

## Essential Oils from the Queensland Flora—Part XI. *Melaleuca viridiflora*, Part II.

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(App.).

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In a previous communication to the Society<sup>1</sup> it was stated that the essential oils of the broad leafed tea tree (*Melaleuca viridiflora*) were being examined and the existence of at least two varieties determined. The first variety already described was found to contain essentially linalol and nerolidol as principal constituents and to show certain resemblance with the essential oil of *M. Smithii*<sup>2</sup> with which there is some confusion of identity. It is noteworthy, however, that in the publication of Baker and Smith regarding *M. Smithii*, no record of the occurrence of linalol is mentioned and presumably this constituent was absent from the oils examined by them from materials obtained near Sydney in N.S.W.

The present communication deals with the essential oil from the more common cineol variety of the broad leafed *Melaleuca*. Other investigators<sup>3</sup> have examined this oil from time to time and various reports of its constituents have been published, particularly with reference to the cineol content, but examination of the result suggests that in most cases the leaves were mixtures and some of the constituents obtained by us were not recorded.

The oil to be described was all obtained from one tree, but similar results were obtained from other trees of the cineol variety, and there appears little doubt at present that there is a constancy of constituents with respect to that variety. Our samples were, however, all obtained from the neighbourhood of Brisbane and it is possible that examination of leaves from other centres may give different results.

The oil as examined by us was found to contain 45.6 per cent. of cineol (Cockings' method) together with d- $\alpha$ -pinene, l-limonene, dipentene,  $\alpha$ -terpineol, sesquiterpene, a crystalline alcohol apparently not previously described and traces of phenol. The crystalline alcohol isolated readily from the last distillation of oil appears to be distinct from eudesmol and to be related to the hydrocarbons of the blue azulene class. It readily loses water and the sesquiterpene obtained gives an azulene on dehydrogenation as well as a reduced hydrocarbon ( $C_{15}H_{26}$ ) but no trace of eudalene or of cadalene. The investigation of this alcohol and the accompanying sesquiterpenes of the oil is being actively pursued and will form the subject of another communication. In the meantime the name "viridiflorol" is tentatively proposed for this alcohol.

In view of the cineol content and the readiness with which its percentage can be increased by distillation the oil can be regarded as a commercial source of cineol.



## EXPERIMENTAL.

Three and a-half cwt. of leaves collected from one tree near Wynnum, Brisbane, were distilled and 2,040 ccs. of oil (1 per cent.) obtained. Towards the end of the distillation solid matter crystallised and was separated from the main oil supply.

The following constants were determined:—

$d_{15.5}$	..	..	.929
$N_{20}^D$	..	..	1.4759
$[\alpha]^D$	..	..	— 2.7
Ester Value	..	..	Nil
Acetyl Value	..	..	23
Cineol	..	..	45.6 per cent. (Cockings Method).

The oil was washed with (a) sodium carbonate and (b) sodium hydroxide solution. A trace of acid and  $\frac{1}{2}$  cc. phenol only were recovered from the alkaline liquors. The phenol gave a greenish colour with ferric chloride, but the small amount present precluded further examination.

As tests also revealed the absence of aldehydes the dried oil—1,420 ccs.—was submitted to fractional distillation under diminished pressure (3 mms.) and the following fractions collected:—

	Temp.	Volume.	$d_{15.5}$	$N_{20}^D$	$[\alpha]^D$
I. ..	0–30°C.	35 ccs.	.9003	1.4703	+ 7
II. ..	30–34°C.	130 ccs.	.9007	1.4652	+ 1.6
III. ..	34–36°C.	173 cc.	.9173	1.4653	— 1.2
IV. ..	36–66°C.	701 ccs.	.9178	1.4629	— 5.6
V. ..	66–68°C.	98 ccs.	.9379	1.4828	— 5.5
VI. ..	68–74°C.	34 ccs.	.9387	1.4850	— 4.5
VII. ..	74–88°C.	86 ccs.	.9348	1.4953	+ 10
VIII. ..	88–110°C.	5 ccs.	not taken	1.4985	not taken
IX. ..	110–114°C.	78 ccs.	.9472	1.4985	+ 19
X. ..	114–116°C.	42 ccs.	.9765	1.4990	0
XI. ..	Residue	12 ccs.			

As the earlier fractions 1-4 were rich in cineol they were washed with 50 per cent. resorcin solution and extraction of the terpene from the resulting solid cakes by petrol ether (b.p. below 60°C.) resorted to. The petrol ether solutions were repeatedly washed with resorcin solution until free from cineol. Considerable difficulty was experienced in removing the large amount of cineol in fraction 4. The cineol 400-500 ccs. was recovered from the resorcin compound and identified in the usual way.

The terpenes after removal of cineol were further fractionated and fractions possessing the following constants ultimately obtained:—

(a)	$d_{15.5}$	.8735
	$N_{20}^D$	1.4700
	$[\alpha]^D$	+ 7
(b)	$d_{15.5}$	.8590
	$N_{20}^D$	1.4720
	$[\alpha]^D$	— 38

The fraction (a) consisted largely of  $\alpha$ -pinene.

