with the usual reagents. From the results of this investigation it appears most probable that the 'tubers' of this species of *Vitis* are simply enlarged root stocks, and as found have comparatively little food value. Cultivation might perhaps improve them somewhat in this respect, but this result is not promising.

We are indebted to Messrs. G. Smith and J. W. Tremain for photographs illustrating the paper.

## EXPLANATION OF PLATES.

Fig. 1—"Tuber" with root attachment.

Fig. 2-Section (transverse) through fresh specimen.

Fig. 3—Transverse section through withered specimens. This shows more distinctly than Fig. 2 the medullary rays.

# THE AUSTRALIAN MELALEUCAS AND THEIR ESSENTIAL OILS.

By RICHARD T. BAKER, F.L.S., Curator, and HENRY G. SMITH, F.C.S., Assistant Curator, Technological

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## Part I.

[With Plates IV. - VII.]

[Read before the Royal Society of N. S. Wales, August 1, 1906.]

THE Melaleucas commonly known as "Tea Trees," and which are distributed throughout the whole continent of Australia, (being found in the dry interior as well as on the mountain ranges and coast districts), may almost be regarded as endemic. M. Leucadendron, which is recorded also for the Indian Archipelago, may have escaped from this austral mainland. It was upon material of this latter species that Linnaeus founded the genus in 1767, and since then over 100 species have been described as Australian,

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and a few from the Pacific Islands, New Caledonia, Tahiti, etc. With so extensive a geographical distribution, they are necessarily a common object in the bush and are well known to settlers who utilise the timber for such economics as corduroy road making, posts, mallets, etc., the wood being very hard and durable in the ground and under water. The bushes are also extensively used for fascine dyke construction, for which they are more suitable than any other Australian shrub. Some species attain tree size, thus furnishing timber of sufficient dimensions for piles, bridging, wharf-decking, etc. The genus affords little study for the ecological student of botany for the species are as much at home on the dry sandstone country as in moist swampy ground or even the rich humus of the shady gulies.

The Melaleuca oils of Australia apparently differ among themselves in regard to their several constituents and the amount, as do the oils of the Eucalypts, although the genus is not so extensive as Eucalyptus, nor does it contain nearly as many species. It is not to be expected therefore that the constituents will be anything so numerous or so diverse, nor is it considered that the inquiry will be of so interesting a nature, when judged from a botanical and chemical standpoint.

It is the intention during these investigations to apply the same methods in the determination of the Melaleuca species and their oils as has already been done by us in our work on the Eucalypts; and as the results are obtained they will be submitted for publication. It is recommended that similar care be taken in the commercial exploitation of the Melaleucas as is necessary with the Eucalypts. With the Eucalypts, the species name, if authentic, should be a guarantee of the quality of the product, and Melaleucas should not depart from this rule. An indiscriminate

mixing of the leaves of species when used commercially will, of course, give no constant product and detract from the value of any standard which might be formulated.

The following species are investigated :—(1) M. thymifolia, Sm. (2) M. linariifolia, Sm.

(1). Melaleuca thymifolia, Sm., B. Fl. iii. p. 134. "Thyme-leaved Tea Tree."

This was one of the very first Melaleucas described from Australia, the description being published by Smith in the Transactions of the Linnean Society in 1797. It is recorded now from the coast ranges and districts from Southern Queensland to the Blue Mountains and Port Jackson, in the neighbourhood of which it is rather plentiful. It is a small shrub with glabrous leaves and inflorescence; the flowers are purple in colour and quite characteristic of the species, and on this account as well as its valuable oil constituent it is a plant worthy of cultivation. The leaves appear almost veinless but are thickly studded with oil glands, which are scattered irregularly throughout the whole underside of the leaves, but quite absent from the upper or concave side, a provision probably of nature to protect them from the volatilising influence of the sun's rays.

**Histology**—The transverse vertical section of the leaf blade here given, affords a good type of histological leaf structure. The ventral and dorsal surfaces are covered with only one well defined layer of epidermal rectangular, elongated cells. On the dorsal side and round the edges of the leaf the epidermal cells appear to have the stronger walls, as those on the ventral surface have evidently a thinner wall structure as they break away in cutting.

