

ON THE CONSTITUENT OF PEPPERMINT ODOUR OCCUR-  
RING IN MANY EUCALYPTUS OILS.—PART I.

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[Received and read before the Royal Society of N. S. Wales, October 3, 1900.]

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AMONG the Eucalypts of Australia there are many species known vernacularly as Peppermints, on account of the marked peppermint odour given by the leaves when crushed, or from the odour of the oil when distilled.

The first Eucalyptus oil was obtained from a New South Wales' species known as the Sydney Peppermint, *Eucalyptus piperita*, Sm., which species grows plentifully in the neighbourhood of Sydney. The following quotation is from page 227 of "White's Voyage to New South Wales," published 1790 :—"The name of Peppermint Tree has been given to this plant by Mr. White on account of the very great resemblance between the essential oil drawn from its leaves and that obtained from the peppermint, *Mentha piperita*, which grows in England. This oil was found by Mr. White to be much more efficacious in removing all cholicky complaints than that of the English peppermint, which he attributes to its being less pungent and more aromatic. A quart of the oil has been sent by him to Mr. Wilson."

Although the leaves of this species have a well marked peppermint odour, yet, the constituent giving this odour is only present in very small quantity in the oil ; this is also the case with many other species, the type *E. amygdalina*, for instance, which is also known in some localities as peppermint. From our experiments we find that this peppermint constituent occurs in greatest amount in the oil obtained from the leaves of *E. dives*, next in that of *E. radiata*, and in somewhat lesser amount from the leaves of



*E. Sieberiana*, and from *E. coriaceæ* and several others. If subsequent investigation should show this constituent to have special value for medicinal or other purposes, it can be obtained commercially from the leaves of both *E. dives* and *E. radiata*, so that the supply can be assured. In the oils of those species mentioned, this peppermint constituent occurs with phellandrene as the principal terpene, and in many of them with an almost entire absence of eucalyptol. Although occurring principally with phellandrene, yet, this terpene need not necessarily be present, as the peppermint constituent has been found occurring in the oil of at least one species in which phellandrene is quite absent; but generally, it may be stated as occurring in the oils of those species which are pronounced phellandrene bearing ones, and which make such a well defined group of *Eucalyptus* trees.

The yield of oil obtained, on a commercial scale, from the leaves and terminal branchlets of *E. dives* ranges from two to three per cent.; the oil is usually almost colourless, owing to the small quantity of free acid present. The crude oil has a low specific gravity 0.882 to 0.888 at 15° C., only a trace of Eucalyptol appears to be present at any time, but there is always much phellandrene. The optical rotation of the crude oil in a 100 mm. tube ranges from  $-55.7^{\circ}$  to  $-63.9^{\circ}$  the higher rotation occurring during the Australian spring months, the lower during the winter months.

On rectifying a sample of the oil of *E. dives* distilled in October, only two per cent. distilled below 172° C.; between 172° and 200° C.<sup>1</sup> 60 per cent. was obtained; between 200° and 227° C. 13 per cent. came over, and between 227° C. and 240° C. 20 per cent. distilled. The peppermint constituent occurs in greatest amount in the fraction 227° to 240° C., and it was thus possible to obtain it in a crude condition by ordinary distillation.

The specific gravity at 15° C. of the fraction 172° - 200° C. was 0.8593, of that obtained between 200° and 227° C. 0.8936, and of that between 227° and 240° C. 0.9318.

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



The optical rotation of the first fraction in a 100 mm. tube was  $-73.85^{\circ}$ , while that of the third fraction had been reduced to  $-9.4^{\circ}$ . A larger quantity of the oil (two litres) was then distilled when practically the same results and percentages were obtained.

The constituents in the fraction  $227^{\circ} - 240^{\circ}$  C. suffered slight decomposition when distilled under atmospheric pressure, as indicated by the odour and the darkening on keeping. When the oil was distilled under reduced pressure no decomposition took place. The oil when thus obtained under reduced pressure is of a slight yellowish colour, having a strong taste and odour of peppermint, and for commercial purposes might be used as thus obtained, or, the same result may be brought about by steam distillation of the fraction  $227^{\circ} - 240^{\circ}$  C. When placed upon the tongue it has a hot and penetrating effect, quickly diffusing a sense of warmth over the chest. When taken in small quantities it appears to act efficaciously in the early stages of a cold. Whether it has value in this or other directions is worthy of determination by the medical profession.