The nitrosyl chloride prepared in the usual way melted at 108°C.



Fraction (b) gave a crystalline tetrabromide.

Fractional crystallisation gave—

dipentene tetrabromide M.P. 125°C.  
and 1-limonene tetrabromide M.P. 105°C.

*Fractions 5 and 6.*—Further fractionation to remove dipentene and 1-limonene gave ultimately a pleasant smelling oil with the following constants:—

$d_{15.5}^D$	.9394
$N_{20}^D$	1.4841
$[\alpha]_D$	— 6

Identity with  $\alpha$  terpineol was established by formation of the nitrosyl chloride M.P. 112°C. and the naphthyl urethane M.P. 144.5°C.

*Fractions 7 and 8*, which gave strong colour tests for sesquiterpene with bromine acetic acid, were further fractionated and finally distilled over potassium.

The following constants were then recorded:—

$d_{15.5}^D$	.9268
$N_{20}^D$	1.4990
$[\alpha]_D$	+ 23.5
b.p.	95°–97°C. 2 mms.

Dehydrogenation with selenium gave a blue azulene hydrocarbon (M.P. of Picate 118°C.) and at the same time a hydrocarbon possessing the following constants:—

$d_{15.5}^D$	.916
$N_{20}^D$	1.4930
$[\alpha]_D$	0

Combustion results [C = 87.1 H = 12.1 per cent.] indicated  $C_{15}H_{26}$  and it appeared obvious that some hydrogenation of sesquiterpene had accompanied the dehydrogenation to azulene. The reducing action of hydrogen selenide in the dehydrogenation of sesquiterpenes has been noticed by other workers and reviewed in the Annual Reports of the Chemical Society, 1936.

No trace of eudalene could be observed and it was concluded that eudesmene was not present.

Ozonisation gave a small yield only of aromadendrone (M.P. of oxime 103°C.) and this sesquiterpene is therefore not the main constituent of the fraction.

Investigation of the sesquiterpene fraction is being actively pursued, but as no solid derivatives have been obtained, and as there is evident relationship to the azulene class of hydrocarbon, it is clear that some more accurate knowledge of the constitution of azulene is a preliminary requisite.

*Viridiflorol.*—In the original steam distillation of the leaves crystalline material was obtained towards the end of the distillation and similarly the last higher boiling fractions of the oil solidified. The solid buttery material was collected, and spread on a porous plate to remove adhering oil and then repeatedly crystallised from methyl alcohol in which and other organic solvents it is rather soluble. It was eventually obtained as a white crystalline mass. M.P. 71°C.



It was at first thought that it was impure eudesmol, but the subsequent examination of the material indicated that it could not be identical with that substance.

The optical rotation in chloroform solution was  $+5.4$  (eudesmol  $+33$ ).

Treatment with formic acid on the water bath for half an hour gave a sesquiterpene with the following constants:—

$d_{15.5}$	.9217
$N_{20}^D$	1.4972
$[\alpha]_D$	$+9$

A deep blue colour reaction was given in acetic acid with bromine vapour.

The alcohol itself under similar conditions developed only a purple colour after some time.

Attempts to prepare the acetate by heating with acetic anhydride were unsuccessful, dehydration taking place. The resulting liquid possessed the following constants:—

$d_{15.5}$	.9315
$N_{20}^D$	1.4978
$[\alpha]_D$	$+32.2$

Combustion results were only approximate for  $C_{15}H_{24}$  and as the liquid possessed a small ester value, it appeared to be a mixture of sesquiterpene with a small amount of acetate. Its density was somewhat higher than that of the sesquiterpene obtained by the formic acid treatment and presumably indicated some admixture with the acetate. Dehydrogenation of the sesquiterpenes obtained by the formic acid and acetic anhydride treatments was accomplished by heating with selenium at  $280^\circ C$ .

In both cases an azulene (M.P. of Picrate  $118^\circ C$ .) was obtained together with a colourless liquid of molecular formula  $C_{15}H_{26}$ . The constants in the case of the hydrocarbons obtained in this way from the sesquiterpene derived by the formic acid treatment were as follows:—

$d_{15.5}$	.9016
$N_{20}^D$	1.4929
$[\alpha]_D$	$-5$
b.p.	$135^\circ C$ . 20 mms.

These results clearly indicate an alcohol apparently corresponding to a hydrocarbon of the azulene class, regarding which no precise constitutional knowledge is at present available, although formulae for azulene have been tentatively suggested.

It is hoped to investigate the constitution of this interesting alcohol and the accompanying sesquiterpenes further.

Our thanks are due to Mr. C. T. White, Government Botanist, for his usual generous assistance in connection with botanical problems. It should be stated that we have adopted the name *Melaleuca viridiflora* in this and the previous paper on his advice.

#### REFERENCES.

- <sup>1</sup> Jones and Haenke. Proc. Roy. Soc. Q., 1936, 41-44.
- <sup>2</sup> Baker and Smith. Proc. Roy. Soc. N.S.W., 1913, 205.
- <sup>3</sup> Cowley. Chem. and Drug., 1910, 76, 832.





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