

ON A NEW AROMATIC ALDEHYDE OCCURRING IN
EUCALYPTUS OILS.

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IN a paper read before this Society in June of this year,¹ the announcement was made that the aldehyde occurring in Eucalyptus oils, and which for a long time had been supposed to be cuminaldehyde, was most probably not that substance, the reasons, then available for that conclusion, being given. I was induced to investigate this subject because it was found that this aldehyde occurs in a very large number of Eucalyptus oils in varying amounts, and is probably present in the majority of them.

In the oils obtained from the true "boxes," *Eucalyptus hemiphloia*, *E. albens*, *E. Woollsiana*, etc., this constituent occurs in greatest amount, and if we take *E. hemiphloia* as the extreme end of the list of those species in which this aldehyde occurs most plentifully, we can descend the scale through the "boxes" into the "gums," and so onward to those species the oils of which contain the greatest quantity of eucalyptol or cineol.

From the results of this research this appears to be quite feasible, as it is probable that the natural eucalyptol in Eucalyptus oils is derived directly or indirectly from this aldehyde, and we may assume that it will eventually be proven that the yellowish tint in Eucalyptus oils of the better class, or those richest in eucalyptol, is due to the original presence of this aldehyde, as the oils containing this aldehyde when rectified are all more or less yellow, and are generally not rich in eucalyptol. Oils very rich in phellandrene, such as *E. dives*, *E. radiata*, etc., do not appear to contain this aldehyde, it being replaced in those oils by the ketone of peppermint odour, consequently these oils are generally almost

¹ On the amyl ester of eudesmic acid occurring in Eucalyptus oils, p. 72.

colourless and often water-white, especially when rectified; they usually also contain very little eucalyptol.

Now oils rich in this aldehyde do not appear to contain phellandrene, as it is not found in the oils of the "boxes" above mentioned, but it does not follow that phellandrene is always absent in the oils of species which contain this aldehyde, in minute quantity, because in several both these constituents have been found together. Phellandrene is a most unsatisfactory constituent when only occurring in small quantity in the oil of any species of *Eucalyptus* at certain times of the year; as at other times of the year no phellandrene can be detected in the oil. It appears to be very unstable, and this fact must always be taken into consideration.

The oils from the "boxes" above named, although containing no phellandrene, and but little pinene, were all lævorotatory, showing that the rotation must be due to the presence of some substance having a high boiling point, and as the principal constituent in the higher fractions appeared to be this aldehyde, it was assumed that the rotation must be due to that substance, and this has been proved to be the case.

The optical rotations in a 100 mm. tube for the oil of *E. hemiphloia*, obtained in September, were as follows:—

Crude oil...	...	...	...	...	= -6·8°
Fraction boiling below 183° C....	...	...	...	...	= -3·2
Fraction 183 - 215° C. ...	...	...	...	...	= -10·3
Fraction 215 - 230° C. ...	...	...	...	...	= -25·0

The optical rotations in a 100 mm. tube for the oil of *E. albens*, obtained in June, were as follows:—

Crude oil...	...	...	...	...	= -6·5°
Fraction boiling below 183° C....	...	...	...	...	= -5·6
Fraction 183 - 225° C. ...	...	...	...	...	= -6·0
Fraction 225 - 255° C. ...	...	...	...	...	= -14·6

Corresponding results were also obtained from the oils of several other species.

The reason why the oil of *E. cnerifolia* of South Australia is lævorotatory is now explained, it is due to the presence of this

aldehyde. Messrs. Faulding and Co., of Adelaide, South Australia, kindly sent us a sample of the crude oil of this species from which the pure aldehyde was obtained. The optical rotations of this oil in a 100 mm. tube, were as follows:—

Crude oil...	...	...	...	...	= - 5·4°
Fraction boiling below 190° C....	...	...	...	...	= - 3·0
Fraction 190 – 220° C. ...	...	...	...	...	= - 5·35

I have seen an analysis of the oil of *E. cnerifolia*, by Mr. R. H. Davis, F.C.S., made several years ago, the most interesting point being where he states the deviation of the oil to be, in a 100 mm. tube, 3·53 degrees to the left.

