

Essential Oils from the Queensland Flora—Part X.—*Melaleuca linariifolia*.

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The essential oil of *Melaleuca linariifolia* has been investigated by Baker and Smith¹ and later by A. R. Penfold² to the latter of whom most of our knowledge of the constituents of this oil are due. As a result of Penfold's investigation with leaves collected near Sydney, the oil was found to contain as principal constituents α and γ terpinene, cymene, terpinenol —4, cineol, sesquiterpene, and sesquiterpene alcohol, and in view of the pleasant odour of the oil and its high germicidal value, it has become of economic importance. The tree also grows in Southern Queensland, notably near Logan Village, and several samples of oil obtained from this latter source have been examined by the author, confirming the results of Penfold, although there appeared to be little, if any, cineol in the oil.

Near Loganlea, however, a second variety of this tree was discovered, the leaves of which possessed a pronounced cineol odour on crushing and later samples of leaves were obtained from Maryborough which gave the same cineol odour.

After confirmation of botanical specimens by Mr. C. T. White, the oil appeared to be worthy of investigation and the results obtained form the subject of this communication.

It is noteworthy that the oil of this new variety bears no resemblance to that of the previously investigated variety, and contains as principal constituents cineol 61 per cent., with lesser quantities of pinene, dipentene, α terpineol, sesquiterpene, and sesquiterpene alcohol. The germicidal value is low and the oil is of little economic value.

EXPERIMENTAL.

Original samples of oil were obtained from the neighbourhood of Loganlea and were submitted as samples by commercial distillers, but the oil from Maryborough was distilled at the University, yield 1.5 per cent. The same results were obtained from both supplies of oil and those of the Maryborough oil only are given below:

The following constants were determined:—

$d_{15.5}$.9180
$[\alpha]_D$	+4.3
N_{20}^D	1.4650
Ester Value	19.6
Acetyl Value	49
Cineol Content	61.5 per cent. (Cockings method)

The oil 900 ccs. was washed with NaOH, which removed only a trace of phenolic body, giving a red-brown colour with ferric chloride and then submitted to fractional distillation at 4 mms. when the following fractions were obtained:—

	Volume.	Temp.	α_D	$d_{15.5}$	N_{20}^D
(1)	.. 665 ccs.	0– 50° C.	+ 2	.9076	1.4605
(2)	.. 48 ccs.	50– 55° C.	+ 2	.9080	1.4648
(3)	.. 100 ccs.	55– 77° C.	+ 14	.9372	1.4800
(4)	.. 45 ccs.	77–110° C.	+ 11	.9458	1.4870
(5)	.. 25 ccs.	110–140° C.	+ 3	.9515	1.4850

Fractions (1) and (2) which contained the bulk of the cineol (80 per cent. content) were extracted with 50 per cent. resorcin solution and the voluminous crystalline cake triturated with petrol ether (50°–60° b.p.). The petrol ether solution was further extracted with resorcin solution and finally dried and fractionated giving a terpene fraction 50 ccs. with the following constants:—

$d_{15.5}$.8546
$[\alpha]_D$	+ 7
N_{20}^D	1.4680

It was found (after further fractionation) to consist of a mixture of pinene and dipentene.

A small head fraction $d_{15.5}$.8596 $\alpha = +9$ gave a good yield of nitrosyl chloride, M.P. 103° C. and consisted largely of pinene, while the residue readily reacted with bromine in acetic acid solution, giving dipentene tetrabromide in excellent yield. The M.P. after crystallisation was 125° C., and no limonene appeared to be present. No other terpenes could be detected.

The solid cineol resorcin compound was decomposed by steam distillation and the cineol 500 ccs. recovered; the constants agreeing chiefly with those recorded for that substance. The o-cresol compound melted at 55° C.

Fraction (3) was further fractionated to remove cineol and the residue possessed the following constants:—

$d_{15.5}$.9389
$[\alpha]_D$	+16
N_{20}^D	1.4814

It was found an analysis to possess the molecular composition $C_{10}H_{18}O$, and in view of its sluggish reaction with sodium as distinct from the ready reaction with potassium judged to be a tertiary alcohol.

Identity with α terpineol was demonstrated by the preparation of the nitrosyl chloride M.P. 115°–116, the phenyl urethane M.P. 113° C. and the naphthyl urethane M.P. 146° C. These derivatives were carefully compared with those from terpinenol — 4 the characteristic alcohol present in the other variety of *Melaleuca linariifolia*, and with those from an authentic sample of α terpineol, but no evidence of the presence of any alcohol other than α terpineol could be obtained.

Fraction (4).—The usual tests for sesquiterpene (bromine vapour in acetic acid solution, &c.) were strongly positive for this fraction. It was repeatedly distilled over metallic potassium and the resultant product possessed the following constants:—

$d_{15.5}$.9359
$[\alpha]_D$	+ 11
N_{20}^D	1.4939

The molecular composition $C_{15}H_{24}$ revealed on analysis, confirmed the presence of sesquiterpene. No solid derivatives could be prepared and as no aromadendrone was obtained on ozonisation, aromadenrene appeared to be absent.

Fraction (5) was treated with metallic potassium until all reaction had ceased and the sesquiterpene removed by distillation at 4 mms. The alcohol recovered from the potassium salt (5 ccs.) possessed the following constants:—

$d_{15.5}$.9404
$[\alpha]_D$	+ 3
N_{20}^D	1.4895
b.p.	120–130°C (4 mms)

It was not further examined but the above results indicate a sesquiterpene alcohol.

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1. BAKER AND SMITH: Royal Society of N.S.W. Vol. XL. (1906), p. 65-69.
 2. A. R. PENFOLD: Royal Society of N.S.W. Vol. LIX. (1925), pp. 306-324.
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