

ON THE CRYSTALLINE CAMPHOR OF EUCALYPTUS
OIL (EUDESMOL), AND THE NATURAL FORMATION
OF EUCALYPTOL.

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IN August 1897, a paper was read before this Society by Mr. R. T. Baker and myself,¹ in which was announced a crystalline camphor or stearoptene isolated by us from the oil of *Eucalyptus piperita*. The specimens then shown only consisted of a few isolated crystals as the camphor does not appear to exist in quantity in the oil of this species. At that time no investigation could be undertaken to determine its constitution, it being obtainable in such minute quantities, but it was thought that it must be a constant constituent in these oils, and that it might be obtainable from other species of Eucalypts in larger quantity.

This surmise was correct, as the camphor has been found to be present in the oils of several species of Eucalyptus, and as will be presently shown, should be isolated, at certain times of the year, from the oils of all those species of Eucalypts whose ultimate constituent is eucalyptol. The results so far obtained in reference to this camphor may assist somewhat towards a more complete knowledge of the chemistry of Eucalyptus oils, and help to explain the differences, found at certain times of the year, in the constituents of the oils of this genus. The differences found existing in the several members, apparently made a correct expression of opinion in reference to them exceedingly difficult, but as our knowledge increases these difficulties partly disappear, and the explanations that can now be given considerably simplify the study of these trees. In the determination of the chemical constituents of the several species of Eucalypts, we have a check

¹ On the Essential oil and the presence of a solid camphor or stearoptene in the "Sydney Peppermint" *Eucalyptus piperita*.

upon their botanical diagnosis, as the chemical constituents of each species appear to be identical under certain conditions, and governed by laws that will eventually be better understood. A large number of facts have accumulated, without exception supporting this statement, and will later be published. It is hoped that by working on material of undoubted authenticity the results may be of permanent value from a commercial as well as a scientific standpoint, and I wish to express my thanks to my colleague, Mr. R. T. Baker, F.L.S., for the botanical diagnosis of the species.

The presence of the camphor, and the natural formation of Eucalyptol.

The oil of *Eucalyptus goniocalyx* was found to be exceedingly rich in eucalyptol, and the presence of eudesmol was very marked. Dextropinene was also present, the oil somewhat resembling, in colour and constituents, that of *E. globulus* and belongs to the same group of trees giving like oils. Phellandrene could not be detected, nor was any to be expected, because in the oils of this class, already determined by me, no phellandrene could be found.

The oil of *Eucalyptus Smithii*¹ was found to be richer in eucalyptol than any oil yet obtained during this research. Eudesmol was present in the oil obtained from the leaves of two consignments, a month separating the dates of the collections, (August and September 1898, from Monga N.S.W., yield of oil 1.345 per cent., mean of four distillations). Dextropinene was present in this oil, and the specific rotation of the rectified oil was $[\alpha]_D + 7.01^\circ$. The constituents which give the oil of *E. globulus* its comparatively high specific gravity were largely absent in this oil, the consequence being that rectified oil of this species, representing 92 per cent. of the crude oil, and containing over 70 per cent. of eucalyptol, only just satisfies the specific gravity requirements of the new British Pharmacopœia, and has a less specific gravity than many other oils containing considerably less eucalyptol; again illustrating the weakness of the specific gravity

¹ See paper by Mr. R. T. Baker, "On three new species of Eucalyptus."—Proc. Linn. Soc. N. S. Wales, June 28, 1899.

standard as fixed. The oils from these two consignments of *E. Smithii* were identical in all constituents, equally rich in eucalyptol and the specific gravity, optical rotation, &c., were practically the same in both. Phellandrene was of course absent.

The oil of a species of eucalyptus, locally known as "Sallow" or "Swamp Gum" and named by my colleague (Mr. Baker) *Eucalyptus camphora* (*loc. cit.*), was rich in eudesmol at the time of year when the leaves were obtained, (2nd September 1898). On redistillation of the crude oil a fraction was obtained, representing 18 per cent., boiling between 280° and 290° C., which in less than one hour had solidified into a solid crystalline mass in the bottle, and which after nine months remains unaltered. The first fraction of this oil contained at that time 33 per cent. of eucalyptol and a large percentage of the pinenes, but had less than 1° of rotation to the right in a 100 mm. tube. Phellandrene was absent.

Besides the species enumerated above, eudesmol has been found by us in the oils of several other Eucalypts that were rich in eucalyptol at the time of distillation, as *E. stricta*, *E. elaeophora*, etc., but, so far eudesmol has not been found in the oil of any species in which eucalyptol is absent, or only present in traces, as *E. dives*, *E. radiata*, *E. dextropinea*, *E. microcorys*, *E. laevopinea*, *E. Dawsonii*, and many others, and it has not been found to be present in any oil without a fair percentage of eucalyptol being present also.

Having considered the oils of those species of eucalyptus found to be rich in eucalyptol, containing eudesmol, and in which phellandrene is absent; we turn to those oils in which phellandrene is present at certain times of the year, and which also contain eucalyptol and nearly always eudesmol.

The oil of the "Red Stringybark" *Eucalyptus macrorhyncha*, when first distilled appears always to contain eudesmol, but in greater abundance at certain times of the year. Eucalyptol is always present; phellandrene can usually be detected; and when the oil is most abundant in the leaf laevopinene is present also.