Stomata are more numerous on the upper surface, giving it a broken appearance in section, and are more clearly shown than generally obtains in most leaf sections. The guard cells are in shape like a pair of anthers and strongly

developed, as also are the numerous and spacious air cavities into which they lead, and these form a marked feature of the section.

Below the epidermal cells of the upper surface are found characteristically arranged cells, *i.e.*, the palisade parenchyma, which is composed of a double row of closely opposed columnar cells, whilst below the lower surface one row of palisade cells only occurs. The palisade parenchyma encloses a loosely disposed area of spongy parenchyma.

The position of the midrib and a lateral vein near each edge of the leaf is well brought out in the plate, and each is seen to be constituted by a fibro-vascular bundle consisting of en. endodermic cells, S. scelerenchymatous conjunctive tissue or woody fibre, T. bast, C. cambium, x. xylem.

G. Briosi in his research on the leaves of *Eucalyptus* globulus, Labill., published by Istituto botanico della R. Universiti di Pavia, (1891) names the cells which I make to be similar to en. as collenchymatous, but as no thickening of the walls at the angles could be found, I have preferred to classify those in this instance as endodermic.

**Essential Oi1**—The yield of oil of this species is considerable, no less than  $82\frac{3}{4}$  ounces of oil being obtained from 227 pounds of leaves with terminal branchlets, equal to  $2\cdot28^{\circ}$ .<sup>1</sup> The material was collected in the month of April in the neighbourhood of Sydney. The crude oil was but slightly coloured, it being yellowish in tint. The rectified oil was colourless. In appearance, odour and taste it differed but slightly from those Eucalyptus oils which are rich in eucalyptol, and which do not contain either the aldehyde aromadendral or the terpene phellan-

<sup>&</sup>lt;sup>1</sup> J. F. Bailey (Queensland Flora) gives the yield of oil as 13 ounces from 112 pounds, which is only about  $\frac{3}{4}$  per cent. The pronounced oil glands in the leaf of this species, however, indicate a large yield of oil.

drene. The oil was rich in cineol, but neither the terpene pinene nor the terpene phellandrene could definitely be determined in it. The amount of esters was small, the saponification number being only 3<sup>1</sup> with the crude oil, and the higher boiling portion did not become acid when distilled under atmospheric pressure. Volatile aldehydes were present but only in very small amount. The optical activity was but slight and to the right, and the refractive index was comparatively low, indicating that there was hardly any constituent present having a high refractive index. This is also shown by the comparative absence of sesquiterpenes in the third fraction.

The oil of this species has a marked resemblance to the better class Eucalyptus oils, and with present methods it would be difficult to detect its presence in those oils if the rectified oil was used for mixing, or even to decide the identity if it were substituted entirely for the superior Eucalyptus oils. The insolubility in 70% alcohol of the crude oil, together with its forming a turbid solution with excess of 80% alcohol, should be a ready means of detection if this is found to be a constant feature with the crude oil of this species, but this difficulty could easily be got over by rectification.

The crude oil had a specific gravity 0.9134 at 15° C.; a refractive index 1.4665 at 23° C., and a rotation in 100 mm. tube at the same temperature  $a_{\rm D} + 2.1^{\circ}$ . On rectification only 1% came over below 172° C. (cor.) but 42% distilled between that temperature and 174° C. This fraction had specific gravity 0.9093 at 15° C.; refractive index 1.4657; and a rotation  $a_{\rm D} + 3.2^{\circ}$ . Between 174 – 183° C., 48% distilled, this had specific gravity 0.9144; refractive index 1.4653; and a rotation  $a_{\rm D} + 1.2^{\circ}$ . Between 183 – 214° C., 6% distilled, this had specific gravity 0.9192; and refractive index 1.4733. The phosphate method gave 53% of cineol in

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the crude oil. The saponification number for the esters was 3.1. A portion of the oil was esterised in the usual way; 1.999 gram of this required .0672 gram KOH, thus giving a saponification number = 33.6. This shows the presence of a fair amount of an alcohol and which gave an odour to the saponified oil with a striking resemblance to that of borneol when treated under the same conditions.

