ON THE AUSTRALIAN MELALEUCAS AND THEIR ESSENTIAL OILS, Part V.

By R. T. BAKER, F.L.S., and H. G. SMITH, F.C.S.

[With Plate VIII.]

[Read before the Royal Society of N. S. Wales, November 5, 1913.]

SUMMARY :---

- 1. Introduction.
- 2. Historical.
- 3. Systematic Botany.
- 4. Remarks on synonymised species.
- 5. Range of species.
- 6. Chemistry of Essential Oils.
 - a. "Cajuput" from M. minor, Linn.
 - b. M. Maideni, R.T.B.
 - c. M. Smithii, R.T.B.

I. Introduction.

Perhaps a more correct title to this paper would be "Melaleuca leucadendron, Linn., its alleged synonyms and their Essential Oils," for that is the ground it covers, but it was thought better not to break the continuity of this series of Melaleuca research in spite of a strong inducement to do so.

The literature published on this particular species shows that much confusion has existed in the minds of systematists, as to what species showing affinity to Linnæus' should be synonymised with, or differentiated from it, and this is specially the case in such botanical works as Bentham's Flora Australiensis, and Hooker's Flora of British India.

To elucidate this difficulty gave us much trouble and absorbed much time. However, we think that having

M-November 5, 1913.

reached the end of our investigations, nothing further remains than to publish the results which are given in this paper.

II. Historical.

The first species described under the generic name Melaleuca was *M. leucadendron* by Linnæus in Mantiss., 105, 1767, from Indian specimens.

There had been imported into Europe from the East, about the beginning of the seventeenth century an oil under the name of "Cajoepoeli" (according to Linnæus' spelling, *infra*) but under a later spelling "Cajuput." At that time and long after its introduction, the botanical origin was ascribed to Linnæus' species (*supra*), as the specimens forwarded to Linnæus were reputed to be taken from trees from which the oil was obtained, and he evidently described it under that impression, as shown by his original specimen now in the possession of the London Linnean Society and labelled by him "Cajoepoeli" and afterwards by Smith as *Melaleuca leucadendron, vera*, a photograph of which is reproduced at the end of this paper, Plate VIII.

This reputed origin of the oil, however, was shown later by Roxburgh to be an error, and that the true source of "Cajuput" was a Melaleuca which he named *M. cajuputi*, but this was found later to be identical with *M. minor*, described earlier in 1813 by Smith in Rees' Cyclop., Vol. XXIII, and so quite a distinct tree from that to which Linnæus had given the above name. However, many European systematists in the last century regarded the two as one, but the early Indian botanists being very emphatic over the matter, always kept them distinct, and our investigations support the latter botanists.

Since the original description by Linnæus was published, several species have been described which had the general facies of his tree but differed in some important characters.

These species, recent botanists working on indoor or herbarium material have synonymised generally under M. *leucadendron*, the list standing as follow:—

minor, Sm.	М.	lancifolia, Turcz.
Cunninghami, Schau.	М.	Cumingiana, Turcz.
saligna, Blume.	М.	lanceolata, R. Br. (Herb.)
viridiflora, Soland.	М.	Sieberi, Schau.
	minor, Sm. Cunninghami, Schau. saligna, Blume. viridiflora, Soland.	minor, Sm.M.Cunninghami, Schau.M.saligna, Blume.M.viridiflora, Soland.M.

The last two are the *M. leucadendron*, var. *parvifolia* Bentham, Flora Australiensis, iii, p. 143.

Having seen recently a statement to the effect that Linnæus' original specimen of *M. leucadendron* was in the Herbarium of the London Linnean Society, in order to settle the question definitely, we wrote to Dr. Daydon Jackson, Secretary to the Society, asking him if he would kindly compare a series which we were sending him, obtained from Sydney and round the East and North Coasts of Australia, of the Melaleucas in dispute, and mark the one or any of them which should prove to be identical with the original.

In his reply he states :--

"I am not able to match any of the specimens you sent, which I now return, but a specimen from Java seems to be the nearest, and I have indicated that with a strip of paper. I also send you a photograph about half-scale of the first sheet in the Linnean Herbarium which bears the words in the hand-writing of Linnæus "Cajoepoeli" = Kajoe-poetih of the natives in a Dutch rendering and = Melaleuca leucadendron. Linnæus also refers to Rumph. Amb., and I put in a tracing of part of tab. 16 of Vol. II, showing the falcate foliage.

"The material before me belonging to the Linnean Herbarium is as follows:—

'1. The first sheet (see photograph); Smith has added at the foot of the sheet, not shown in photograph, *M. leucadendron vera*. J.E.S.'"

