $C_{10}H_{16}O$.
·910–·925	−6° to −14°	**Thujone** $C_{10}H_{16}O$; fenchone $C_{10}H_{16}O$; pinene $C_{10}H_{16}O$; traces of esters ; carvone $C_{10}H_{14}O$.
·900–·950	laevo rotary	**Thymol** $C_{10}H_{14}O$; carvacrol $C_{10}H_{14}O$; menthone $C_{10}H_{18}$; linalol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; cymene $C_{10}H_{14}$; bornyl acetate $C_{12}H_{20}O_2$; pinene $C_{10}H_{16}$.
·940	dextro-rotary	
·855–·870	+10° to +15°	**Turmerol** $C_{19}H_{28}O$(?) ; phellandrene $C_{10}H_{16}$.
·855–·870	−18° to −40°	**Pinene** $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
·860–·870	+15° to +20°	**Pinene** $C_{10}H_{16}$.
870–·875	to +20°	**Pinene** $C_{10}H_{16}$; sylvestrene $C_{10}H_{16}$.
		Sylvestrene $C_{10}H_{16}$; pinene $C_{10}H_{16}$.
·930–·960	−8° to −15°	Pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; borneol $C_{10}H_{18}O$ and its esters ; terpineol $C_{10}H_{18}O$; a sesquiterpene alcohol $C_{15}H_{26}O$; alcohol $C_{10}H_{20}O_2$.
·985–·995	−8° to −15°	Pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$ and its esters ; a sesquiterpene ; kessyl acetate $C_{16}H_{26}O_3$.
·890–·900	practically inactive	**Citral** $C_{10}H_{16}O$.
1·010–1·030	+25° to +40°	
1·177–1·187	0° to −1°	**Methyl salicylate** $C_8H_8O_3$ and traces of other bodies (see page 225).
1·177–1·187	inactive	
·930–·935	—	**Cineol** $C_{10}H_{18}O$; dipentene $C_{10}H_{16}$ (?).
·925–·955	—	**Thujone** $C_{10}H_{16}O$; thujyl alcohol $C_{10}H_{18}O$ and its esters ; phellandrene $C_{10}H_{16}$; pinene $C_{10}H_{16}$.
·990–1·010	—	Cineol $C_{10}H_{18}O$.

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