

## Essential Oils from the Queensland Flora, Part IX.—*Melaleuca viridiflora*, Part I.

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Investigations of the essential oil from the broad leafed tea tree, which is a very common tree in Eastern Australia, have been carried out by several workers, and the main constituents of the oils examined by them placed on record.<sup>1</sup> Botanical investigation has likewise proceeded and the tree is referred to in this paper as *Melaleuca viridiflora*, although other names, such as *Melaleuca Leucadendron* (var. *lancifolia*) and *Melaleuca Maidenii* have from time to time figured in the literature. Owing to the reported high cineol content of the oil, it has never been of economic value, but in view of several inconsistencies which appeared in the results of various workers, it appeared desirable to make a new and systematic investigation of the whole problem of the essential oils. In this work the authors have had the co-operation of the Forestry Department, which supplied many of the consignments of leaves and assisted the investigation as far as possible. It soon became apparent that at least two varieties of *Melaleuca viridiflora* existed, one in which cineol was the principal constituent, but the other contained no cineol, and trees of this type were readily differentiated from the cineol variety by the marked difference of odour of the crushed leaves. This particular variety was first located from a consignment of leaves from the neighbourhood of Maryborough, and fortunately the leaves were collected from two trees only which were kept separate until their identity was established. Trees of this same type were subsequently discovered in close proximity to Brisbane and, while a complete survey of the Brisbane area has not yet been carried out, it would appear that its distribution is considerably less than that of the cineol variety, although the two varieties grow together.

The investigation of the oil from this variety has been completed and forms the subject of this paper. It is intended to submit the results obtained from the examination of the cineol and possibly other varieties at a later date.

The oil described in this paper has been found to consist almost exclusively of the two alcohols linalol and nerolidol with a little sesquiterpene, citral and traces of a phenol. As the alcohols can be readily separated from one another and appear uncontaminated with other substances, the oil may be regarded as a convenient source of these alcohols, and in view of the linalol content (at least 50 per cent.) is of undoubted economic value.

It appears likely that the oils examined by previous workers were mixtures of the two varieties mentioned above, as indiscriminate picking of leaves was no doubt indulged in by collectors.

### EXPERIMENTAL.

One and a-quarter cwt. of leaves collected at Antigua (near Maryborough) on 18th June, 1935, gave 700 ccs. of oil, while 200 lb. collected near Brisbane gave 1,000 ccs. of oil, the yield being in each case

approximately 1 per cent. In the case of the Maryborough consignment the leaves were from two trees only and kept separate till their identity was established, while with the Brisbane leaves, careful selection of trees was resorted to in order to obtain samples from the same variety.

The following constants were recorded:—

|                                | Maryborough Sample. |    |    | Brisbane Sample. |    |         |
|--------------------------------|---------------------|----|----|------------------|----|---------|
| $d_{15.5}$                     | ..                  | .. | .. | .8764            | .. | .880    |
| $N_{20}^D$                     | ..                  | .. | .. | 1.4700           | .. | 1.4719  |
| $[\alpha]_D$                   | ..                  | .. | .. | + 15.5           | .. | + 14.26 |
| Ester Value                    | ..                  | .. |    | Nil              | .. | Nil     |
| Acetyl Value                   | ..                  | .. |    | 146.2            | .. | 150     |
| $[\alpha]_D$ after acetylation |                     |    |    | — 2              | .. | — 2     |

Both oils possessed a pleasant rose-like odour due to the presence of linalol.

The oils were washed with dilute  $\text{Na}_2\text{CO}_3$ , and then dilute  $\text{NaOH}$  solutions. The  $\text{NaOH}$  washing gave in each case about  $\frac{1}{2}$  ccs. of dark-coloured oil smelling of eugenol. The colour reaction with ferric chloride solution was reddish-brown (eugenol gives a green). Tests for  $\beta$  diketones were negative. A small quantity of crude benzoyl derivative was obtained, but it could not be sufficiently purified for identification.

The oil 790 ccs. (Brisbane sample only described as the Maryborough oil gave similar results) was next submitted to fractional distillation under diminished pressure 4 mm. and the following fractions collected:—

|                  | Temp.         | Vol.     | $d_{15.5}$ | $N_{20}^D$ | $\alpha_D$ |
|------------------|---------------|----------|------------|------------|------------|
| I.               | .. 0–59°C.    | 18 ccs.  | .884       | 1.4654     | + 9.39     |
| II.              | .. 59–62°C.   | 355 ccs. | .868       | 1.4607     | + 16.70    |
| III.             | .. 68–118°C.  | 20 ccs.  | .900       | 1.4780     | + 5.29     |
| IV.              | .. 118–121°C. | 370 ccs. | .884       | 1.4785     | + 11.54    |
| Resinous Residue |               | 25 ccs.  |            |            |            |

Repeated refractionation ultimately resolved the various fractions into two main fractions (b) and (d) with a small head fraction (a) and a sesquiterpene fraction (c).

The small head fraction (a) 10 ccs. possessed the following constants:—

|            |        |
|------------|--------|
| $d_{15.5}$ | .8858  |
| $N_{20}^D$ | 1.4660 |
| $\alpha =$ | + 6.65 |
| b.p. app.  | 186°C. |

Examination revealed the presence of linalol (as would be expected in view of fraction (b), which required, therefore, that some constituent of density higher than .8858 should be present. Cineol was naturally suspected under these circumstances, but only negative tests were obtained and similarly tests for pinene and other terpenes were negative.