In the spring time phellandrene appears in greatest amount in the oil of this species, while in the autumn it is almost or quite absent. As the phellandrene diminishes in this oil, the eucalyptol increases in quantity, other alterations also taking place. In a paper¹ by Mr. Baker and myself, published July 1898, analyses are given of the oil of this species, in which a good quantity of eudesmol had been found. A reference to that paper will shew that only about 48 per cent. distilled below 183° C., and that the oils contained a fairly large fraction boiling above 268° C. consisting largely of eudesmol. It was from the high boiling constituents of this oil that the eudesmol was obtained for the purpose of this research. On opening some months afterwards, the glass stoppered bottle in which the crude oil had been stored, it was found that there had been absorption of the oxygen from the air filling the vacant space above the oil, there being apparent suction on the stopper of the bottle; little notice was taken of this at the time, but the same thing having occurred again investigation of the contents was made to determine if possible the result of the alteration. It was then found that the greater portion of the high boiling fraction containing the eudesmol had disappeared, and that the oil had become much richer in eucalyptol. The following is the analysis of this oil after having been kept in the crude condition for nine months. No pinenes were found, nor could phellandrene be detected. On redistillation only a few drops came over below 170° C., but between that temperature and 175.5° C. 27 per cent. had distilled, and by 182.8° C. 74 per cent. had been obtained against 48 per cent. distilling below 182.8° C. when originally investigated. The fractions were divided as follows:—

Below	175.5° C.	= 27 per cent.	= First fraction
Then to	182.8° C.	= 47	„ = Second „
„	268.6° C.	= 10	„ = Third „
„	276.8° C.	= 11	„ ... Fourth „

The fourth fraction only contained eudesmol in very small quantity at this second distillation, and only crystallised on long standing.

¹ On the Stringybark Trees of N.S. Wales—Proc. Roy. Soc. N.S. Wales, July 6, 1898.

Specific gravity, First fraction = $\cdot 9124$ @ 15° C.

„ „ Second „ = $\cdot 9164$ „

„ „ Third „ = $\cdot 9188$ „

„ „ Fourth „ = $\cdot 9446$ „

„ „ Crude oil = $\cdot 9307$ „

$[\alpha]_D + 2\cdot 33^{\circ}$ for first fraction and $[\alpha]_D + 2\cdot 14^{\circ}$ for second fraction.

Eucalyptol First fraction = 68.5 per cent.

„ Second „ = 71.1 „

Originally the mean of several determinations of first and second fractions gave 51 per cent. of eucalyptol.

It will be seen that the first fraction is almost as rich in eucalyptol as the second, and this is also found to be the case in those oils that are exceedingly rich in eucalyptol at time of distillation, *E. Smithii* particularly.

From these results it is apparent that by the alteration of the high boiling constituents, marked changes have taken place. The rotation has become more dextrorotatory, the specific gravity of the lower boiling fractions has increased, the increase in eucalyptol content is most marked, and the eudesmol has practically vanished.

The investigation of the oil of *E. eugeniioides* further emphasises the specific alteration undergone by this class of oils on keeping in the crude state under certain conditions. This oil is that marked No. 2 of *E. eugeniioides* in the paper previously referred to (the Stringybark trees of N. S. Wales). Unfortunately a full investigation was not made of that particular oil at the time, but enough data are given to determine the direction of change. The same absorption of oxygen was apparent as in the oil of *E. macrorhyncha* and the alteration of the constituents was in the same direction as found in that oil. No eudesmol was originally detected in this oil, but there appears little doubt but that it should be found, if carefully sought for, as it exists in other oils of the class to which this species belongs, viz.:—*E. macrorhyncha*, *E. piperita*, and *E. amygdalina* (not the species from which much of the supposed “amygdalina oil” that has been sent to Europe under that name was obtained, as the tree from which

this so-called "amygdalina oil" has been distilled, is now proved by botanical characters and chemical evidence to be specifically distinct from *E. amygdalina* of Labillardière, and is *Eucalyptus dives* of Schauer, which species was founded on immature trees).

On redistilling this sample of the oil of *E. eugenoides* after nearly two years, 5th July, 1899, 96 per cent. distilled below 182° C., the fraction being very rich in eucalyptol. The crude oil which originally only contained 28·4 per cent. of eucalyptol, now contained 62·5 per cent. eucalyptol, a marked increase. The rotation had changed but little in this oil, being slightly more dextrorotatory ($[\alpha]_D + 5\cdot5^\circ$) than when originally determined. The specific gravity of the crude oil was ·9171 @ 15° C., and of the large fraction ·9127 a slight increase on that of the crude oil.¹

In the alteration of the other sample of the oil of *E. eugenoides*, marked No. 1 in paper referred to, we are able to show the necessity of a small quantity of oxygen to bring about the desired change in the formation of eucalyptol. After the completion of the original investigation on these oils, the crude oil remaining was stored in the dark with other oils, and remained untouched for nearly two years. A marked improvement in the eucalyptol content having taken place with the oil, No. 2 sample of *E. eugenoides*; investigation of oil No. 1 was then made, with the result that the same alteration had not then taken place with this oil as in that of No. 2, it was but little richer in eucalyptol than when first distilled, containing then under 40 per cent. eucalyptol. It appeared only possible to account for this discrepancy by the fact that the bottle containing No. 1 oil was quite full when put away, whereas the bottle containing No. 2 oil was less than half full and besides had been opened two or three times during the time. This pointed to the fact that oxygen was necessary to bring about the