There is a remarkable constancy (within certain limits) in the characters of the oils obtained from identical species of Eucalypts. We have numerous instances of this fact, one of which will now suffice, that of the “Mallee Box,” *E. Woollsiana*, the oil of which contains this aldehyde in fair quantity. This is a species growing in the western portion of this State, and has just been named and described by my colleague Mr. R. T. Baker, F.L.S.¹ In working out this species, four different quantities of material were obtained from various localities where it grows plentifully; the results from these were as follows:—

	No. 1.	No. 2.	No. 3.	No. 4.
Yield in percentage of oil on a commercial basis ...	0·493	0·4435	0·524	0·517
Rotation crude oil, 100 mm. tube ...	- 12·2	- 9·5	- 15·8	- 12·7
Specific gravity, at 15° C. ...	0·889	0·8917	0·8947	0·8977

These oils were all free from phellandrene, and the rotation shows them all to contain about the same amount of the aldehyde. Only a small quantity of eucalyptol was present in either sample. This constancy in constituents of the oils of the various species of Eucalypts can be taken advantage of, in obtaining those several constituents now known to occur in the oils of this remarkable group of trees.

¹ Proc. Linn. Soc. N. S. Wales., 1900.

So far as the Eucalypts of New South Wales are concerned, it is now fairly well known in which particular species any constituent occurs in greatest amount. This fact was taken advantage of in the preparation of this aldehyde. Our researches had shown that this aldehyde occurs probably in greatest amount in the oil obtained from *E. hemiphloia*. Our sample of *E. hemiphloia* had been obtained from Emu Plains. But as this species grows in abundance at Belmore, in the neighbourhood of Sydney, and this locality is easy of access, fresh material was obtained from there, with the result that the oil was found to be practically identical with that obtained a year previous from Emu Plains.

It is well known that the oil of *E. cneoroifolia* of South Australia is rich in eucalyptol. In the fraction of the oil of *E. hemiphloia* distilling below 183° C. (representing 73 per cent. of crude oil) 24 per cent. of eucalyptol was found, while the same fraction of the oil of *E. albens* contained 37 per cent. of eucalyptol. Our results indicate that in the majority of instances the maximum amount of eucalyptol in Eucalyptus oil is reached during the fall of the year and towards the winter months, but that as the spring advances and the trees become more vigorous in growth, the minimum amount of eucalyptol is present, while the yield of oil obtainable from the leaves is greater, the tendency being for the constituents to form eucalyptol as the year advances.

When the pure aldehyde was treated with an alkaline solution of potassium permanganate, oxidation took place rapidly with the generation of a considerable amount of heat. One of the products thus formed was apparently eucalyptol, and although (owing to want of sufficient material) it has not yet been isolated so that its physical characters might be determined, yet, from its characteristic odour and pungency I have no doubt but that eucalyptol is formed when the aldehyde is thus treated. Several determinations were made and always with the same result. When the oxidation was carried out with potassium bichromate in sulphuric acid, the acid formed was quite different from that obtained by potassium permanganate; eucalyptol was not formed by this

method, simple oxidation of the aldehyde group to carboxyl alone taking place, this was proved by the analysis of the silver salt of the acid. These results open up a very interesting line for research, and further investigations will eventually be undertaken on this subject.

In a paper¹ read before this Society, August 2nd, 1899, p. 90, it was shown that by natural oxidation of the oil of *E. eugenoides* eucalyptol had been formed. This interesting fact has also been noticed in the oil obtained from the "Red Box" of Rylstone, *E. ovalifolia*, an oil which contains this aldehyde, but in which phellandrene is also present. Eighteen months after distillation and analysis, having occasion to again investigate the sample, it was found that the oil had increased considerably in eucalyptol content, and that the rectified oil had reduced its rotation in 100 mm. tube -14.1° to -12° . As phellandrene was originally present in this oil, the laevorotation was of course partly due to that substance and partly to the presence of the aldehyde.

By acting upon an alcoholic solution of the aldehyde with sodium an odoriferous oil was obtained; this is probably the alcohol corresponding to the aldehyde. Subsequent investigation will prove whether it is that substance. The oil of *E. patentinervis* has already been shown to contain an aromatic alcohol (amyl ester of eudesmic acid, *loc. cit.*) which could not satisfactorily be located; the saponified oil had an odour identical with that of the oil obtained by reduction of the aldehyde, and it is thus probable that this alcohol occurs naturally in some Eucalyptus oils.

EXPERIMENTAL.

