

ON THE AMYL ESTER OF EUDESMIC ACID, OCCURRING IN  
EUCALYPTUS OILS.

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IN a paper by Mr. R. T. Baker and myself "On the Stringybark Trees of New South Wales," read before this Society, July 1898, we show that an ester must be present in the oil of *Eucalyptus macrorhyncha*. We had several times detected the presence of esters in other Eucalyptus oils but always in too minute quantities to allow them to be isolated with any success.

The investigation into the constituents of these oils, now being undertaken on material obtained from undoubted species, enables the statement to be made, that most probably esters are present in all Eucalyptus oils, and it is to be supposed, therefore, that to these the characteristic odour of Eucalyptus oil is largely due.

There is an organic connection between the constituents of the oils of the genus Eucalyptus, and it appears almost certain that most if not all of those constituents occurring in minute quantities in the oils of some species, are present in larger amount in the oils of other species. It is certainly so with the two pinenes present in these oils, with lævo-phellandrene,<sup>1</sup> with eudesmol, with (?) cuminaldehyde, with eucalyptol and with other constituents which have been isolated during this research; the chemistry of these, however, is not yet completed.

The ester that forms the subject of this paper has been detected in several oils in increasing amount. The oil of the "Black Gum"

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<sup>1</sup> Investigation of the oils of most of the New South Wales species of Eucalyptus points to the fact that dextro-phellandrene does not occur in these oils.

*Eucalyptus aggregata*, contains the ester in sufficient quantity to enable its constituents to be isolated and determined.

Unfortunately the yield of oil is small in those species of *Eucalyptus* giving this ester in largest amount. The leaves of the "Black Gum" *E. aggregata*, from which this oil was obtained, were sent by the Museum collector, Mr. Bäuerlen, in the month of October, from Fagan's Creek, near Braidwood, in this colony. Four hundred pounds of leaves were received, but the amount of oil obtained was only two and a half ounces, equal to 0.04 per cent. More material was not obtainable later, without great trouble and expense, as trees of this species do not occur within easy distance of Sydney. More leaves of the "Black Gum" will be obtained at the first opportunity and the chemistry of the acid completed, a research I would like to reserve to myself.

It is probable, however, that we may yet find other species of *Eucalyptus* containing this ester in fairly large quantities. The oils of *E. botryoides* and of *E. saligna* contain an ester in fair amount; it is present in the oil of *E. rostrata*, and in the oils of several other species its presence can be proved.

The determination of this ester explains much in reference to *Eucalyptus* oil that previously seemed obscure. It is most probable that the amyl alcohol of this ester is connected with the valeraldehyde known to be present in these oils, and it may, perhaps, be found eventually, that the (?) cuminaldehyde, existing in so many of these *Eucalyptus* oils, has some connection with the acid of the ester. In the oil of *E. rostrata* both the ester and (?) cuminaldehyde occur together. The presence of this aldehyde is much more frequent in these oils than was previously supposed.

[Since this paper was prepared I have been investigating the aromatic aldehyde found in many *Eucalyptus* oils. This constituent was previously supposed to be cuminaldehyde and its odour and reactions certainly suggested that substance; but further research points to the fact that it is not ordinary cuminaldehyde. When isolated in a pure condition its odour is more

aromatic than cuminaldehyde, and it differs from that aldehyde in having a somewhat high rotation to the left, a less specific gravity, a lower boiling point, and its oxime melts at a much higher temperature. It is now being further investigated.]<sup>1</sup>

It must not be thought that the odour of some *Eucalyptus* oils is entirely due to this ester. In the oil of *E. patentinervis* a very small quantity of an ester is present, but the odour of the saponified oil is excellent, resembling somewhat that of Bergamot oil, and there is little doubt but that either linaloöl or geraniol is present. Acetylation of the oil showed no less than 16.5 per cent. of free alcohol to be present in the oil of this species, calculated as linaloöl. A small quantity of citral was removed from the oil of this species (*E. patentinervis*) by acid sodium sulphite, and determined by the formation of the alcy- $\beta$ -naphthocinchonic acid characteristic of citral,<sup>2</sup> and it seems reasonable to suppose that this citral has some connection with the aromatic alcohol present in the oil of this species. The leaves have a lemon odour when crushed and are quite aromatic. It was previously supposed that botanically *E. patentinervis* was connected with *E. resinifera* but the chemical determination of the constituents of its oil shows it to have no immediate connection with that species, but to be allied to *E. botryoides* and perhaps more closely to *E. saligna*.