The peppermint constituent when obtained as pure as possible, possesses an odour of peppermint which is much more pronounced when diffused, but the peppermint taste is increased exceedingly, and it is also much more pungent than the oil of the fraction from which it was obtained. It is most probably, owing to the strong odour given by this constituent when diffused, that has caused the name "peppermint" to be attached to so many different species of *Eucalyptus*. The oil of many of these species, however, does not contain the constituent in sufficient quantities to enable it to be isolated, or even readily detected; and it is probable that many of the constituents found in larger amount in some *Eucalyptus* oils are also present in minute quantities in a great many others, their characteristic odour being more readily detected in the leaf than in the oil after extraction.

The only chemical references to this peppermint constituent, that I can find are in Messrs. Schimmel & Co's. semi-annual reports for April 1888, and April 1890, where referring to the



oil of *E. hæmastoma*, they say, that probably this contains menthone. There appears to be but one constituent in Eucalyptus oils having this peppermint odour. We have distilled the oil from the leaves of *E. hæmastoma* from two localities and failed to detect this peppermint constituent in the oil. This species grows plentifully in New South Wales, and is known as "White or Scribbly Gum." Mr. Smith, the author of this species, named *E. hæmastoma* in 1797, no doubt from trees growing at Sydney, in the neighbourhood of which it occurs plentifully, and as the characteristic constituents of identical species of Eucalyptus appear to be constant, there can be no doubt that the oil referred to by Schimmel & Co. was not obtained from *E. hæmastoma*, but from another species.

The question of constancy of chemical constituents in oils of the same species of Eucalypts will be fully discussed in the forthcoming work by Mr. R. T. Baker and myself.

Now that this peppermint constituent has been isolated it is found not to be menthone, as it has a much higher specific gravity, a higher boiling point, has probably no rotation, and the crystalline product obtained on reduction by sodium in alcoholic solution is not menthol, but quite a distinct substance and most probably new. Its taste and odour also differ from menthone. In boiling point and specific gravity it more closely resembles pulegone, but the same differences present themselves as with menthone. We are indebted to Messrs. Schimmel & Co. of Leipzig for samples of both menthone and pulegone, that firm having presented to the Technological Museum a very fine collection of the several constituents occurring in essential oils. It is probable that the peppermint constituent found in Eucalyptus oils is a new ketone, and in the second part of this paper I purpose dealing more fully with its chemical reactions and peculiarities.

#### EXPERIMENTAL.

##### *Purification of the constituent.*

The fraction 227° – 240° C. was frequently agitated for about three weeks with a saturated solution of sodium bisulphite, adding



a little alcohol. The combination did not readily take place. After some days a crystalline compound formed which continued to increase. On adding water the crystals dissolved, the unacted upon oil separating. The aqueous portion was removed and decomposed with caustic soda solution. An oil at once separated in good quantity showing that a compound had been formed. The separated oil was well washed and then steam distilled. As thus obtained it is almost colourless, and has an intense peppermint taste and peppermint odour; it is soluble in alcohol, ether, and ordinary solvents, and is slightly soluble in water.

*Optical rotation.*

The rotation in a 100 mm. tube was  $-0.35^{\circ}$ . It is probable that the constituent itself is inactive, and that the slight rotation was caused by the presence of a minute quantity of the aromatic aldehyde present in these oils, previously supposed to be cuminaldehyde; this itself is laevorotatory and would be extracted with sodium bisulphite together with the peppermint constituent, and be present in the final product. That a small quantity of an aldehyde is present is indicated by the slight pink colour obtained when tested by Schiff's reaction, but the quantity present can be but small as this aldehyde answers to Schiff's reaction readily, besides easily forming a crystalline oxime. It has not been possible so far to form a crystalline oxime with the peppermint constituent, it remaining persistently as a thick oil; when dissolved in alcohol it had no rotation.