Preparation of the pure aldehyde.—1000 cc. of the crude oil of *Eucalyptus hemiphloia* obtained at Belmore, near Sydney, in September, was distilled. Constituents boiling below 190° C. were removed, the remainder was agitated with acid sodium sulphite and a crystalline mass thus obtained. After twenty-four hours this was purified by well washing with ether-alcohol, drying the

¹ On the crystalline camphor of Eucalyptus oil (eudesmol) and natural formation of eucalyptol (cineol).

crystalline mass on porous plate, and decomposing with sodium carbonate. The separated oil was well washed and then steam-distilled; 33 cc. of the aldehyde was thus obtained from a litre of crude oil, equal to 3.3 per cent. The aldehyde was slightly yellowish in tint, very mobile, and had a not unpleasant odour, being more aromatic than cuminaldehyde. It is soluble in the usual solvents for such substances.

Specific gravity of the aldehyde.—The aldehyde was carefully cooled to 15° C. in a pyknometer standardised at 15° C. The specific gravity was 0.9478. Another determination in a different pyknometer gave 0.9476, this was also cooled to 15° C., this gives a mean specific gravity of 0.9477 at 15° C.

Specific rotation of the aldehyde.—The rotation of the aldehyde in a 100 mm. tube at 22° C. was -46.6° , thus the specific rotation is $[\alpha]_D -49.19^\circ$.

Preparation of the oxime.—The aldehyde was dissolved in alcohol a saturated aqueous solution of hydroxylamine hydrochloride added, and then a solution of sodium carbonate. This was afterwards heated some time at about 80° C. and poured into water; the oily substance which separated soon crystallised in fine colourless crystals, showing faces having a fine lustre. The crystals were then drained on a porous plate, when they were obtained almost pure. The crystals were purified from alcohol until of constant melting point. The pure oxime melted at 84° C. When the base was separated with caustic potash instead of sodium carbonate, identical crystals were obtained, but the oily product was much darker and the yield of crystals was not so large.

This is the only aldehyde of this character occurring in this class of oils, as several of the higher boiling fractions from various oils were added together, including those of *E. cneoroifolia*, *E. albens*, and *E. Woollsiana*. The aldehyde was extracted with acid sodium sulphite in the usual way, purified, and the oxime formed; this oxime also melted at 84° C.

Preparation of the hydrazone.—The aldehyde reacts readily with phenylhydrazine. The hydrazone was prepared as follows: The aldehyde was dissolved in glacial acetic acid and phenylhydrazine added; the solution was then heated on the water bath with the addition of a little sodium acetate. On adding dilute acetic acid a copious yellow crystalline mass was obtained, this was well washed with acetic acid, dried on slab and purified several times from alcohol. The hydrazone melted quite sharply at 105°C . with decomposition. The determination of the melting point was best taken on cover-slip on the surface of mercury, the closed tube method not being so satisfactory.

Preparation of the naphthocinchoninic acid.—A solution of β -naphthylamine in absolute alcohol was added to a mixture of the aldehyde and pyruvic acid also dissolved in absolute alcohol, this was heated on the water bath with upright condenser. In less than fifteen minutes after the alcohol boiled, a yellow crystalline mass had formed, this was filtered off and washed with ether until quite pure. The alkyl- β -naphthocinchoninic acid thus formed was sulphur-yellow in colour, it melted sharply at 247°C . with decomposition. The formation of the product with this aldehyde is easy of accomplishment, the reaction taking place readily.

Boiling point of the aldehyde.—The boiling point of the aldehyde was 210°C ., it is doubtful if the aldehyde be at all decomposed at this temperature, but at an increased temperature sufficient to entirely volatilise it slight decomposition takes place; for this reason attempts to determine its vapour density were not satisfactory, concordant results not being obtained.

The aldehyde reduced an alkaline silver solution with the formation of a mirror, and it also answered to Schiff's reaction.

Analysis of the aldehyde.—The aldehyde on analysis gave the following results:—

0.1416 gave 0.4101 CO_2 and 0.1293 H_2O

$\text{C} = 79.03$; $\text{H} = 10.141$

0.1271 gave 0.3711 CO_2 and 0.1157 H_2O

$\text{C} = 79.62$; $\text{H} = 10.119$

From the mean of these results, or from either, we may consider the formula for the aldehyde to be $C_{10}H_{14}O$, especially as this formula was confirmed by analysis of the silver salt of the corresponding acid.

$C_{10}H_{14}O$ requires 80 C., and 9.33 H. per cent.

