

ON THE AUSTRALIAN MELALEUCAS AND THEIR ESSENTIAL OILS, PART VI.

By R. T. BAKER and H. G. SMITH.

With Plate I.

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Introduction.

The two species upon which this paper is founded are *Melaleuca ericifolia*, Sm. and *M. Deanei*, F.v.M., both being found in Eastern Australia.

1. MELALEUCA ERICIFOLIA, Sm.

Botany.

This species was one of the first recorded from Australia being described by Dr. Smith in the Transactions of the Linnean Society, iii, 276, 1797, and a figure of it is given in Exot. Bot. t. 34. The diagnosis of this plant in Bentham's Flora Australiensis, Vol. III, p. 159, agrees very well with the botanical material upon which this paper is based, so that no description is here necessary. Bentham mentions a varietal form, viz.:—*erubescens*.

The chemical results, however, were not obtained from this red flowered form, but the plant with white flowers.

Geographical Distribution.

It is one of the widest distributed species of the genus, as Bailey records it from Queensland in his Flora of that State; Mueller for South Australia in his Second Census, whilst Robert Brown, Mueller and J. D. Hooker record it for New South Wales, Victoria and Tasmania respectively.

Chemistry of Essential Oil.

An essential oil was first distilled from the leaves and terminal branchlets of this Australian species of *Melaleuca* by Mr. J. Bosisto, (Proc. Roy. Soc. Victoria, July 1862).

Considerable investigation was undertaken about that time concerning some of the properties of this oil, such as its solvent action on resins, and for burning in lamps, (The Technologist 3, 1863, p. 17). Mr. Bosisto states that from 100 lbs of leaves and branchlets he obtained 5 ounces of a very limpid and almost colourless oil, partaking much of "cajuput" flavour; that with age it improved greatly giving more the aroma of the flowers. The specific gravity of this sample is recorded by him as 0.899.

In a paper on Essential Oils by Dr. J. H. Gladstone, (Journ. Chem. Soc., 17, 1864, p. 1) the constants for the oil of this *Melaleuca* are given. The specimen had been forwarded to London for display in the Exhibition of 1862, and with others was handed to Dr. Gladstone for investigation. The specific gravity recorded by him was 0.903 at 15.5° C.; refractive index $n_D = 1.4712$; and rotation in a tube 10 inches long +26°—or corrected for 1 decimetre tube +10.23°.

Beyond the additional statement that the oil of *Melaleuca ericifolia* bears a striking resemblance to the "cajuput" of commerce, obtained from *Melaleuca leucadendron* of the Moluccas,¹ (The Technologist *loc. cit.*); and the remark by Dr. Gladstone, (Journ. Chem. Soc. 25, 1872, p. 1), "that the same oxidised compound as occurs in oil of "Cajuput" was evidently the principal constituent in the oil derived from *Melaleuca ericifolia*," nothing further appears to have been known as to the chemical properties of the oil of this Australian species.

It was thought desirable, therefore, that an investigation should be undertaken, so that the chemical composition and economic possibilities of the oil of this species of *Melaleuca* might be determined.

¹ Evidently *Melaleuca minor*, Sm. See Part V of this series of papers. This Journal 1913.

The knowledge concerning the chemical composition of oil of "cajuput" is now somewhat complete, and during recent years chemists have devoted considerable effort towards the elucidation of this problem. This question is more fully considered in Part V of this series of papers on the Australian Melaleucas and their oils, and an analysis given of a sample of oil of "cajuput," sent to us by Dr. M. Treub of the Royal Botanic Gardens, Buitenzorg, Java, (This Journal, 1913).

The elementary composition of the principal constituent in "cajuput" oil of commerce was correctly recorded as $C_{10}H_{18}O$ by Blanchet as early as 1833 (Annalen 7, p. 161). It was named cajuputene hydrate by Schmidl (Journ. Chem. Soc. 14, 1862, p. 63). Dr. Gladstone named it cajuputol (Journ. Chem. Soc. 25, 1872, p. 1). Its identity with cineol was shown by Wallach, (Ann. 225, 1884, p. 315).