This photograph throws some doubt on *M. leucadendron*, Linn., as being an Australian species, but comparing it with specimens in the National Herbaria of Sydney and Melbourne, from Arnheim Land, Napier, Broome Bay, Burdekin, Escape Cliff, these appear somewhat to match it, but until material is obtained from India, the home of the original, and compared botanically and chemically with Australian material, in our opinion the name *M. leucadendron*, Linn. should be held in abeyance as applying to an Australian species.

Morphologically therefore, it is not any of those investigated by us nor does it agree chemically.

That the Melaleuca on the N.W. Coast of the Continent differs from that of other Eastern Coast species is evident from the remarks of Mr. W. S. Campbell, which appeared in the "Sydney Morning Herald of October 6th, 1913, who when describing a trip to those parts of the Continent, states:—

"Here and throughout the country, in the many favourable moist places, the tea tree, *Melaleuca leucadendron*, abounds. Along the banks of rivers, creeks, and many lagoons and swampy localities, it attains a great height and diameter. Overhanging the water amongst other vegetation, with its silvery green, pendulous leaves, it adds greatly to the beauty of many beautiful places. *This tree seems to differ to some extent from that bearing the same name in New South Wales*, and which is very common about the coast, the leaves being more willowy-like."

Concerning these Tea-trees, Mr. W. H. Tibbits, L.S., Woollahra, writes:---

"These trees also grow in the Cape York Peninsula and out from Cooktown." This tree is very probably *M. saligna*, Schau.

III. Systematic Botany.

Bentham evidently experienced great difficulty in classifying his material under this species (M. leucadendron) AUSTRALIAN MELALEUCAS AND THEIR ESSENTIAL OILS. 197

when preparing his Flora Australiensis, for there he states, Vol. III, p. 142:-

"This species, widely spread and abundant in the Indian Archipelago and Malayan Peninsula, varies exceedingly in the size, shape and texture of the leaves, in the young shoots, very silky-villous or woolly, or the whole quite glabrous; in the short and dense or long and interrupted spikes; in the size of the flowers; in the greenish-yellow, whitish, pink, or purple stamens, etc, and at first sight it is difficult to believe that they all can be forms of one species, but on examination none of these varieties are sufficiently constant or so combined as to allow of distinct races."

J. F. Duthie who wrote the Myrtaceæ portion of Hooker's Flora of British India, reproduces these remarks, Vol. II, p. 463, and divides the species into two varieties, viz: var. *leucadendron*, var. *minor*.

The only difference he makes in these two forms is that the former has glabrous spikes, whilst in the latter they are villous.

De Candolle in his Prodromus, Part III. p. 212, lists M. leucadendron, Linn. and M. minor, Smith, giving specific differences practically similar to the varietal ones of Duthie; more recently Bailey makes three varieties, viz:—var. lancifolia, var. saligna, var. Cunninghami.

Not only are we inclined to regard M. leucadendron, Linn. as extra-Australian, but also M. minor, Smith,—the source of Cajuput oil; but in order to throw further light on the subject, specimens were obtained from Dr. M. Treub, Director of the Department of Agriculture, Buitenzorg, Java, who very kindly sent us full material—flowering and fruiting specimens and a large supply of oil obtained from that species, or M. cajuputi as he states.

This botanical material matches very well the coloured figure of *M. minor*, Sm., in Bentley and Trimen, Medicinal Plants, Vol. 11, p. 108. The leaves are of rather a thin texture, almost membraneous, rarely 4" long, mostly under 3" and about $\frac{1}{2}$ " wide, ovate, straight, now and again falcate. Venation fine, varying in number from 3 to 5 prominent ones, the flowering rachis having a white silky pubescence, flowers distant.

This, evidently, then is the true M. minor of Smith and at any rate is the species from which cajuput oil is obtained, for the analysis of this specimen of oil agrees with the published analyses of cajuput oil, and differs from those of all Australian Tea Trees going under the name of M. *leucadendron*. It must also be stated that Treub's specimens differ botanically from any Australian material **seen** by us.

IV. Remarks on the Species Synonymised under M. leucadendron, Linn., by various Authors.

M. LEUCADENDRON, Linn.

This species, as far as our knowledge goes, we regard as extra-Australian.

M. MINOR, Sm. (M. cajuputi, Roxb.)

This species also for the same reason should be regarded as extra-Australian.

M. CUNNINGHAMI, Schau.

This species is placed by Bentham in Fl. Austr., iii, 143, (loc. cit.) under M. leucadendron, Linn., but the original locality and description (Walp. Rep. ii, 927) show conclusively that it is M. viridiflora, Solander.