The crude oil was not soluble in 10 volumes 70% alcohol, or any quantity below that amount, but the rectified oil, distilling below 183° C., was soluble in 1.3 volumes of 70% alcohol and remained clear with 10 volumes. With 1 volume of 80% alcohol, or with the same amount of 90% alcohol, the crude oil dissolved but became very turbid with  $1\frac{1}{2}$  volumes and did not clear again with 10 volumes. The rectified oil was soluble in all proportions with both 80 and 90% alcohol. This peculiarity of solubility in alcohol distinguishes the crude oil of this species of Melaleuca from any of the crude Eucalyptus oils rich in eucalyptol. As the third fraction was soluble in 1.2 volumes 70% alcohol, it appears that the constituent which is insoluble in alcohol is not volatile under ordinary distillation. The crude oil of M. linariifolia was soluble in excess of 80% alcohol, thus differing from the oil of this species.

The comparative absence of high boiling constituents in the oil of M. thymifolia accounts for the somewhat low specific gravity, and it cannot therefore replace oil of cajuput while the pharmacopoeia standard remains as at present, a standard in which the specific gravity, 0.922 to 0.930 is required. Whether there is now any need for such a standard is questionable.

(2). Melaleuca linariifolia, Sm., B. Fl., iii. p. 140. "Tea Tree." This is one of the tallest of tea trees and occurs in the coast district of New South Wales and Southern Queensland.

E-Aug. 1, 1906.

It is well described by Bentham in the "Flora Australiensis," (loc. cit.) and so need not again be described here. A passing reference however might be made to the marginal and lateral veins of the leaf which are distinctly marked, but are not referred to by Bentham (loc. cit.) The material upon which this research is founded was obtained at Gosford and was carefully examined in order to correctly establish its botanical identity. There can be no doubt that the chemical results are founded on botanical material true to specific name i.e., M. linariifolia, Sm. Like its congener described in this paper it was one of the first Melaleucas recorded, being described by Smith synchronously with that species, M. thymifolia. The oil glands are evidently less numerous than those of M. thymifolia, but are just as prominent in the lower as the upper surface of the leaf, and the yield of oil is considerably less than in that species.

**Histology**—The histological characters of the leaves of this species differ in a few particulars from those of M. thymifolia. The palisade parenchyma occupies much less of the leaf structure, the difference being occupied by a greater development of spongy tissue. The oil glands, whilst fewer in number, are much larger than those of M. thymifolia, an individual gland extending almost from the ventral to the dorsal surface.

Collenchymatous cells which are entirely absent in the sections of *M. thymifolia*, are here very numerous between the midrib and the dorsal epidermis, a character common in the leaves of *Eucalyptus globulus*, Labill.

The large air cavities, so distinctive a feature in the leaves of M. thymifolia are almost quite absent in this species, the more numerous and larger air cavities of the spongy parenchyma probably compensating for this deficiency.

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We have to acknowledge our indebtedness to Mr. S. J. Johnston, B.Sc., for kindly cutting the section upon which the above histologic remarks are based.

**Essential Oil**—The yield of oil obtained from the leaves with terminal branchlets of this tree was 1.214%, 260 pounds of material giving  $50\frac{1}{2}$  ounces of oil.<sup>1</sup>

The material was collected at Gosford, a few miles north of Sydney, and in the month of September. The crude oil was pale yellow it being of a light lemon tint, and had a turpentine-like odour which was much more strongly marked than with the oil of M. thymifolia. The rectified oil was colourless. The cineol content was low; phellandrene could not be detected, nor was evidence obtained of the presence of pinene. The higher boiling portion contained a sesquiterpene which in its colour reaction with bromine (a few drops dissolved in acetic acid and the fumes of bromine passed into the liquid, a violet colour at once forms which falls through the liquid, the whole becoming deep violet changing to indigo blue after some time), correspond to the sesquiterpene of Eucalyptus oils. Volatile aldehydes were present in the first few drops distilling but the amount was very small. The optical activity was slight and to the right, and the refractive index higher than with the oil of M. thymifolia; this was due to the larger amount of high boiling constituents present. The oil of this species is largely a terpene one, but an alcohol was present which evidently corresponded with that occurring in the oil of M. thymifolia.