¹ The temperature at which the original specific gravity was given in the paper is 22° C. This can be readily corrected, as by a determination of a *Eucalyptus* oil at all temperatures between 10° C. and 22° C. it was found that the increase below 15° C. and the decrease above that temperature was almost identically ·00075 for every degree of temperature, water at 15° C.

change. To test the accuracy of this surmise the oil No. 1 was transferred to a large bottle which it only half filled, and by occasionally shaking and removing the stopper, change soon commenced; so much so, that in two weeks the improvement in eucalyptol could be readily detected, and on the expiration of one month the oil was analysed with the following result:—

On redistillation only a few drops came over below 167° C., by 170° 4 per cent. had been obtained; between that temperature and 176.5° there distilled 70 per cent., and at 181° 88 per cent. had come over. The oil distilling between 171° and 181° was taken as one fraction. This was slightly yellowish in tint, but brilliant in appearance and had a pleasant odour and taste. The specific gravity of the rectified oil was $\cdot 9102$ at 15° C., specific rotation $[\alpha]_D + 3.85^{\circ}$ and it contained 58 per cent. of eucalyptol. The crude oil had a specific gravity $\cdot 9202$ at 15° C. (an increase in specific gravity on original determination), specific rotation $[\alpha]_D + 4.5^{\circ}$ (a slight dextrorotatory increase) and contained at this time ($31.7.99$) 55 per cent. of eucalyptol, an increase in eucalyptol of nearly 24 per cent. from time of distillation from the leaves, and an increase in eucalyptol of about 15 per cent. in one month by alteration under the conditions described. It is evident that the change is not yet completed in this oil, but more time could not be given, and another analysis will be eventually made. It will be observed that the other sample of the crude oil of *E. eugenoides* contained 62.5 per cent. of eucalyptol, equal to about 65 per cent. in the rectified portion, as the maximum of alteration. The maximum content of eucalyptol in the rectified portion of any *Eucalyptus* oil appears to be about 70 per cent. (the fraction representing about 80 to 85 per cent. of the whole), and although this amount of eucalyptol is very rarely found to be present, yet it appears that on natural alteration of oils like *E. macrorhyncha*, *E. eugenoides*, etc., this standard may be reached by judicious management. It may be that eventually we shall obtain complete control of these results, and that the oil from prolific yielders will be made to reach this standard.

From the results of the oil of *E. eugenioides* it is seen that the formation of eucalyptol in the crude oils of this class does not apparently take place without oxygen being present. How much oxygen is necessary to bring about the maximum change is a problem to be solved.

In the paper on *E. piperita* (*loc. cit.*) eudesmol, eucalyptol 26 per cent., and phellandrene were shown to be present in the oil at the time of distillation. It is possible in the oil of this species to show the result of alteration in the formation of eucalyptol while in the leaf. On 26th July 1898 (the end of our Australian winter) a consignment of the leaves of *E. piperita* was received from Currawang Creek, near Braidwood, N. S. Wales, the oil of which on analysis contained no phellandrene, and the presence of an extraordinarily large amount of eucalyptol was found, but no eudesmol could be detected at that time. The oil on redistillation gave a fraction boiling between 172° and 180° C., representing 75 per cent. of the crude oil, which fraction had a specific gravity .915 at 15° C., specific rotation $[\alpha]_D + 3.66^\circ$ and contained 70 per cent. eucalyptol. The rectified oil is almost colourless, exceedingly brilliant in appearance and as rich in eucalyptol as any; it resembles the oil of *E. macrorhyncha* and other first quality oils of this class. In appearance, taste, odour and eucalyptol content, the oils of this class of *Eucalyptus*, when obtained under correct conditions are of superior quality, and it appears that by taking advantage of known natural alterations in the constituents of these oils, or by keeping the crude oils under certain conditions until the maximum alteration has taken place, that we may govern the formation of the constituents required, even if we do not succeed eventually in bringing about the required alteration at once by artificial means.

From the consideration of the facts enumerated above, it appears certain that the *Eucalyptus* camphor (eudesmol) is an intermediate product in the natural formation of eucalyptol, and as such is not to be expected to be present always in constant proportions. It will be shown presently that the formula of eudesmol is $C_{10}H_{16}O$

and that it is isomeric with ordinary camphor, but has no rotation.