From this it would appear that Schauer had not access to the British Museum drawings and descriptions.

M. SALIGNA, Schau.

This is described by Schauer in Walp. Rep., ii, 927, and the locality is the same as *M. Cunninghami*—Endeavour River. It is therefore tropical, and from a drawing of the original by Dr. Daydon Jackson, London Linnean Society sent to us, is different from any we have yet seen. (See excerpt of article by Mr. W. S. Campbell, *supra*.)

M. MAIDENI, R. T. B., Proc. Linn. Soc., N.S.W., 1913. This is commonly known as the "Broad-leaved Tea Tree" throughout its geographical distribution, although at Port Macquarie it is known as the "Bell Bowery Tea-tree." It grows to a large size and produces an excellent pale, hard close-grained timber suitable for boat-building, carriage and general cabinet work, and is also very durable in the ground.

M. SMITHII, R. T. B., Proc. Linn. Soc., N.S.W., 1913.

This is commonly known as the "Broad-leaved Tea Tree" throughout its geographical distribution. It also, like *M*. *Maideni* grows to a large size and produces an excellent pale, hard close-grained timber, suitable for boat-building, carriage and general cabinet work, and is also durable in the ground, but has a well marked or pronounced sapwood.

From amongst the material collected at this Institution in connection with the species of Linnæus, we have separated these two forms, which we cannot place with any of the species here enumerated (infra), and these have been systematically described by one of us in the Proc. Linn. Soc., N.S.W., September, 1913, under the name of M. *Maideni* and M. *Smithii*.

M. VIRIDIFLORA, Soland.

This name first appears in Gaertn. Fruct. i, 173, (1788), under M. angustifolia, Gaertn., to which Bentham, Flora Australiensis, Vol. III, p. 142, gives specific rank. Index Kewensis synonymises the name under M. angustifolia, Gaertn., but this is without doubt an error, for in Britten's Botany of Cook's Voyages, published by the British Museum in 1901, an original drawing of M. viridiflora, Sol. is reproduced. This and the accompanying text prove conclusively it is not M. angustifolia, Gaertn., which is also figured in

the same work. Neither is it *M. leucadendron*, Linn. The original locality (*loc. cit.*) is Bustard Bay, Endeavour River, and some fine specimens of it are extant in the Sydney Herbarium, with leaves measuring up to 7'' long and 3'' wide, being identical with that portrayed in Britten's reproductions. The leaves are the broadest and most coriaceous of all the Melaleucas known to us.

There can be no doubt that it is a distinct species, and the name should stand.

Recently, there has been a species named from New Caledonia by Brongniart and Gris as *M. viridiflora*. By the law of priority this name must give place to that of Solander, as the tree, judging from specimens in the Sydney Botanic Garden Herbarium from New Caledonia under this name are certainly not the true *M. viridiflora* of Solander. The New Caledonian specimen should be given a new name.

M. lanceolata, R. Br. and M. Sieberi, Schau. are the M. leucadendron var. parvifolia of Bentham (loc. cit.).

As a result of these investigations, and an examination of material in the Sydney and Melbourne Herbaria, we find the valid species now to stand as follow:—

M. leucadendron, Linn.	M. Maideni, R. T. Baker.
M. minor, Sm (syn. M. cajuputi,	M. Smithii, R. T. Baker.
Roxb.)	M. viridiflora, Soland.
M. saligna, Blume.	M. lanceolata, R. Br.

V. Range of Species.

- M. LEUCADENDRON, Linn.—Extra-Australian, although it is possible that this species may occur around the tropical shores of the Continent.
- M. MINOR, Sm.-East Indies and so is not Australian.
- M. VIRIDIFLORA, Soland-Tropical shores of Australia.
- M. VIRIDIFLORA, Brong. et Gris. (see note) New Caledonia.
- M. CUNNINGHAMI, Schau.-Identical with M. viridiflora.
- M. SALIGNA, Schau.—Mouth of tropical rivers of N.W. and N. Coasts.

- M. MAIDENI, R.T.B. M. leucadendron, var. lancifolia, Bail.-Casino, Port Macquarie, Brisbane and well North.
- M. SMITHII, R. T. B.-Port Jackson, Terrigal, Gosford.
- M. LANCIFOLIA, Turcz.-Philippine Islands.
- M. CUMINGIANA, Turcz.-Philippine Islands.
- M. LANCEOLATA, R. Br. (Herb.) (M. Sieberi, Schau.)-Neighbourhood of Port Jackson.

VI. Chemistry of Essential Oils.

(a) "Cajuput" from MELALEUCA MINOR.