"Cajuput" of commerce is essentially a heavy oil, the specific gravity mostly ranging between 0.92 and 0.93; it is usually slightly lævorotatory, and contains an excess of 50 per cent. of cineol when determined by the phosphoric acid method. In addition to the cineol the aromatic alcohol terpineol is present in small amount, while the terpene pinene appears to be the lævorotatory form.

Although the oil of *Melaleuca ericifolia* contains both cineol and terpineol—the latter in the dextrorotatory form, yet, it can replace in no way the "cajuput" oil of commerce for pharmaceutical purposes, as the amount of cineol in the crude oil is less than 10 per cent., and the excess of terpenes, consisting of dextrorotatory pinene and dextrorotatory limonene, causes the specific gravity to be far too low for it to conform to official requirements for "cajuput." The somewhat large amount of terpineol which it contains gives to it a much more aromatic odour than possesses that of "cajuput," and in consequence it may be considered more

suitable for perfumery purposes than for medicine. Unfortunately the yield of oil is somewhat small, and the minute leaves, peculiar to the species, is also a character detrimental to profitable distillation. Another feature which may also militate against its industrial employment is the fact that commercially prepared terpineol can now be purchased at a comparatively cheap rate.

Summarising the results here recorded it may be stated that the oil of *Melaleuca ericifolia* differs from the oil of "cajuput" in the following directions:—

- (a) by having a much lower specific gravity.
- (b) by the terpenes being strongly dextrorotatory.
- (c) by containing dextrorotatory terpineol in some quantity.
- (d) by containing considerably less cineol, and
- (e) by the chief oxygenated constituent being terpineol and not cineol.

Experimental.

The material for this investigation was collected at Kogarah, near Sydney, New South Wales, in February, 1916, and was from the white flowering form of this species. The yield of oil from the fresh leaves and terminal branchlets was 41 ounces from 306 lbs. of material, equal to 0·84 per cent. The crude oil was of a very light-amber colour, and had an odour with some resemblance to that of "cajuput," although more aromatic, a character due to the presence of the terpineol. This constituent being present in some quantity causes the oil to be less mobile than are, for instance, the majority of the cineol bearing oils of the Eucalypts.

The following constants were obtained with the crude oil:

Specific gravity at 15° C. = 0·8938

Optical rotation $a_D + 13\cdot3^\circ$

Refractive index at 20° = 1·4705.

The cineol was less than 10 per cent., and the oil was insoluble in 10 volumes 70 per cent. alcohol, but soluble in 1 volume 80 per cent. alcohol. The saponification number was 6.96 indicating 2.4 per cent. of terpinyl-acetate. The free alcohol was determined by boiling the oil for $1\frac{1}{2}$ hours with acetic anhydride and anhydrous sodium acetate in the usual manner; the saponification number had then increased to 100.4. It is recognised, however, that acetic anhydride acts upon terpineol as a dehydrating agent, with the formation of dipentene and other bodies, and according to Heusler (the Terpenes, p. 259), the amount of terpinyl-acetate formed by the usual method of acetylating is about 84 per cent. of theory; if this statement is accepted as correct for the oil of this *Melaleuca*, then nearly 30 per cent. of free terpineol was present, assuming the whole alcohol to be that substance.

The slight colour of the crude oil was due to the phenol acting upon the iron of the digester during the process of distillation, and, in order to identify this substance, 178 grams of oil were agitated with dilute alkali in the usual manner; the phenol weighed 0.49 gram, equal to 0.27 per cent. The product was liquid and had an odour, and gave colour reactions with ferric chloride, somewhat closely resembling those given by tasmanol—the liquid phenol of *Eucalyptus* oils.

The test for aromatic aldehydes gave a negative result, the oil being agitated with a 30 per cent. solution of sodium bisulphite for several hours.