Eucalyptus globulus belongs to a group of Eucalypts, of which we have several in this colony, the oils of which have great resemblance to each other and when distilled are always rich in eucalyptol, they contain dextropinene in varying quantities and are free from phellandrene. In this group the alteration of the constituents through eudesmol to eucalyptol is rapid and but little reserve material of high boiling constituents is stored in the leaf, although both in the case of *E. goniocalyx* and *E. Smithii* eudesmol was found. It is probable for this reason that phellandrene is found to be always absent in the oils of the globulus group, which on distillation appear to generally contain nearly their maximum amount of eucalyptol, and therefore undergo little alteration on keeping. In those oils like *E. macrorhyncha*, *E. piperita*, *E. eugenoides*, etc., which contain a fair percentage of eucalyptol, and mostly some phellandrene, the change is not usually completed at time of distillation, and we can thus trace the process of alteration of the constituents and the formation of the ultimate product, eucalyptol.¹ In the redistillation of those oils under atmospheric pressure, besides the water always given off at about 100° C., it is found that water is again always split off from the constituents boiling at a high temperature particularly that fraction containing eudesmol. The constitution of eudesmol indicates that the oxygen atom is attached to the molecule previous to the formation of eucalyptol. Which particular terpene is necessary to this formation of eucalyptol is uncertain, but phellandrene cannot be detected when the apparent maximum of alteration has taken place. It is found that the pinene present in the oils of the group of Eucalypts to which *E. macrorhyncha* belongs is always lævopinene, whereas in the oils of the globulus group the pinene always appears to be dextropinene, and the indication thus is that it is the lævo-terpenes

¹ In this paper I have not dealt with that group of Eucalypts whose oils consist very largely of phellandrene, nor those whose oils consist very largely of pinene.

that are necessary to this alteration, and this probably accounts for the fact that the oils of the globulus group are always dextrorotatory, as it is found that when the maximum of eucalyptol has been reached in the oils of *E. piperita*, *E. macrorhyncha*, etc., that the oils are always dextrorotatory, and in about the same proportion as is found in the oils of the globulus group. As a result of experiments on the terpenes, by Armstrong and Tilden,¹ they arrive at the conclusion that American turpentine contains a substance which either has a less dextrorotatory power or is lævorotatory, and which is more readily polymerised than its chief constituent. This also appears to be the case with the pinenes of *Eucalyptus* oils.

If eudesmol is the intermediate stage in the formation of eucalyptol, we ought to find that those oils which have been found to contain eudesmol in quantity should, at certain times of the year, become rich in eucalyptol, and that has been found to be so. The oil of *Eucalyptus camphora* distilled from material sent from Delegate, Feb. 1899, was found to be rich in eucalyptol, the oil much resembling that of *E. globulus*, eudesmol was only present in small amount at that time of the year. This is probably the case with *E. Smithii* also, and it is to be expected that the oil from this tree will be found rich in eudesmol at certain times of the year, as when distilled only a small quantity was present, but the maximum eucalyptol had been practically reached at that time, and 97 per cent. was obtained on redistillation boiling below 180° C. so that the constituents boiling at a high temperature were practically absent. The crude oil had almost the same specific gravity as the large fraction, and the first portion distilling was almost as rich in eucalyptol as the last portion.

EXPERIMENTAL.

Preparation of the pure Eudesmol.

The oil of *Eucalyptus macrorhyncha* was taken for the preparation of this camphor, but any oil rich in eudesmol, as *E. camphora*, would do as well. The constituents boiling below 188 – 190° C.

¹ Chem. Journ., xxxv., 733.

were removed by distillation from the crude oil, and the remainder (about 40 per cent.) poured from the still into shallow glass vessels and left a few days to crystallise. It then formed a soft crystalline mass of the consistency of butter. This was then spread upon porous plates to absorb the fluid portions. This was found to be important as a very small quantity of adhering terpenes makes subsequent purification difficult. When the adhering oil had been absorbed a whitish product was obtained. This was dissolved in alcohol, water added until slight turbidity remained, and left in open vessels to crystallise. This was found the better way as by adding excess of water an oily product was obtained very difficult to crystallise. On standing a day or two the camphor crystallised, this was removed as a cake, the mother liquor being used for a further crop of crystals. The adhering liquid was removed by porous plates and the process repeated until a perfectly snow-white product was obtained, having the correct melting point $79 - 80^{\circ} \text{C}$.

The crystalline substance is quite white, silky in lustre, and beautiful in appearance. It is very soft and inclining to a paraffin nature, the crystals are fairly well developed, acicular, and when sufficiently transparent to allow light to pass, polarize partly in colours, and extinguish parallel. Only a comparatively small amount of crystals could be obtained of this nature, the remainder on purification consisting of small interlaced crystals giving the product a matted appearance. In its purified state it is exceedingly light. When the fraction containing the eudesmol was first obtained from the oils of *E. macrorhyncha* and *E. camphora* it was thought that we might obtain the camphor in good quantity, as the fraction crystallised into a solid mass on standing, but this was more apparent than real, as when purified only a comparatively small amount of eudesmol had been obtained, and it would be necessary to distill a very large quantity of oil to enable one pound of pure eudesmol to be obtained.

Eudesmol is insoluble in water and alkaline solutions. It is soluble in chloroform, petroleum ether, ether, alcohol, glacial acetic

acid (crystallises out again on adding water), acetone, benzene, olive oil and oils generally. The volatile solvents all leave the eudesmol in a crystalline condition on evaporation, either at once or crystallisation soon takes place on standing.

Melting Point.