This oil which was sent to us by Dr. M. Treub, of the Royal Botanic Gardens, Buitenzorg, Java, was labelled "KAJOEPOETIH-OLIE." The oil was in appearance and odour identical with that of ordinary "cajuput" of com-It had a distinct green colour, due entirely to merce. the presence of copper; the copper was removed and determined as such. The odour of cineol was most marked, and the secondary odour of the oil had a strong resemblance to that of terpineol. The crude oil had the following characteristics :--

Specific gravity at 15° C. = 0.9198.

Rotation $a_{\rm p} = -2.4^{\circ}$

Refractive index at 22° C. = 1.4666.

Saponification number = 5.46.

Cineol, determined by resorcinol method, =68 per cent. Soluble in $1\frac{1}{4}$ volumes of 70 per cent. alcohol by weight at 20° C.

On rectification, the first portion contained some aldehyde, strongly indicating valeric aldehyde, but benzaldehyde was not detected. The lower boiling terpenes were lævo-rotatory. Below 195° C. (Corr.) 77 per cent. distilled. This portion boiling between $215-260^{\circ}$ (15 per cent.) was slightly dextro-rotatory, the rotation $a_{\rm p} = +0.5^{\circ}$, the sp. gr. = 0.9237, and refractive index at $22^{\circ} = 1.4875$.

These results agree with those usually recognised for "cajuput" oil, and do not agree with those obtained with the oils of the supposed forms of *Melaleuca leucadendron* growing in New South Wales and Southern Queensland, showing that these latter trees are not identical with the Melaleuca which supplies the well-known "cajuput" oil. The above investigation was carried out for comparison.

(b) MELALEUCA MAIDENI.

This tree which occurs in Northern New South Wales and in Southern Queensland, is that known in Queensland as *M. leucadendron* var. *lancifolia*, and the oil has been distilled in small quantities from the leaves of this species by Mr. Ingham of Brisbane; a sample distilled by him was analysed by Mr. R. C. Cowley, F.C.S., the results being published in the "Chemist and Druggist" of 28th May, 1910. We have investigated the oil of this tree from the following localities, and three several times of the year.

Port Macquarie, New South Wales, 30/11/1910.

Casino, New South Wales, 27/12/1911.

Port Macquarie, New South Wales, 15/1/1912.

The oils from these three specimens agree very well in general characters; this can be seen from the following table. The material was cut as for commercial oil distillation.

Crude Oils.	Yield per cent.	8p. gr. at 15° C.	Cineol per cent.	Solubility in Alcohol by Weight.	Rotation a _D	Sap, No.	Refractive index.
Port Macquarie (1910)	1.79	0.9199	39	7 vols. 70%	$-4^{\circ}.2$	3.8	1.4744 at 23°
Casino (1911)	1.26	0.9227	26	1 vol. 80%	$-0^{\circ}.7$	3.2	1.4800 at 22°
Port Macquarie	1.17	0.9234	31	1 vol. 80%	-1°.9	5.1	1.4769 at 23°
(1912)						-	

Mr. Cowley's figures for his sample of oil of this species were:—Sp. gr. 0'922; Rot. $a_{\rm D} = -3^{\circ}$; ref. ind. 1'4623; cineol 45 per cent.

The crude oil of this species was but little coloured. As the leaves were distilled from iron the oil was not green,

and did not, of course, contain copper like ordinary "cajuput" oil. The odour reminds somewhat of "cajuput" but the secondary odour is distinctive. It contains much less cineol than ordinary "cajuput." The lower boiling terpenes consist principally of lævo-rotatory pinene and lævo-rotatory limonene. Some aldehydes were present in the first portion distilling, and the odour of benzaldehyde was easily detected. The high boiling fraction contained a considerable quantity of an alcohol, but the indications for the presence of terpineol were not good, particularly as only a small amount distilled between $190-255^{\circ}$ C. After the latter temperature, a considerable quantity distilled, ranging from 30 to 40 per cent. of the total This high boiling fraction apparently contains a fair oil. quantity of the sesquiterpene alcohol which is such a pronounced constituent in the oil of the Sydney form, (M. Smithii). The dextro-rotation of this high boiling fraction, its high boiling point, together with the ascertained presence of an alcohol, indicate that this is so, although the physical results suggest the presence also of a sesquiterpene belonging to the closed chain series.