On rectification under atmospheric pressure 2 per cent. distilled below 168° (uncor.), consisting principally of water and volatile aldehydes. Between $168-190^{\circ}$ 52 per cent. distilled; this fraction was colourless and consisted principally of dextrorotatory pinene (nitrosochloride melting at 103°); dextrorotatory limonene and dipentene (tetrabromide

melting at 109°), but contained cineol and some terpineol. Between $190-215^{\circ}$ 26 per cent. distilled, the fraction consisting largely of terpineol. The temperature then rose considerably, and between $243-268^{\circ}$ 15 per cent. distilled, the fraction consisting largely of a sesquiterpene.

The three main fractions gave the following results:—

	Sp. gr. 15° .	Rotation a_D	Ref. index at 23°
First fraction	0.8832	$+14.3^{\circ}$	1.4628
Second „	0.8857	$+11.5^{\circ}$	1.4650
Third „	0.9229	$+10.6^{\circ}$	1.4933

To identify the terpenes the first fraction was first agitated with a 50 per cent. aqueous solution of resorcinol until all absorbable constituents were removed.

The odour of terpineol was distinctly marked in the oil of the second fraction, and in order to identify this alcohol the phenylurethane was prepared, this melted at 111° C. Another portion was shaken with a well cooled mixture of equal parts of sulphuric acid and water in small quantities at a time. The unabsorbed oil was removed and the acid solution diluted with 4 volumes of water and stood on one side. Next day an abundance of crystals had formed which were purified and shown to be terpin-hydrate.

In order to separate the terpineol in a fairly pure condition another 100 c.c. of the crude oil were distilled, and the portion boiling above 190° subjected to distillation under reduced pressure; 12 c.c. were thus obtained boiling between $108-115^{\circ}$ at 20 mm. the bath at $155-160^{\circ}$. This fraction had rotation $a_D +14.8^{\circ}$, and specific gravity 0.932; while the odour was distinctly that of terpineol.

2. MELALEUCA DEANEI, F.v.M.

Botany.

(a) *Systematic*.—This species was described by Mueller in Proc. Linn. Soc. N.S.W., 1886, p. 1107, and no additional

data have come to light concerning it since that time showing that it is a rare species. The spikes of white downy buds and pale flowers make it an attractive shrub and one worthy of cultivation.

Mueller in his description (*loc. cit.*) states that the leaves are three nerved," but in this feature of venation just a slight point appears to have escaped his observation, viz:— that in some cases the leaves are six or more veined.

(b) *Histology*.—A section of the leaf shows a particular uniformity of anatomical structure. The palisade parenchyma forms a band of a single row around the leaf below a rather narrow epidermis. The vascular bundles are surrounded by xylemic or woody fibres, bounded on the main bundles by supporting tissue, between them and the dorsal and ventral epidermis of the leaf. The mesophyll or spongy parenchyma is composed of thin walled cells, irregularly hexagonal as seen in the section.

A dark deposit characterises some of the sections, this substance being found in the lumen of the woody fibres surrounding the bundles, but occurring more particularly in the mesophyll cells bordering the parenchymatous palisade layers. This substance is evidently not restricted or deposited in any special leaf tissue of the species investigated in this series of papers, viz:—*M. thymifolia*, *M. linariifolia*, *M. nodosa*, *M. uncinata*, *M. bracteata*, *M. trichostachys*, and *M. genistifolia*. It has not, however, been found in *M. gibbosa*, nor *M. pauciflora*, and it was not till after reading the first two papers that it was considered as a manganese compound. A summary of its occurrence in the respective species may not be out of place here. Under *M. uncinata* will be found one of the finest series of microphotographs showing this substance, being very conspicuous in the epidermal cells, spongy parenchyma, and is in such abundance in the cells surrounding

the bundle as to form a dark or black ring around it, (Vol. XLI, pl. xix to xxv). In *M. trichostachys* it is shown, (Vol. XLIV, pl. xlii, xliii), scattered throughout the spongy parenchyma and no where else, whilst in *M. bracteata*, the same paper, it is depicted in the epidermal cells and the centre of the spongy parenchyma, and in the same tissue are seen deposits of it in *M. genistifolia*, and where also only a few indications of it are found in *M. nodosa*.