Perfectly purified eudesmol melts at $79 - 80^{\circ}\text{C}$. The crystallised substance from dilute alcohol, from acetic acid, and the sublimed material, all melted at that temperature, and by no method of purification was 80°C . exceeded. The tendency to give lower melting points was most troublesome, necessitating many scores of determinations on different material. Minute portions of the high boiling terpenes are prone to be retained, and these lower the melting point considerably. The best method of taking the melting point was found to be as follows:—the camphor was melted at the lowest possible temperature, and a portion drawn into a capillary tube and allowed to perfectly crystallise again in the tube; 3 mm. of the column was then retained; the tube was attached to the thermometer and suspended in water which was slowly heated. The substance was considered to have reached its melting point at the instant when it began to rise in the tube.

Sublimation.

Purified eudesmol, melting at $79 - 80^{\circ}\text{C}$. was taken. This sublimed readily, care being taken to keep the upper glass cool; fine crystals of a good length were obtained. It was found that when the sublimation was carried out at the lowest possible temperature, that the sublimate melted at the same temperature as at first, but that if heated too much, the melting point of the sublimate had been lowered; this was found to be the case under all conditions, the tendency being to form substances having a lower melting point. Sublimation takes place at a little above 100°C .; a distinct sublimate was obtained by heating in a tube closed at one end when suspended in boiling water for some time.

The melting point of the sublimate being lowered by overheating, an attempt was made to determine at what temperature this decomposition commenced. A small U tube was taken with one

limb a little longer than the other, and the end of the longer limb closed. A small portion of eudesmol was then melted in the closed end and the remainder filled with mercury; this was attached to a thermometer and the whole immersed in glycerol. On heating it was found that slight decomposition commenced at about 180°C . and continued to slowly increase until 250°C . had been reached, when the determination was stopped. No alteration, therefore, takes place at 150°C ., and eudesmol sublimes readily below that temperature.

Rotation.

Eudesmol has no rotation; 2.5 grams dissolved in 50 grams of alcohol had no action on a ray of polarised light in a 200 mm. tube.

Analysis of Eudesmol.

The material was melted in the platinum boat at the lowest possible temperature. Results of five of the determinations made are given—

0.1725	gave	0.5006	CO_2	and	0.1764	H_2O .	C. = 79.13;	H = 11.36
0.2324	„	0.6704	„	„	0.2294	„	„ 78.66;	„ 10.97
0.1962	„	0.5646	„	„	0.1951	„	„ 78.44;	„ 11.06
0.1611	„	0.4657	„	„	0.1622	„	„ 78.83;	„ 11.17
0.1608	„	0.4624	„	„	0.1614	„	„ 78.42;	„ 11.15

$\text{C}_{10}\text{H}_{16}\text{O}$ requires 78.94 C., and 10.53 H. per cent.

Mean of the above analyses C = 78.7 and H = 11.14 per cent.

The material used for determinations Nos. 4 and 5 was that previously used for the molecular determination; it was regenerated from the acetic acid solution by the addition of water.

Molecular determination.

The molecular determination was made by the cryoscopic method, glacial acetic acid being used.

Eudesmol taken = 0.3855 gram.

Acid = 29 grams.

Acid alone, first time freezing = 5.56°

„ „ second „ „ = 5.54°

„ „ third „ „ = 5.53°

After solution of the eudesmol

First time freezing = 5.22°

Second „ „ = 5.185°

Third „ „ = 5.185°

\therefore Molecular value = 150

$C_{10}H_{16}O$ = 152

Di-nitro compound.

On the addition of strong nitric acid to eudesmol, little change takes place at once in the cold. After a little time it darkens somewhat, the eudesmol becoming liquid and changing to a purple colour. On gently heating until reaction commenced, the colour changed at once to yellow with rapid solution of the substance and evolution of dark brown fumes. After about fifteen minutes the action apparently ceased and if kept cool no more brown fumes escaped. On addition of water a yellow crystalline mass was at once formed. The filtrate remained yellow. The nitro-compound is slightly soluble in cold water, more readily in hot water. It is soluble in alkaline solutions and reprecipitated on acidifying. It was purified from alcohol. When dry it is of a primrose colour. It is soluble in alcohol, ether and acetone, but does not form a well defined crystalline substance with these solvents. It melts at $90^{\circ} C.$, but changes to a deep orange colour at $75^{\circ} C.$

A determination of the nitrogen gave results as follows :—

Material taken = .1147 gram.

Moist nitrogen obtained = 11.5 cc.

Barometer = 767 mm.

Temperature of gas = $16^{\circ} C.$

\therefore Nitrogen = 11.8 per cent.

$C_{10}H_{14}(NO_2)_2O$ requires nitrogen 11.57 per cent.

Dibromide.

The purified eudesmol was dissolved in a small quantity of glacial acetic acid and bromine added. This was readily and quietly absorbed, no substitution taking place. The bromide is an addition product. The rise of temperature was prevented as much as possible. The bromide soon separated as a semi-solid

substance especially on shaking and adding a few drops of water. The bromide was then boiled repeatedly with water, with very dilute potash solution, and with dilute alcohol. It was then purified from chloroform, and as it did not form a well defined crystalline compound it was again boiled with water and with dilute alcohol. When cold it was a plastic mass, sufficiently hard to rattle like shot in a bottle. It is of a yellowish-brown colour. It is exceedingly soluble in chloroform and in ether, but difficultly soluble in alcohol, and not at all if the alcohol be at all dilute. It melts at 55° to 56° C.; the melting point was taken with minute spheres on the surface of mercury; with the aid of a lens the exact melting point was readily seen.