The sample from Port Macquarie (30/11/10) was rectified; a small amount of acid water and some aldehydes came over below 157° C. Between 157 - 173° C. 26 per cent. distilled; between 173 - 183° 38 per cent. The thermometer then quickly rose to 250°, only 1 per cent. distilling. Between 250 - 270° 30 per cent. distilled. The three main fractions gave the following results :—

SI	o. gr. at 15° C.	Rotation $a_{\rm D}$	Ref. index at 22°C.
First fraction	0.8914	- 5°.8	1.4628
Second fractio	n 0 · 9005	- 10°.4	1.4632
Third fraction	0.9257	$+ 11^{\circ}.2$	1.4956

The cineol was determined by the resorcinol method in a portion boiling below 190° C., the result indicating 39 per

cent. of that constituent in the crude oil. The saponification number for the ester plus the free acid was 3.8.

The low boiling portion was repeatedly shaken with 50 per cent. resorcinol to remove the cineol, the residue well washed, dried and redistilled.

Between $157 - 132^{\circ}$ C. 6.5 cc. were obtained, and between $162 - 175^{\circ} 10$ cc. distilled. These gave the following results:—

Sp. g	r. at 15° C.	Rotation $a_{\rm D}$	Ref. index at 20°C.
First fraction	0.8602	- 9°.2	1.4684
Second fraction	0.8603	- 18°.6	1.4701

These fractions were again rectified and 5 cc. obtained, distilling below 158° C.

This portion had rotation $a_{\rm D} - 7^{\circ}.6$; and refractive index at $20^{\circ} = 1.4683$. The nitrosochloride was prepared with it and this melted at $103 - 4^{\circ}$. It is thus evident that the pinene is lævo-rotatory, although less so than is the limonene.

The results obtained with the high boiling fraction suggest that a sesquiterpene is present in some quantity, although its identity remains at present undetermined.

The oil obtained from the Casino material was also rectified, the results being in close agreement with those given by the Port Macquarie sample. The high boiling fraction was, however, somewhat larger in amount (43 per cent.) and no less than 35 per cent. distilled above 265° C. This high boiling fraction had specific gravity at $15^{\circ} = 0.9355$; rotation $a_{\rm p} + 11^{\circ}.1$, and refractive index 1.4959. The somewhat smaller amount of eucalyptol (26 per cent.) in this oil is due to this increased amount of the high boiling fraction.

The oil from the Port Macquarie (15/1/12) material was also rectified, the fractions, together with their physical

AUSTRALIAN MELALEUCAS AND THEIR ESSENTIAL OILS. 205

characters, being in close agreement with those obtained with the other two samples above. The high boiling fraction (35 per cent., 30 per cent. distilling above 265° C.) had rotation $a_{\rm D} + 16^{\circ}.6$, specific gravity at $15^{\circ} = 0.9412$ and refractive index 1.4971. The cineol present in the crude oil was 31 per cent.

The saponification number of the ester by boiling was 5[•]1, while that of the acetylated oil, after boiling two hours with acetic anhydride and sodium acetate in the usual way, was 42[•]4. Assuming that the alcohol of the original ester was identical with the free alcohol, there was 16[•]8 per cent. of a sesquiterpene alcohol ($C_{15}H_{26}O$) in this sample of the crude oil of this species, and from the figures given above, this alcohol is assumed to correspond to that occurring so plentifully in the oil of *M. Smithii*.

(c) MELALEUCA SMITHII.

This is the common broad leaved Melaleuca growing in the neighbourhood of Sydney, Gosford, Terrigal and surrounding districts. How much further north of the last locality it extends is not yet known, but its southern limit is not much below Sydney.

We have investigated the oil of this tree from three localities, and the results thus obtained agree very well with each other, but differ considerably from those of the northern form (M. Maideni) and show no resemblance to "cajuput" oil, as can be seen from the following.

Locality.	Yield per cent.	Sp. gr. at 15°	Cineol per cent.	Solubility in Alcohol by Weight.	$a_{\rm D}$	Refractive index at 22°	Sap. No.
Rose Bay, Sydney 18/12/1911.	0.607	0.8815	about	1.7 vols.70%	+11°.8	1.4812	3.1
Terrigal, N.S.W. 21/12/1911.	0.923	0.9003	less than 2	2 vols. 70%	$+6^{\circ}.7$	1.4824	3.3
Gosford, N.S.W. 20/9/1899.	0.492	0.8976	about 5	2 vols. 70%	+5°.8	1.4806	6.2