The presence of a small quantity of this aldehyde in the oil of *E. dives* again illustrates the persistency with which minute quantities of the several constituents maintain their presence in these oils.

*Specific gravity.*

The specific gravity of the purified material was .9393 at  $\frac{17^{\circ}}{15^{\circ}}\text{C}$ .

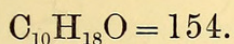
*Boiling point.*

The purified material boils at  $224 - 225^{\circ}\text{C}$ .



*Molecular value.*

1.1816 gramme in 27.3 grammes of glacial acetic acid gave a depression in the freezing point of 1.085 degrees; the molecular value from this is 155.

*The crystalline substance formed on reduction.*

On treating a solution in alcohol with metallic sodium, and afterwards adding water, the thick oily substance which separated was seen, after some time, to contain crystals. The aqueous portion was removed and the oily mass treated with slightly diluted alcohol in the cold. The crystals were but slightly acted upon and it was thus possible to remove the adhering oily impurities by dilute alcohol alone. That the crystals can be thus purified, was seen by the fact that as thus obtained, they melted at the correct temperature. The crystals are but slightly soluble in ether, so that they can be thus purified also. The crystals were found to be exceedingly soluble in chloroform from which on evaporation oblique needle crystals were obtained. The best method of purification was found to be to remove all adhering impurities by alcohol and ether, drying, and afterwards dissolving in chloroform, filtering, and allowing to crystallise. The crystals were colourless, they were slightly soluble in acetic ether, insoluble in acetone, and insoluble in alkalis.

The melting point was 155 - 156° C.; the substance did not decompose on melting, and on cooling crystallised very finely in long prisms of radiating crystals, which polarised exceedingly well. Its slight solubility in both alcohol and ether may be characteristic.

*Determination of the alcohol in fraction 227 - 240° C.*

An attempt to isolate an alcohol from this fraction with phthalic anhydride was not successful, no alcoholic substance being obtained. A portion of the oil of this fraction was then boiled for three hours with acetic anhydride and anhydrous sodium acetate, treating in the usual way and saponifying the product, 1.3236 grammes of the oil thus obtained was heated half an-hour with 10 cc.



alcoholic potash of known value, and titrated with semi-normal sulphuric acid, the saponification figure was 42.3 from which, taking the molecular weight of the ester as 196, we obtain 14.8 per cent. of ester or 12.0 per cent. of alcohol originally existing in this fraction, considering the molecular formula to be  $C_{10}H_{18}O$ . Only a very small quantity of ester is present originally in the crude oil of *E. dives*, so that an aromatic alcohol is shown to be present in small amount in this oil.

I wish to express my thanks to my colleague Mr. R. T. Baker, F.L.S., for botanical assistance in the preparation of this paper.

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ON AN EUCALYPTUS OIL CONTAINING 60 PER CENT. OF  
GERANYL ACETATE.

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[Read before the Royal Society of N. S. Wales, November 7, 1900.]

IN a paper by Mr. R. T. Baker and myself, "On the Darwinias of Port Jackson and their essential oils," read before this Society, December 6th, 1899, we showed that geraniol occurs in large quantities in the oil distilled from the leaves of *Darwinia fascicularis*; this alcohol can, therefore, be obtained in commercial quantities from plants belonging to the Myrtaceæ.

The indigenous flora of Australia is exceedingly rich in plants belonging to this natural order, and it is thus probable that we shall eventually find other plants belonging to the Myrtaceæ, besides *Darwinia fascicularis* and the present Eucalyptus, from which geraniol may be obtainable on a commercial scale.

During the research on the Eucalypts of New South Wales and their essential oils, now being undertaken at this Museum, the



Smith, Henry George. 1900. "On the constituent of peppermint odour occurring in many Eucalyptus oils, Part I." *Journal and proceedings of the Royal Society of New South Wales* 34, 136–142. <https://doi.org/10.5962/p.359342>.

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