A determination of the bromine in 0.2008 gram of the bromide gave $0.2470 \text{ AgBr.} = 0.1051 \text{ Br} = 52.34 \text{ Br per cent.}$

$\text{C}_{10}\text{H}_{16}\text{Br}_2\text{O}$ requires 51.3 Br per cent.

Eudesmol does not apparently form a nitrosochloride, as amyl nitrite in acetic and hydrochloric acids failed to react, no crystals being obtained even on long cooling to -10° C.

When eudesmol was treated with phenylhydrazine no alteration of the original material took place.

It was not possible to introduce other hydrogen atoms into the eudesmol molecule by ordinary methods. When a solution in alcohol was treated with sodium no alteration took place, the regenerated material being identical with that taken. Several other methods were tried but without effect. It appears, therefore, that the oxygen atom is not ketonic, as eudesmol cannot be reduced to an alcohol. This coincides with the known peculiarities of eucalyptol as that substance does not apparently contain an hydroxyl group, so that the remaining H_2 required to form eucalyptol from eudesmol must be attached to the molecule of the latter in another way. Alcoholic potash effects no alteration in eudesmol even on boiling for a long time.

Oxidation.

On heating eudesmol with dilute nitric acid, energetic action took place with evolution of brown fumes, and rapid solution of

the camphor. On continued boiling no crystalline product was obtained. The acid solution was boiled continuously for two days, and even then no crystalline product was obtained. On addition of water no precipitate was formed. The nitric acid was removed by evaporation, and to the small quantity remaining, still in solution, water was added; a minute quantity of a camphoraceous substitute was obtained, but no crystals were precipitated. This camphoraceous substance does not appear to be the unaltered material, as it melted below 40°C . The filtrate was evaporated to dryness on the water bath, water again added, filtered, and this process repeated a few times. The filtrate on again evaporating to dryness crystallised in microscopic crystals on standing. These crystals were soluble in cold water to an acid solution, which on addition of barium chloride and ammonia gave no precipitate in the cold, but on boiling a precipitate was soon obtained. This was filtered off, washed, treated with hydrochloric acid and the solution agitated with ether. On evaporation of the ethereal solution the residue showed microscopic crystals, this was again crystallised from water. The product was a mass of microscopic needles resembling camphoronic acid. No oxalic acid was obtained. To be sure the crystals were camphoronic acid, that acid was formed from ordinary camphor in the usual way, and treated under exactly the same conditions; the product resembled in every respect that obtained from eudesmol, with the exception that the melting point of the product from eudesmol ($165 - 168^{\circ}\text{C}$.) was a few degrees higher than that from camphor, and that on repeated crystallisation rather better defined crystals were obtained with the acid from eudesmol. From the results by Aschan¹ and by Perkin and Thorpe it is shown that the *i*-camphoronic acid melts at a higher temperature than either *d*- or *l*-forms, and that the *i*-acid has better defined crystals. It thus seems that the acid derived from eudesmol will be found, when sufficient shall have been obtained, to be *i*-camphoronic acid. Eudesmol is readily oxidised by chromic acid. The oxidation products of eudesmol

¹ Ber. 1895, xxviii., 16 and 224.

are interesting and the want of material has alone prevented me completing their investigation at this time, but I hope to continue the research later. The nitro-compound is also worthy of further inquiry.

On fusing eudesmol with potash at 180° C., the volatile acid obtained on acidifying with sulphuric acid and distilling was acetic acid. No iso-butyric acid was detected.

THEORETICAL CONSIDERATIONS.

The isolation of eudesmol from several members of the "globulus group" of Eucalypts, (those species whose oils are rich in eucalyptol at time of distillation), the natural alteration of the eudesmol fraction from oils like that of *E. macrorhyncha* with the corresponding formation of eucalyptol, and the other facts described in the body of this paper, show eudesmol to be intermediate in the formation of eucalyptol in Eucalyptus oils.

Eudesmol has a formula $C_{10}H_{16}O$, is isomeric with camphor, and contains two atoms of hydrogen less than eucalyptol.

The ease with which eudesmol forms a di-bromide as an additive compound (attempts to form a higher bromide were not successful), indicates that the molecule is unsaturated, but that the linking must be different from the double linking of the terpenes is shown by eudesmol not forming a nitrosochloride. The pinenes of Eucalyptus oils readily form nitrosochlorides. Eudesmol not reacting with phenylhydrazine indicates that the oxygen atom is not ketonic, but that it is combined in the molecule in some other way. The non-success in all attempts to introduce hydrogen atoms into the eudesmol molecule by ordinary methods, and its inertness to the action of sodium generally, makes it appear probable that the oxygen atom is combined to more than one carbon atom. It may be that cymene plays some part in the formation of eudesmol. Cymene has been shown to occur in the oil of *E. globulus*¹ and thus in other Eucalyptus oils, because *Eucalyptus globulus* is only one member of a class whose oils are identical in composition.

¹ Faust and Homeyer, Ber. VII., 1429.