It appears certain however by analogy with other oils containing linalol that some linalol monoxide ( $d_{15.5}$  .9520) would be present.<sup>2</sup> Aerial oxidation of linalol while still in the tree is stated to give rise to small amounts of linalol monoxide. In all probability fraction (a)

consisted of linalol with some contamination with monoxide sufficient to raise the density to that indicated.

Fraction (b) consisted essentially of linalol. The following constants were determined:—

|              |              |
|--------------|--------------|
| $d_{15.5}$   | ·868         |
| $N_{20}^D$   | 1.4607       |
| $[\alpha]_D$ | + 18.5       |
| b.p.         | 60°C. 4 mms. |

The fraction was submitted to critical examination in the following experiments:—

*Primary alcohols.*—Extraction with phthalic anhydride in benzene solution gave no indication of primary alcohols.

*Terpenes.*—Purification of the linalol was accomplished by the formation of sodium linalol; the non-alcoholic portion being then removed by vacuum distillation. Dihydromyrcene (a by-product of the action of sodium on linalol) was identified by means of its tetra bromide M.P. 88°C. The constants for this dihydromyrcene were as follows:—

|            |        |
|------------|--------|
| $d_{15.5}$ | ·783   |
| $N_{20}^D$ | 1.4523 |

indicating that it was almost pure and that there could not be any appreciable quantities of non-alcoholic bodies in fraction (b). Linalol purified from its sodium compound possessed the following constants:—

|              |        |
|--------------|--------|
| $d_{15.5}$   | ·869   |
| $N_{20}^D$   | 1.4618 |
| $[\alpha]_D$ | + 18.5 |

which do not differ markedly from those of the original fraction.

*Identification of Linalol.*—The phenyl and naphthyl urethanes (M.P's 66°, 54°C.) were prepared and oxidation with dichromate gave good yields of citral. M.P. of semicarbazone 164°C. *Acetylation.* The acetylation of the fraction gave geranyl acetate as main product while the rotation became slightly negative in accordance with the well-known behaviour of linalol in this reaction.

*Acetic Acid Benzidine Test.*—The main linalol fraction gave a pronounced test with acetic acid benzidine solution, indicating the presence of an aldehyde. This test was also readily given by a sample of commercial linalol, but not with linalol prepared from sodium linalol. Extraction with semicarbazide acetate solution gave on isolation about  $\frac{1}{2}$  per cent. of aldehyde material which gave a pronounced benzidine test similar to that of citral (which substance is a normal oxidation product of linalol). It appears therefore that the linalol is contaminated with small amounts of citral insufficient for isolation.

*Fraction (c).*—20 ccs. of this fraction were available. The following constants were determined:—

|              |                  |
|--------------|------------------|
| $d_{15.5}$   | ·900             |
| $N_{20}^D$   | 1.4780           |
| $[\alpha]_D$ | + 5.29           |
| b.p.         | 68–118°C. 4 mms. |

The bromine-acetic acid test for sesquiterpene was strongly positive. The usual method of removing alcohols from sesquiterpene fractions,

that is distillation over sodium, could not be used in this instance owing to the production of hydrocarbons from linalol and nerolidol (fraction *d*) by the action of sodium.

No solid derivatives could be obtained, and the fraction apparently consisted of some sesquiterpene in admixture with linalol and nerolidol.

*Fraction (d).*—360 ccs. possessed the following constants:—

|              |        |
|--------------|--------|
| $d_{15.5}$   | ·8836  |
| $N_{20}^D$   | 1·4782 |
| $[\alpha]_D$ | + 1·5  |

Identification of this fraction with nerolidol (melaleucol) has already been described in this Journal.<sup>3</sup>

Purification of nerolidol by the sodium method (as described above for linalol) gave as by-product a hydrocarbon with the following constants:—

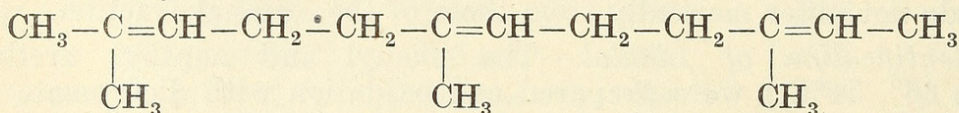
|              |        |
|--------------|--------|
| $d_{15.5}$   | ·8335  |
| $N_{20}^D$   | 1·4700 |
| $[\alpha]_D$ | 0      |

[Found C = 87·4 H = 12·6  $C_{15}H_{26}$  requires C = 87·3 H = 12·6.]

This hydrocarbon gave a characteristic solid bromide M.P. 131°C. by addition of bromide.

The percentage of bromide was 69·5 per cent. and evidently corresponded with a hexa bromide [Br. = 69·9].

Although this hydrocarbon does not appear to have been previously described, its constitution by analogy with dihydromyrcene and linalol is that of dihydrofarnesene.



This hydrocarbon was subsequently prepared by reduction of farnesene (from nerolidol via farnesol) with sodium and alcohol, and the same hexabromide prepared, M.P. 131°C., alone or in admixture with the abovementioned sample.

Our thanks are due to Mr. C. T. White, Government Botanist, for critical examination of the leaves submitted as samples.

<sup>1</sup> The Essential Oils (Finnemore) 556, 557.

<sup>2</sup> Schimmel & Co. Reports 1912. October, 80.

<sup>3</sup> Jones and Harvey. R.S.Q. 1936 2-3.



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