Oxidation of the aldehyde with potassium bichromate.—It was found that an alkaline solution of potassium permanganate acted very energetically on the aldehyde, so potassium bichromate in sulphuric acid was used instead; this substance acted much more slowly. By heating directly over a low flame using an upright condenser, or for some hours on the water-bath, a dark coloured cake eventually formed on the surface of the liquid, on cooling, this became quite brittle. The solid portion was collected, powdered, boiled in a dilute soda solution when the chromium salt was decomposed. The filtrate was acidified with hydrochloric acid, when a colourless acid was precipitated, this was well washed with water and purified from dilute alcohol from which it was obtained in interlaced crystals which gave the material a soft matted appearance. The purified substance melted sharply at $110^{\circ}C$.; on allowing the melted acid to cool, it crystallised in stout microscopic prisms which melted again at $110^{\circ}C$. The acid was soluble in boiling water, but little soluble in cold water, very soluble in alcohol and in ether, from which it crystallised well. The acid is saturated, as its aqueous solution did not bleach bromine water. The ammonium salt crystallised well, it formed a silver salt readily, also a light blue copper salt with copper sulphate; barium and calcium chlorides did not give precipitates. Ferric chloride gave no coloration in alcoholic solution. The formula for this acid is $C_{10}H_{14}O_2$ the aldehyde group alone being oxidised to carboxyl; this is shown by the determination of the silver salt. 0.1905 gramme of the silver salt gave 0.0755 gramme metallic silver, equal to 39.63 per cent. silver, $C_{10}H_{13}AgO_2$ contains 39.49 per cent. silver. The molecular weight of the silver salt = 272 giving a molecular value for the acid between 165 and 166. $C_{10}H_{14}O_2 = 166$. This is, therefore, the corresponding acid of the aldehyde, or aromadendric acid.

Oxidation of the aldehyde with potassium permanganate.—The aldehyde was readily and energetically attacked by an alkaline solution of potassium permanganate. The odour of the original aldehyde soon changed to one indicating somewhat that of cinnamon. This odour soon vanished and was eventually replaced by the characteristic odour of pure eucalyptol. The excess of permanganate was reduced, the clear filtrate acidified with hydrochloric acid and evaporated down to a small bulk; a white solid acid was thus obtained, this was filtered off, well washed, and purified from a boiling mixture of two parts alcohol and one part water; on boiling off the alcohol most of the acid precipitated, it being not readily soluble in boiling water. It was easily soluble in alcohol and in ether. This acid melted at $259-260^{\circ}\text{C}$. with formation of the anhydride. The acid readily sublimed on melting, forming a well crystallised sublimate which melted at 152°C . Both the acid and the anhydride are crystallised bodies before and also after melting. The anhydride readily sublimed, it being easily driven from one watch glass to another; it dissolved easily in a small quantity of boiling water, and crystallised out beautifully on cooling, it being practically insoluble in cold water; it was very soluble in alcohol and in ether. The original acid was apparently not regenerated by boiling the anhydride in water, as the separated crystals melted again at the same temperature as the sublimate. The anhydride commenced to sublime at about 135°C ., but if the heating was somewhat rapid it melted sharply at 152°C .

From the characters of the acid and its anhydride, formed by the oxidation of the aldehyde with potassium permanganate, and the formation at the same time of eucalyptol, it might be considered that the products were cineolic acid and its corresponding anhydride; but the melting points obtained do not agree with those given for cineolic acid and its anhydride, consequently further investigation of these oxidation products is required.

The name proposed for this aldehyde is *aromadendral*, utilising the name for the genus given by Dr. W. Anderson, the surgeon of Captain Cook's second and third expeditions. The correspond-

ing alcohol would then be *aromadendrol*. The acid obtained by oxidising the aldehyde group with potassium bichromate is thus *aromadendric acid*. It would have been preferable if the name eucalyptal could have been adopted, but there are already two substances that have been given the name eucalyptic acid, namely: that of L. Rummel for a substance obtained from the wood of *E. globulus* (art. *E. globulus*, *Eucalyptographia*), and that of H. Weber for one from the leaves of *E. globulus* (Wittstein's *Organic constituents*, p. 80). Utilisation of the most appropriate nomenclature is thus barred.

I wish to express my thanks to my colleague Mr. R. T. Baker, F.L.S., for botanical help in the preparation of this paper, and also for the material, which is thus of undoubted authenticity.



Smith, Henry George. 1900. "On a new aromatic aldehyde occurring in Eucalyptus oils." *Journal and proceedings of the Royal Society of New South Wales* 34, 286–295. <https://doi.org/10.5962/p.359350>.

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