In the list of known constituents of the oil of *E. globulus*, published by Schimmel and Co., report April 1897, we find amyl alcohol mentioned, it may be considered that this amyl alcohol was originally derived from the ester now being described, and goes to show that even in an oil like that of *E. globulus* an ester is present at some time, although when distilled these oils usually consist largely of pinene and eucalyptol.

*The oil of Eucalyptus aggregata.*

The crude oil of the "Black Gum" *E. aggregata*, is very fluid, much like water in that respect, it is light orange-brown in colour

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<sup>1</sup> Added 25 July, 1900.

<sup>2</sup> There is no doubt but that citral does occur naturally in some *Eucalyptus* oils.

and the odour has but little resemblance to ordinary Eucalyptus oil. It has a high specific gravity for an Eucalyptus oil, and it was this peculiarity that first directed attention to it. On distillation under atmospheric pressure 26 per cent. was obtained, distilling between  $156^{\circ}$  and  $164^{\circ}$  C.,<sup>1</sup> this was principally dextropinene, proved by its boiling point, formation and character of its nitrosochloride, its odour and other tests; only 12 per cent. was obtained, distilling between  $164^{\circ}$  and  $245^{\circ}$  C. while 22 per cent. distilled between  $245^{\circ}$  and  $292^{\circ}$  C.; the remainder was poured from the still and became semi-crystalline on cooling. The portion adhering to the still was removed by ether. The crystalline residue was reserved for further determination.

The specific gravity of the crude oil at  $15^{\circ}$  C. was 0.956

„	„	fraction $156^{\circ} - 164^{\circ}$ C. at $15^{\circ}$ C.	= 0.866
„	„	„ $164^{\circ} - 245^{\circ}$ C.	„ = 0.8769
„	„	„ $245^{\circ} - 292^{\circ}$ C.	„ = 0.9868

Specific rotation, fraction  $156^{\circ} - 164^{\circ}$  C. =  $[\alpha]_D + 27.13^{\circ}$ .

Light did not pass with the crude oil.

Phellandrene could not be detected in this oil, and eucalyptol also appears to be quite absent. The principal constituents present are dextropinene and the ester, with perhaps some polymerised terpenes. A small quantity of a new constituent is also present, this has not yet been determined, but it has been isolated from the oils of several other species of Eucalyptus in some of which it occurs in fairly large quantities.

*Determination of Ester in the oil of E. aggregata.*

As it was evident that an acid had been separated at the high temperature used during the distillation, determinations of the ester in the original oil were made. The oil was boiled for half an hour with a known quantity of alcoholic potash, standardised by semi-normal sulphuric acid, a condenser being used in the ordinary way.

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<sup>1</sup> These temperatures have been corrected to the nearest whole degree.

- (1) 1.017 gramme oil required 0.1148 gramme potash, therefore saponification figure = 112.8.
- (2) 3.2378 gramme oil required 0.3612 gramme potash, saponification figure = 111.6.

The result of the analysis of the acid gave a molecular formula  $C_{14}H_{18}O_2$  as determined by its silver salt. Amyl alcohol is the alcohol of the ester, and considering the acid as monocarboxylic, the formula of the ester would be  $C_{13}H_{17}COOC_5H_{11}$  with a molecular value of 288, therefore the percentage of ester in the oil of *E. aggregata* is for No. 1 determination 58 per cent., for No. 2 equivalent to 57.4 per cent. or a mean value of 57.7 per cent.; this is assuming no other ester to be present in the oil.

*Determination of the alcohol of the ester.*

A portion of the oil of *E. aggregata* was boiled for some time with aqueous potash, a good reflux condenser being used. The solution was then distilled. The aqueous solution obtained was surmounted by an oily substance in which the odour of amyl alcohol could be detected. The aqueous solution, which gave the iodoform reaction, was separated from the oily portion and redistilled. Nothing was obtained boiling below  $100^{\circ}C$ .; the distillate contained a few oily globules; neither methyl nor ethyl alcohol was present. The distillate gave the iodoform reaction readily, and on boiling it with sulphuric acid and sodium acetate the solution had the characteristic odour of amyl acetate. The oily portion of the first distillate was redistilled, it commenced to distil at  $130^{\circ}C$ ., and the portion distilling between  $130^{\circ} - 135^{\circ}C$ . was collected; although masked somewhat by the presence of a portion of the other constituents of the oil it had the odour and gave the reactions for amyl alcohol. When oxidised with potassium bichromate and sulphuric acid, and treated in the usual way, the acid obtained had the characteristic odour and reactions of valeric acid. The alcohol of this ester is therefore amyl alcohol.