The crude oil had a specific gravity 0.9129 at  $15^{\circ}$  C., a refractive index 1.4741 at  $22^{\circ}$  C., and a rotation in 100 mm. tube  $a_{\rm D} + 2.5^{\circ}$ . On rectification only 1 cc. distilled below 172° C., (cor.) but between  $172-175^{\circ}$  C. 17 cc. distilled.

<sup>&</sup>lt;sup>1</sup> In the *Technologist*, Vol. III and other places, the yield is given as about 1.5 per cent.

This fraction had specific gravity 0.8976; refractive index 1.4681; and rotation  $a_{\rm D} + 3.0^{\circ}$ . Between  $175 - 183^{\circ}$  C.,  $52^{\circ}$  distilled, this had specific gravity 0.9003; refractive index 1.4692, and rotation  $a_{\rm D} + 2.9^{\circ}$ . Between  $183 - 250^{\circ}$  C.,  $23^{\circ}$  distilled, this had specific gravity 0.9136; refractive index 1.476; and rotation  $a_{\rm D} + 4.4^{\circ}$ . Between  $250 - 258^{\circ}$  C.,  $4^{\circ}$  distilled, this consisted largely of the sesquiterpene; it had specific gravity 0.9233; and refractive index 1.5011. It was distinctly acid, thus showing the presence of an ester. By the phosphate method the crude oil contained  $16^{\circ}$  of cineol. The saponification number for the esters in the crude oil was 6.4.

A portion of the oil was esterised; 2.0134 grams of this required 0.0812 gram potash, saponification number = 40.3. The amount of the alcohol in the oil of this species is thus a little more than with that of *M. thymifolia*. The crude oil was insoluble in 10 volumes 70% alcohol. It was soluble in 1 volume 80% alcohol and was only very slightly turbid with 10 volumes.

# EXPLANATION OF PLATES.

Transverse Sections of Leaves. Melaleuca thymifolia.

- Fig. 1—Shows the irregular occurrence of three oil glands in the leaf tissue.
- Fig. 2—Shows oil glands in a different position to those in fig. 1 and also the large number of air cavities on the ventral surface. The guard cells are also very clearly seen.
- Fig. 3-This section contains two large oil glands.
- Fig. 4—Here only one small oil gland is seen in that portion of the leaf sectioned; the air cavities are very numerous.

Figs. 1 to 4 are all magnified 50 diameters.

- Fig. 9—An enlarged portion of the edge of a leaf blade of M. thymifolia,  $\times$  250.
- Fig. 10—Rough sketch of Fig. 9,  $\times$  250. (a) Epidermic cells. (b) Palisade parenchyma. (c) Spongy parenchyma. (d) Vascular

bundle. (e) Air cavity. (f) Guard cells of stoma. (g) Oil gland.

Fig. 11—Rough sketch, central vascular bundle × 250. (e) Endodermic cells. (s) Sheath of sclerenchymatous conjunctive tissue or wood fibre. (t) Sieve tube of the bast, phloem.
(c) Cambium. (x) Xylem.

## Melaleuca linariifolia.

- Fig. 5—This shows the leaf structure of this species, and the large size of the oil glands.
- Fig. 6—Only one gland is sectioned in this portion of the leaf blade.
- Fig. 7.—A small oil gland is shown near the central vascular bundle.
- Fig. 8-No oil glands shown.

Figs. 5 to 8 are all magnified 70 diameters.

# PORT SYDNEY.

By LAWRENCE HARGRAVE. [With Plate VIII.]

[Read before the Royal Society of N. S. Wales, September 5, 1906.]

WITHOUT preamble I place before you the following statements as being axiomatic; and the plan and sections annexed as sufficient for any patriotic New South Walesman to thoroughly grasp the situation and see that the railway and eastern quay of Port Sydney are wanted by the city, now; and the rest of the work at an early date by the State and the continent.

- 1. The wharfage accommodation of Sydney is inadequate to the immediate future requirements of the State.
- 2. That lengthening and dredging existing wharves and berths in sites tortuous of approach and already crowded by ferries will only increase the congestion.



Baker, Richard T. 1906. "The Australian melaleucas and their essential oils." *Journal and proceedings of the Royal Society of New South Wales* 40, 60–69. <u>https://doi.org/10.5962/p.359469</u>.

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