L-PHELLANDRENE IN THE OIL OF MELALEUCA ACUMINATA. 159

## ON THE OCCURRENCE OF L-PHELLANDRENE IN THE OIL OF MELALEUCA ACUMINATA.

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[Read before the Royal Society of N. S. Wales, October 4, 1922.]

SHORTLY prior to my retirement from the Technological Museum there was received from Professor A. J. Perkins of the Agricultural Department of South Australia, a sample of the oil of *Melaleuca acuminata* for report, which had been distilled in Kangaroo Island, where this Melaleuca is known as "Lavender Bush."

There is a considerable industry carried on in Kangaroo Island in the distillation of Eucalyptus oil from leaves of *Eucalyptus cneorifolia* and *E. odorata*, and it was suggested that perhaps this Melaleuca might produce an oil of equal value.

As the chief terpene was found to be phellandrene it was thought desirable that permanent record should be made of the fact, particularly as this appears to be the first time that phellandrene has been found in the oils of species belonging to this genus.

In April, 1892, Messrs. Schimmel & Co. received from Messrs. Cumming & Co. of Adelaide, a sample of the oil of this species, and record (Semi-annual report, April) the specific gravity as 0.892, and rotation  $a_{\rm D} - 15^{\circ}$  2', also that it contained much cineol; but no attempt appears to have been made to identify the terpenes.

It will be observed how closely these constants agree with those now recorded, which again supports the conclusion of relative constancy of the oil products of individual species grown under natural conditions. The amount of oil obtained from one 400 gallon square iron tank was 17 pounds; the weight of material distilled was not stated, but was probably about 900 to 1000 pounds, giving a yield of about 1.7 to 2 per cent. The crude oil was almost colourless, very mobile, and contained a considerable amount of cineol. It had specific gravity at  $15^{\circ} = 0.8935$ ; rotation  $a_{\rm D} - 12.8^{\circ}$ ; refractive index at 20° = 1.4690; acid number 1.1; saponification number 4.5; saponification number of esterised oil 21.2. Cineol determined by the resorcinol method in the portion boiling below 190°, and calculated for the crude oil, was 43.7 per cent.

On rectifying under atmospheric pressure only a few drops distilled below 165° (uncor.); between  $165-170^{\circ}$  30 per cent. distilled; between  $170-190^{\circ}$  62 per cent. came over, and between  $190-220^{\circ}$  2.5 per cent. distilled. The first two fractions gave the following results:—

	Sp. gr. at 15°	Rot. a <sub>D</sub>	Ref. ind. at 20°
First fraction	0.8825	$-13.5^{\circ}$	1.4661
Second "	0.8922	$-13.2^{\circ}$	1.4685

The third fraction was added to the residue and the saponification number determined, this was 15.9, indicating the ester to be high boiling.

Terpenes.—It was found that the cineol phosphate compound could be separated from the terpene portion. The method adopted was to slowly treat the rectified oil in a beaker with phosphoric acid until judged to be in excess. The pasty mixture was then warmed until the greater portion of the cineol phosphate separated, the liquid portion poured off and the beaker containing it placed in ice water until the remaining cineol phosphate crystallised out. The remaining liquid was then well shaken with a 50 per cent. by weight aqueous solution of resorcinol, in order to remove any remaining cineol or alcoholic bodies that might be present; the terpenes were then well washed, dried and filtered.

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On rectifying the terpenes as thus prepared practically nothing distilled below  $166^{\circ}$  (uncor.). Between  $166-168^{\circ}$ 39 per cent. distilled; between  $168-172^{\circ}$  39 per cent. came over, leaving 22 per cent. boiling above  $172^{\circ}$ . The two fractions gave the following results:—

	Sp, gr. at 15°	Rot. $a_{\rm D}$	Ref. ind. at 20°
First fraction	0.8568	$-20.8^{\circ}$	1.4735
Second ,,	0.8542	$-21.2^{\circ}$	1.4794

Apparently a very small quantity of pinene was present in the first fraction, judging from the boiling point and physical constants; but the reaction for phellandrene was most distinctive. The nitrosite was prepared using sodium nitrite and acetic acid in the usual way, and when purified by dissolving in chloroform and precipitating with methyl alcohol, melted at 105-6°. It was dextrorotatory and 0.1552 gram. in 10 c.c. chloroform rotated the ray 1.0° to the left in a decimetre tube; the specific rotation was thus  $[a]_{\rm p}$  $+64.4^{\circ}$ .

It is thus evident that the principal terpene in the oil of Melaleuca acuminata is lævo-phellandrene, and judging from some of its reactions it is probable that when completely investigated this phellandrene will be found not to be identical in constitution with the l-phellandrene occuring in the oils of species belonging to the "Peppermint group" of Eucalypts. This matter is to receive further investigation.

The ester and free alcohol in the oil of this Melaleuca were but small in amount, as was also the sesquiterpene. The alcohol was high boiling and probably terpineol.

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