*Determination of the acid of the ester.*

The fraction obtained distilling between  $245^{\circ} - 292^{\circ}C$ . was agitated with aqueous potash, the alkaline solution was acidified

with hydrochloric acid, when a soft paraffin-like substance separated, this soon became crystalline. The separated oil, after agitating with the potash solution, was saponified with alcoholic potash in the usual way, water added and the aqueous solution acidified, more of the crystalline acid was thus obtained showing that some of the ester had distilled unchanged, it may be mechanically.

The residue left in the still above  $292^{\circ}$  C. was agitated with aqueous potash, and on acidifying the alkaline solution a fairly large quantity of the crystalline acid was obtained. On saponifying the portion insoluble in aqueous potash in the usual way and acidifying the solution, only a very small quantity of the crystalline acid was obtained, showing that the greater portion of the ester had been decomposed by the temperature at which the oil had been distilled. The crystalline substance thus obtained was the acid of the ester occurring in this oil, and on purifying each of the portions obtained as described above, an identical crystallised acid was obtained. No phenols could be detected.

The purification of the acid was carried out as follows:—The crystalline substance, obtained by acidifying the potash solution, was dissolved in alcohol and boiled with the addition of a little animal charcoal, filtered, and allowed to crystallise. The crystals were separated, dissolved in boiling water, and filtered boiling hot. On cooling the acid was deposited in crystals, recrystallisation from boiling water was repeated two or three times, a product of constant melting point was thus obtained. It is very necessary to obtain the crystals thus, as the impurities present cannot otherwise be removed, and these lower the melting point considerably. If purification be carried out as described above, the melting point of the crystals obtained in any direction will be constant. The same crystals were obtained when the original oil was saponified with alcoholic potash, and also when aqueous potash was used for determining the alcohol.

The acid is quite white and in general appearance is not much unlike salicylic acid, it crystallises in rhombic prisms and these

polarize brightly in colours. The melting point of the crystals is  $160^{\circ}$  C. (uncor.) and a crystalline mass is again formed on cooling. The melting point is that of the individual crystals adhering to the inner side of the tube, the melting point of the mass in the tube is not sharp, and an error of two degrees might easily occur. The acid is a very weak one, but it is exceeding soluble in ammonia and the alkalis. It is very sparingly soluble in cold water, easily soluble in hot water, in alcohol, in ether, in acetone and chloroform, but it is insoluble in benzene, in petroleum spirit (even on boiling) and in carbon bisulphide (slightly on boiling).

*Sublimation*—The acid sublimes with difficulty and at rather a high temperature, it sublimes unchanged.

*Ammonium salt*—The acid is exceedingly soluble in ammonia, the solution was evaporated to dryness over sulphuric acid, it crystallised very well, it is not readily soluble in cold water, but is so in hot water; it does not separate out again at once on cooling, thus differing from the acid itself.

*Ferric salt*—The aqueous solution of the ammonium salt was used, ferric chloride gives a light orange precipitate insoluble even in a large quantity of water.

*Copper salt*—Sulphate of copper gives a light bluish-green precipitate in the aqueous solution of the ammonium salt.

*Silver salt*—When nitrate of silver is added to the aqueous solution of the ammonium salt fine crystallisation of the silver salt soon takes place, the crystals are white but become pinkish on exposure to light.

Neither barium chloride nor calcium chloride gives a precipitate.

*Solubility of the acid in water at  $20^{\circ}$  C.*

The pure acid was dissolved in boiling distilled water, and when at the temperature given the crystals which had separated were removed by filtration; 25.48 grammes of the filtrate gave 0.0188 gramme solid, equivalent to 0.0738 per cent., or the acid required 1,355 parts of water at  $20^{\circ}$  C. to dissolve one part of acid.

*Determination of the Bromide.*

On adding bromide water to the aqueous solution of the acid it was at once bleached; the acid is, therefore unsaturated. The acid was dissolved in hot water and bromine added until in excess. The bromide was very soluble in hot water, on cooling and standing a crystalline mass was obtained, this was almost colourless, it melted at  $102^{\circ} - 103^{\circ} \text{ C}$ . The determination of this bromide was made by ignition with lime in the usual way. 0.1576 gramme bromide taken, total silver bromide obtained 0.1546 gramme or 0.0658 gramme bromine, equivalent to 41.75 per cent. bromine.  $\text{C}_{14}\text{H}_{18}\text{Br}_2\text{O}_2$  requires 42.6 per cent. bromine. This indicates a dibromide. The reactions showed the bromine to be present in the side chain.