Crystals of calcium oxalate are fairly plentiful, the first recorded in a *Melaleuca* leaf. Oil glands are numerous and irregularly scattered throughout the leaf tissues. They vary in size, being larger towards the midrib where their diameter in some cases almost equals the width of the leaf. Towards and around the edge their size is much smaller.

Geographical Distribution.

The original locality is given as Lane Cove, Port Jackson, H. Deane, but Camfield (Proc. Linn. Soc., N.S.W., 1901), records it between Arncliffe and National Park. Mr. F. W. Williams obtained the material from which the chemical results were obtained at Cook's River. It is thus seen to be a rare species, and with the encroachment of the city will probably in the near future be exterminated.

Chemistry of Essential Oil.

The material for this investigation was collected at Cook's River, near Canterbury, New South Wales, in the month of March. It was to the courtesy of Mr. F. W. Williams that we were able to obtain it from this locality, and he kindly assisted the collector of the Technological Museum to procure the leaves for distillation.

Two separate collections were made, one from the young growth, or "suckers," which had sprung from the trees felled about 18 months previously; the other consisting of mature leaves and terminal branchlets from old trees.

The oil glands were pronounced and numerous in the leaves of the younger material, but sparsely distributed in those of the old trees, and it was to this peculiarity that great variations in the yields of oil were experienced. This variation in oil content in the leaves of the younger growth and in those from old trees is not restricted to the of *Melaleucas*, and we had previously found this peculiarity to obtain with certain species of *Eucalyptus*, particularly *E. rubida*.

The yield of oil from 72 lbs. of leaves and terminal branchlets from old trees was less than half a cubic centimetre of a dark coloured oil, and it was even necessary to remove it from the distillate by agitating with petroleum ether. The yield from the young material was equal to 0·7 per cent. of a reddish-brown oil with a pronounced terpene odour. It was found to consist very largely of dextro-rotatory pinene, together with a little cineol and a high-boiling alcohol, most probably terpineol judging from the odour.

The crude oil from the young material had the following constants:—

Specific gravity at 15° C. = 0·8888.

Rotation $a_D + 22\cdot7^\circ$

Refractive index at 22° = 1·4646.

It required 7 volumes 80 per cent. alcohol to form a clear solution. The saponification number for the esters was 5·7, equal to 2 per cent. of terpinyl-acetate. After boiling with acetic anhydride and anhydrous sodium acetate in the usual manner the saponification number was 18·6, indicating about 4 per cent. of free terpineol, if the alcoholic constituent is considered to consist wholly of that substance.

On rectification under atmospheric pressure no less than 33 per cent. distilled between 155 and 158° (uncor.) and 60 per cent. between 158 and 185°.

These two fractions gave the following constants:—

	Sp. gr. at 15°.	Rotation α_D	Ref. index at 16°
First fraction	0·8708	+31·2°	1·4660
Second „	0·8830	+21·6°	1·4658

The cineol was determined in the second fraction by the resorcinol method, giving a result equal to 19·5 per cent. of the crude oil, but a phosphoric acid determination only gave a result equal to 15 per cent. cineol in the crude oil. It is thus evident other bodies in addition to the cineol were absorbed by the resorcinol. The alcohol was probably terpineol and was in the dextrorotatory form.

That the greater portion of the oil consisted principally of dextrorotatory pinene was demonstrated in the following manner:—The rectified oil was agitated for some considerable time with a 50 per cent. cold aqueous solution of resorcinol until absorbable bodies were removed. The remaining oil had specific gravity at 15° = 0·8640; rotation α_D + 33·6°; refractive index at 15° = 1·4674, and gave a nitrosochloride melting at 104°.

Although these results are interesting as demonstrating great diversity in the essential oils of the *Melaleucas*, yet, it is apparent that *Melaleuca Deanei* can have no economic value as an oil producing plant, the chief constituent being pinene, and oxygenated bodies are only present in very small amount.



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