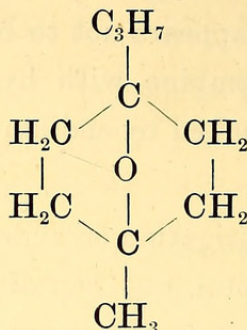
Cymene is closely connected with the pinenes, and has been shown to contain iso- and not normal propyl.¹ It may be too that dipentene takes some part in this alteration. Eucalyptol, which is identical with cineol,² appears not to be either a ketone or an alcohol, as it does not combine with hydroxylamine or phenylhydrazine. It is not attacked by sodium nor by benzoyl chloride below 120°.

The results of this investigation on eudesmol point to a structure allied to that of eucalyptol, but containing two atoms less of hydrogen. The oxygen atom of eucalyptol enters the molecule during the formation of eudesmol, and if cymene be the structure upon which eudesmol is built, then the two added hydrogen atoms enter the molecule at the same time as the oxygen atom. When those Eucalyptus oils which contain a fairly large percentage of high boiling constituents are distilled under atmospheric pressure, the fraction boiling above 250° C. almost in every case splits off a portion of water, and it thus appears that water is present in fairly loose chemical combination with the constituents which compose the high boiling portion of the oils. That it is this water, or its elements, that assists in the formation of eucalyptol appears certain, if it is not so, then it is difficult to account for the formation of eucalyptol in those Eucalyptus oils when kept in their crude condition in a closely stoppered bottle, or to account otherwise for the increase in them of from twenty to thirty per cent. of eucalyptol. That the alteration is from higher boiling constituents to those boiling at a lower temperature is shown in the analyses given, and this must necessarily be so if eucalyptol is the final product as supposed. It has been shown by the investigation on the oil of *E. eugenoides* that oxygen is necessary to start this change. That the increase in eucalyptol content means also a diminution of certain of the terpenes has also been shown.

¹ Widman, Ber. xxiv., 439.

² The name eucalyptol has been retained in this paper to indicate the precise origin of the material, Eucalyptus oils. It may be that cineol found in the Melaleucas may have a like origin as both genera belong to the N.O. Myrtaceæ.

Cineol, and therefore eucalyptol, was supposed by Brühl¹ to contain no double linkings, and owing to its optical inactivity, and for other reasons, he suggested for it the following formula :



The oxygen atom entering the molecule during the formation of eudesmol, that substance must have a formula corresponding to eucalyptol. Eudesmol has no rotation, so that it probably does not contain an asymmetric carbon atom, or that the molecule has a racemic modification. It is difficult to depict for eudesmol a corresponding structure to cineol, having one double linking on the terpene type, without the presence of an asymmetric carbon atom which would indicate activity.

After arriving at the composition of eudesmol and having determined its close connection with eucalyptol, it appeared to me, on considering its reactions, that the difficulty might probably be met by suggesting the quadrivalence of the oxygen atom, as this appears to be in a different state of combination in both eudesmol and eucalyptol than is found to be the case in any allied substance. The question of the valency of an oxygen atom under certain conditions has also been considered by others.

Brühl² advocated the quadrivalence of oxygen in hydrogen peroxide. J. F. Heyes³ advocated the quadrivalence of oxygen in reference to some peroxides.

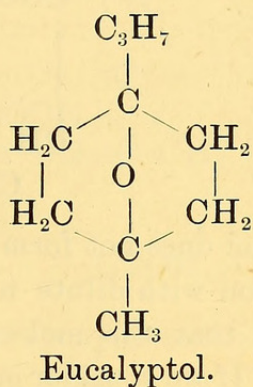
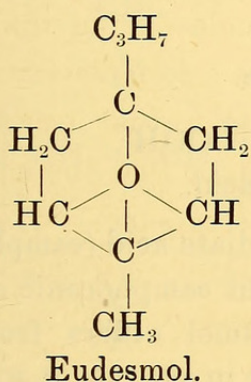
In a paper read before the Chemical Society on June 1st, 1899, on "The salts of dimethylpyrone and the quadrivalence of oxygen," by Dr. J. N. Collie, F.R.S. and Thomas Tickle, the authors are

¹ Brühl, Ber. xxi., 461. ² Brühl, Ber. 1897, xxx., 160

³ Phil. Mag., 1888, xxv., 221.

inclined to believe that the constitution of these compounds is similar to that of the salts of nitrogenous and other bases. This, however, assumes that oxygen may behave as a quadrivalent element. In favour of this hypothesis, the authors instance such compounds as dimethyl ether hydrochloride, diethyl ether hydriodide, ether peroxide, etc.

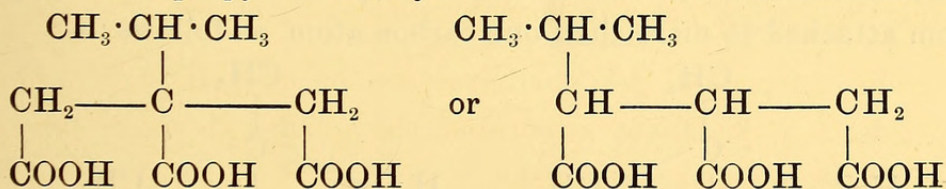
If the oxygen atom in eudesmol be depicted as quadrivalent, then by taking Brühl's formula for eucalyptol the following constitutional formulæ might be suggested, considering iso-propyl present as in cymene.



This would necessitate the arrangement of the fourth affinity of the carbon atoms of the nucleus on the centric formula.