The cineol was determined by the resorcinol method in the portion distilling below 260° C. (15 per cent.) of the Gosford sample, but when calculated for the crude oil showed that not more than 5 per cent. of that constituent was present. The reactions for cineol were readily obtained in this portion of the oil. With the other samples (Rose Bay and Terrigal) a smaller amount distilled below 265°. The other constituents in the oil do not appear to be absorbed by resorcinol, and not more than 2 per cent. of cineol in the Terrigal and less than that in the Rose Bay oil was determined to be present by this method. That a little cineol was present was shown by the first portion giving the reaction for that substance with bromine. The terpenes were a little more pronounced in the Gosford sample, and this may perhaps be accounted for by the distillation of the leaves not having been carried so far as with the others, this is suggested also by the lesser yield of oil. The aldehydes obtained in the first portions distilling always contained a substance with the odour of benzaldehyde, and to endeavour to locate this, a portion of the crude oil was frequently agitated during two days, with a solution of acid sodium sulphite. A very small amount of a crystalline substance separated, which was collected with difficulty. When decomposed with soda a marked odour of benzaldehyde was obtained, but the amount available was too small to proceed further. It may be assumed, however, that benzaldehyde is the aldehyde having this odour occurring in the oil of this Melaleuca. The small amount of terpenes in the oil of this species consists of lævo-rotatory pinene, lævo-rotatory limonene and dipentene, thus agreeing in this respect with those found in the oil of M. Maideni. They were both determined in the oil of the Gosford sample.

The sesquiterpene alcohol. The principal constituent in the oil of this species is a liquid sesquiterpene alcohol, which, from its physical characters and properties, appears

AUSTRALIAN MELALEUCAS AND THEIR ESSENTIAL OILS. 207

to belong to the aliphatic series. The odour is somewhat pleasant, although weak in this respect. When diluted with alcohol and spread thinly on a watch glass, the odour becomes a little more defined and delicate and remains persistent for several days.

This appears to be the first time that a substance of this nature has been noticed occurring in the leaf oils of plants, and it is only very recently that similar constituents have been determined as existing in the odoriferous oils of cer-In "Die ätherischen Ole" of Gildemeister tain flowers. and Hoffman, 2nd edition, p. 416, these substances are referred to, and the statement is there made that up to the present time (1910) they have only seldom been observed, but it is presumed that with extended investigations they will be more frequently found. Two of these alcohols are mentioned in the work referred to, Nerolidol¹ found in the higher boiling portions of Orange flower oil, which had, boiling point 276 - 277°, 128 - 129° (6mm.); spec. gr. 0.880; rotation $a_{\rm p}$ + 13°.32; and Farnesol which occurs in the oil of Ambrette seeds, in Linden flower oil, in the oils of the flowers of various kinds of Acacias, and probably also in Rose oil. Haarmann and Reimer,² show the boiling point to be 160° (10 mm.); sp. gr. at 18° 0.885; $n_{\rm D}$ 1.488; rotation $a_{\rm p} + 0^{\circ}$. An investigation has just been undertaken by M. Kerschbaum on farnesol.³ This author assumes that farnesol acts as a fixing material for the more volatile constituents of the flower, and attributes the sweet scent of Linden flowers to the presence of these sesquiterpene alcohols, which delicate odour is brought out by extreme dilution assisted by the oxidising influences of the air.

¹ Hesse and Zeitschel, Journ. f. prakt. Chem. 11, 66 (1902), 504.

² Patent No. 149603 and Chem. Zentralbl. 1904, 1, 975.

³ Ber. Deut. Chem. Gesell., 1913, p. 1732.

He suggests the following formula for farnesol, which it will be seen is an extension to the geraniol grouping:— CH_3 :

 $CH_{3} \rightarrow C: CH.CH_{2}.CH_{2}.C: CH.CH_{2} - CH_{2}.C: CH.CH_{2}OH.CH_{2}OH.CH_{3}O$

Harries and Haarman (Ber. 1913, p. 1737) have also investigated the structure of farnesol by oxidation with ozone, and agree with the above formula.

It will be seen that farnesol does not contain an asymmetric carbon atom, and is thus inactive. The alcohol in the leaf oil of Melaleuca Smithii is dextro-rotatory, so that the molecule contains an asymmetric carbon atom, and thus must be a different substance to farnesol. The characters recorded for nerolidol (above) appear to agree more closely with those so far obtained with the alcohol from the oil of this Melaleuca. The difference in molecular structure between these substances may perhaps correspond to that between geraniol and linalool, as a tertiary carbon atom appears to be present, but considerable work is necessary to be carried out with this alcohol before its characteristics and its molecular structure can be ascertained; and we know very little, as yet, about the molecule of nerolidol.

We propose the name *melaleucol* for the dextro-rotatory aliphatic sesquiterpene alcohol which occurs in the leaf oil of this species of Melaleuca.

Melaleucol is an almost colourless, slightly viscous oil, with a weak, but somewhat pleasant odour. When dissolved in chloroform, or in glacial acetic acid, it takes up a large amount of bromine, and is thus highly unsaturated. This was also shown by the permanganate reaction.