*Molecular value of the acid.*

On adding silver nitrate to the cold aqueous solution of the acid no precipitate was obtained, the silver salt being soluble in dilute aqueous solution. The method adopted was to add a little water to some of the pure acid crystals, and then just sufficient ammonia to dissolve the acid. On adding two or three drops of silver nitrate solution a curdy precipitate formed at once, the solution was removed from this and silver nitrate added in excess; fine crystallisation rapidly took place, this was finally crystallised from water. The silver salt is exceedingly soluble in hot water and is fairly soluble in cold water. 0.0762 gramme of the silver salt gave 0.0258 gramme metallic silver on ignition, equivalent to 33.86 per cent.; the molecular weight of the acid from this determination is 212. 0.0204 gramme silver salt gave 0.0068 gramme silver, equivalent to 33.33 per cent., molecular weight of acid from this is 217.

An acid with a formula  $\text{C}_{14}\text{H}_{18}\text{O}_2$  has a molecular weight 218, and  $\text{C}_{13}\text{H}_{17}\text{COOAg}$  contains 33.23 per cent. silver.

*Action of Nitric Acid.*

On treating the acid crystals with nitric acid they at once dissolved with formation of a crimson colour, this soon changed to orange, on heating it became almost colourless. On adding

water, colourless crystals were obtained; these were little soluble in cold water but soluble in alcohol. It is doubtful if this was a nitro-compound. The crystals are microscopic needles, acid to litmus, and melted at  $113^{\circ}$  C.; on powdering the fused material it again melted at the same temperature. This is near the melting point of cumic acid, and if it be that acid, then ordinary oxidation of the side chain had taken place.

*Theoretical.*

As shown above, the molecular weight of the acid of the ester is near 215. The alcohol present is amyl-alcohol, so that the formula for this ester is  $C_{13}H_{17}COOC_5H_{11}$  assuming the acid to be monobasic. The only consideration is that of the structure of the acid. Eudesmic acid is unsaturated, taking up bromine to form a dibromide. It is not a member of the series of fatty acids, and its characters remove it from the acrylic series. Probably it belongs to the series of acids homologous with cinnamic acid. The formula for cumyl-angelic acid is  $C_{14}H_{18}O_2$  having a molecular weight of 218, this approaches very closely the molecular weight found for eudesmic acid. [An aldehyde resembling]<sup>1</sup> cuminaldehyde is frequently found occurring in Eucalyptus oils, and it may be that this has some connection with eudesmic acid. Perkin<sup>2</sup> describes a series of acids he had formed from cuminaldehyde. The cumyl or cumenylacrylic acid  $C_{12}H_{14}O_2$  thus obtained consisted of white needles melting at  $157^{\circ} - 158^{\circ}$  C., and giving reactions somewhat resembling those obtained from eudesmic acid. The results show some resemblance between the two acids, but there are many differences between them; the observed molecular weight might suggest cumyl-angelic acid as the more probable. The cumenyl-angelic acid formed by Perkin melted at  $123^{\circ}$  C.; probably the side chain in eudesmic acid constitutes an isomeric form of angelic acid, this may explain the differences in melting points. When the research on this acid is continued, Perkin's experiments will be repeated. The crystalline acid, obtained by the action of nitric acid, had the characters of cumic acid. If this is eventually

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<sup>1</sup> Added 25th July, 1900.    <sup>2</sup> Journ. Chem. Soc., xxxi, 388.

shown to be that acid then the side chain in eudesmic acid is in the para position relatively to the iso-propyl. This will be decided when more material has been obtained.

The name, eudesmic acid, is from Robert Brown's name for the genus "Eudesmia." L'Heritier's name "Eucalyptus," however, had priority.

I would like to express my thanks to my colleague Mr. R. T. Baker, F.L.S., for botanical assistance in the preparation of this paper, it being necessarily of the greatest importance that the material worked upon should be true to name.

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#### NOTE ON A NEW METEORITE FROM NEW SOUTH WALES.

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[With Plate I.]

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[Read before the Royal Society of N. S. Wales, June 6, 1900.]

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THE meteorite, the subject of this note, was found early in January of this year, about two miles from Bugaldi Post Office, fifteen miles north-west of Coonabarabran by Mr. W. Gould. I am indebted to Mr. Robert Wilcox, Postmaster of Bugaldi for the data in connection with the discovery of it. This gentleman obtained all particulars for me from Mr. Gould. and it was through his agency that it came into the possession of the Museum.

Mr. Wilcox writing me when despatching the specimen to Sydney, states:—"The stone or supposed meteorite was found showing on the surface of the ground. It was noticed by the ground being torn and broken on such a hard ridge. It had penetrated the ground and rose out. It was found about two



Smith, Henry George. 1900. "On the amyl ester of eudeamic acid, occurring in Eucalyptus oils." *Journal and proceedings of the Royal Society of New South Wales* 34, 72–81. <https://doi.org/10.5962/p.359335>.

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