As eudesmol on oxidation with nitric acid gives camphoronic acid as one of its oxidation products, we may perhaps derive some assistance by considering the probable formula for that acid.

Bredt¹ from investigation of its salts considered camphoronic acid to be isopropyltricarballic acid and to have the formula

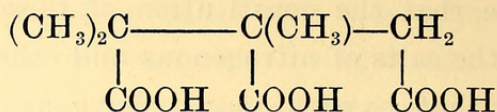


thinking the first of these the more probable.

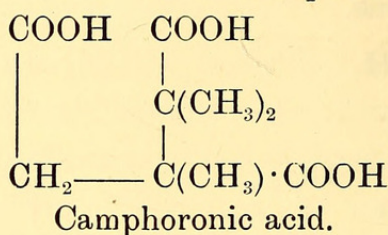
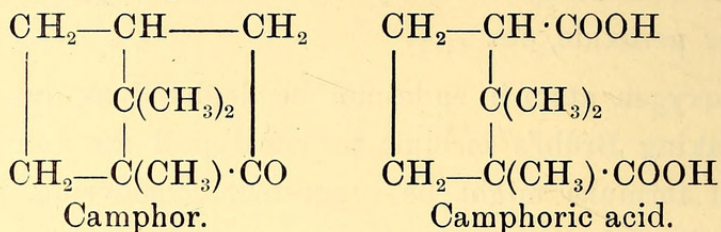
In an important paper on the synthesis of *i*-camphoronic acid by Perkin and Thorpe² it is shown that camphoronic acid has the constitution of a trimethyltricarballic acid of the formula

¹ Annalen, 1884, 226, 249 - 261.

² Journ. Chem. Soc., 1897, 1169.

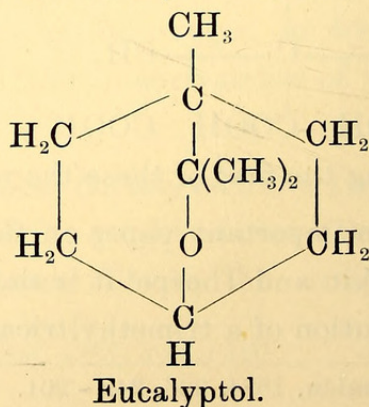
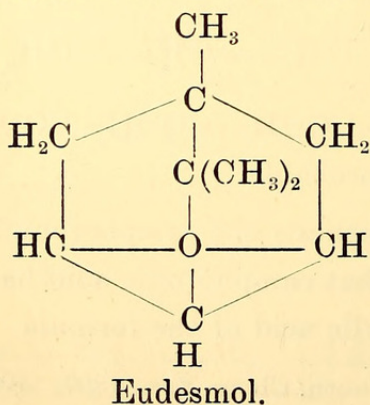


as was first suggested by Bredt¹ who represented camphor, camphoric acid and camphoronic acid as follows:—



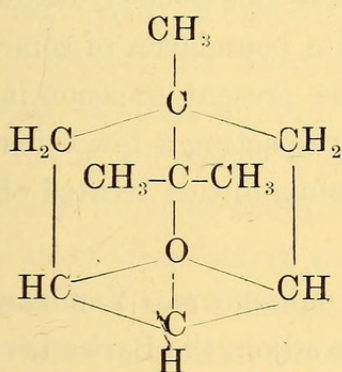
Eudesmol does not form the intermediate acid (camphoric acid) on oxidation with dilute nitric acid, but camphoronic acid, again indicating that the molecule of eudesmol differs from that of camphor. If we consider eudesmol to be in agreement with Brühl's formula for eucalyptol, the camphoronic acid derived from it would require to be depicted as isopropyltricarballic acid.

If we accept Bredt's formula for camphoronic acid to be trimethyltricarballic acid, and which formula is supported by the synthetical production of Perkin and Thorpe, then Brühl's formula for eucalyptol cannot be considered to be correct, and eudesmol will require to be constructed in a form corresponding somewhat with Bredt's formula for camphor, but with the oxygen atom attached to more than one carbon atom, as follows:—

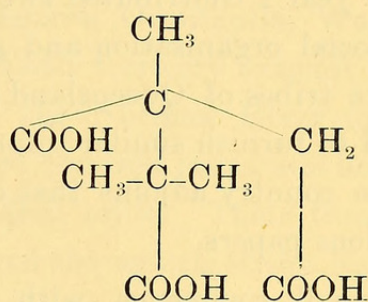


¹ Ber. 1893, xxvi., 3049.

The comparative ease with which oxidising agents act upon the eudesmol molecule, together with its instability, denote its susceptibility to attack, the tendency evidently being for the oxygen atom to become divalent, or in its most stable form. If we accept the possibility that the first action of the oxidising agent is to destroy the symmetry of the molecule by attacking it in its weakest point, the oxygen atom becoming attached to one of the three lower carbon atoms, then the chain would be broken and camphoronic acid as trimethyltricarballic acid could be constructed from eudesmol.



Eudesmol.



Camphoronic acid.



Smith, Henry George. 1899. "On the crystalline camphor of Eucalyptus oil (eudesmol), and the natural formation of eucalyptol." *Journal and proceedings of the Royal Society of New South Wales* 33, 86–107.

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