So far, no satisfactory combination with this alcohol has been obtained, so that it has not yet been isolated in a perfectly pure condition. When freshly extracted from

AUSTRALIAN MELALEUCAS AND THEIR ESSENTIAL OILS. 209

the leaf it boils under atmospheric pressure at $275 - 277^{\circ}$ C. with scarcely any decomposition, but the older oil splits off water more readily. Under reduced pressure the main fraction boiled at $163 - 165^{\circ}$ at 33 mm.

Analysis gave the following results:—0.1855 gram. gave 0.5526 gram. CO_2 and 0.1936 gram. H_2O . C=81.24 and H=11.6 per cent. $C_{15}H_{26}O$ requires C=81.08 and H=11.71per cent.

The specific gravity of the directly distilled alcohol, boiling within one degree of temperature, was 0.886 at 15° C. and the refractive index at $20^{\circ} = 1.488$. These figures roughly indicate a molecular refraction corresponding to that required for a sesquiterpene alcohol with three double linkings. The essential oil of this Melaleuca is thus shown to differ in constituents from that of any other species of Melaleuca so far determined, and consequently the product of this tree promises to be of considerable scientific interest, and possibly of commercial value. Further work will now be done upon it.

ROSE BAY TREES (18/12/1911).

The sample of oil from the Rose Bay material was but little coloured, being of a light lemon-yellow. The odour had no resemblance to that of "cajuput," being somewhat delicate and perhaps characteristic.

Although somewhat viscid in character, and consisting almost entirely of high boiling constituents, yet, the specific gravity of the crude oil was exceptionally low. The yield of oil from the leaves with terminal branchlets was 0.61 per cent. The crude oil had

Specific gravity at 15° C. = 0.8815. Rotation $a_{\rm D} = + 11^{\circ}$.8. Refractive index at $22^{\circ} = 1.4812$. Soluble in 1.7 volumes 70 per cent. alcohol by weight. Saponification number for ester and free acid = 3.04. N-November 5, 1913. • On rectification under atmospheric pressure, only 2 per cent. distilled below 265° C. This portion contained, besides some water, a little aldehyde (in which the odour of benzaldehyde was readily detected), a very little cineol and some terpenes. Between $265 - 273^{\circ}$ C. only 2 cc. distilled; but between $273 - 277^{\circ}$ no less than 70 per cent. distilled, and between $277 - 280^{\circ}$ 12 per cent. more came over. The last two fractions gave the following results:— Sp. gr. at 15°C. Rotation $a_{\rm p}$ Ref. ind, 23°C.

	0	2		
Fraction $(265 - 277^{\circ})$	0.8882	$+ 9^{\circ}.7$	1.4830	
Fraction $(277-280^\circ)$	0.8937	$+ 12^{\circ}.4$	1.4876	

A portion of the crude oil was boiled with acetic anhydride and anhydrous sodium acetate for $1\frac{3}{4}$ hours in the usual way, well washed and dried. 1.5732 gram. required 0.2184 gram. KOH. so that the saponification number from this was 138.8; representing 55 per cent. of an alcohol (C₁₅H₂₆O). Another acetylated sample of the oil gave corresponding results. More than half the oil thus consisted of this sesquiterpene alcohol. Probably the greater portion of the remainder of the oil consisted of the corresponding sesquiterpene to this alcohol; this is suggested from the figures for specific gravity, boiling point, etc., so far obtained. It also seems as if the sesquiterpene has a higher rotation than has the alcohol. This will be proved later.

TERRIGAL TREES (21/12/1911).

The sample of oil from the Terrigal material (60 miles north of Sydney), was identical in appearance, colour, and odour with that from Rose Bay, and it had the same slight viscous behaviour. The yield of oil from the leaves and terminal branchlets was 0.923 per cent. This is higher than that obtained from the Rose Bay material, perhaps due to a difference in the age of the trees, or to location. A somewhat larger amount of terpenes was present in this oil, as was found also to be the case with the oil from the Gosford material. The crude oil gave the following results:-

Specific gravity at 15° C. = 0.9003.

Rotation $a_{\rm D} = +6^{\circ}.7$.

Refractive index at $23^{\circ} = 1.4819$.

Soluble in two volumes 70 per cent. alcohol by weight. Saponification number for ester and free acid = 3.3.

The lower dextro-rotation in this oil is due to the larger amount of lævo-rotatory terpenes (pinene and limonene) in this oil than in that from the Rose Bay material, thus neutralising to a certain extent the dextro-rotation of the alcohol.

On rectification, two per cent. came over below 183° C.; this consisted of water, aldehydes (benzaldehyde distinctly noticed) cineol and terpenes. Between $183-265^{\circ}$ 9 per cent. distilled. The terpenes were proved in the Gosford material to consist of lævo-rotatory pinene and lævorotatory limonene and dipentene. Between 265 and 274° 10 per cent. came over, and between $274-277^{\circ}$ no less than 56 per cent. distilled. (This fraction consisted largely of the sesquiterpene alcohol characteristic of this species.) Between $275-280^{\circ}$ 15 per cent. distilled. These fractions gave the following results :—

5	Sp. gr. at 15° C.	Rotation $a_{\rm D}$	Ref. index at 22°C.
First fraction	n 0.8702	- 19°.4	1.4719
Second fracti	ion 0.8980	$+ 6^{\circ}.9$	1.4834
Third fraction	n 0 · 9074	$+ 12^{\circ}.6$	1.4871
Fourth fracti	ion 0.9075	$+ 7^{\circ}.4$	1.4898

A portion of the crude oil was boiled for two hours with acetic anhydride and sodium acetate in the ordinary way, and the acetylated oil prepared as usual. 1.5316 gram. required 0.1624 gram. KOH, therefore the saponification number = 106.04, representing 42 per cent. of an alcohol ($C_{15}H_{26}O$). Thus nearly half this oil consisted of this

R. T. BAKER AND H. G. SMITH.

aliphatic sesquiterpene alcohol. As with the Rose Bay oil the highest boiling portions gave indications for the presence of a sesquiterpene corresponding to that of the alcohol.

GOSFORD TREES (20/9/1899).

The sample of oil from the Gosford material (a few miles from Terrigal) was identical in odour, colour and appearance with those from Terrigal and Rose Bay. It approached more closely in constituents to the Terrigal sample, and this might be expected from the somewhat close proximity of these two localities. This sample of oil had been distilled fourteen years, but beyond a few preliminary tests nothing had been done with it. Although stored for such a long time in the Technological Museum, yet, it apparently had undergone little alteration, and the figures here given are in conformity with those of the other samples which were freshly distilled. It will be seen that this oil differs greatly from that of M. Maideni and does not agree at all with ordinary "cajuput." The terpenes in the lower boiling portion were lævo-rotatory pinene, lævo-rotatory limonene and dipentene. Benzaldehyde was also detected by the odour in the portion first distilling. Cineol was present but only about 5 per cent. in the crude oil; it was determined by the resorcinol method in the portion distilling below 260°. The crude oil gave the following results:-

Specific gravity at 15° C. = 0.8976.

Rotation $a_{\rm D} = +5^{\circ}.8$.

Refractive index at $22^{\circ} = 1.4806$.

Soluble in two volumes 70 per cent. alcohol by weight. Saponification number for ester and free acid = 6.5.

On rectification, 2 per cent. of water, aldehydes, terpenes and cineol, came over below 173° C. Between $173-183^{\circ}8$ per cent. distilled; between $183-193^{\circ}6$ per cent. distilled; the thermometer then rose rapidly to 260° with only 1 per cent. more (this 7 per cent. thus forming one fraction). Between 260 and 270° only 8 per cent. came over, but between $270-277^{\circ}$ no less than 65 per cent. of the total distilled, 73 per cent. thus forming the third fraction. These fractions gave the following results :—

	Sp. gr. at 15°C.	Rotation $a_{\rm D}$	Ref. ind. at 22°C.
First fraction	(8%) 0.8768	- 14°.5	1.4679
Second fractic	on (7%) 0.8784	- 19°.6	1.4720
Third fraction	(73%) 0.9028	$+ 11^{\circ}.6$	1•4851

To obtain sufficient of the lower boiling constituents for determination, another 100 cc. were rectified with the above results. The amounts distilling below 260° (30 cc.) were added together, the cineol determined, and the remainder, with the unabsorbed portion, distilled to 177° C. The cineol was removed from this by repeated agitation with 50 per cent. resorcinol, the unabsorbed portion washed and dried. On again distilling, about half came over between $155-162^{\circ}$, another fair portion between $170-177^{\circ}$. With these the following results were obtained:—

	Sp. gr. at 15°C.	Rot. $a_{\rm D}$	Ref. ind. at 24°C.
First portion $(155-162^{\circ})$	0.8604	$-10^{\circ}.6$	1.4668
Second portion $(170 - 177^{\circ})$	0.8534	$-20^{\circ}.1$	1.4718

The nitrosochloride was prepared with the first portion and this when finally purified melted at $103-4^{\circ}$, pinene was thus present. The tetrabromide was formed with the second portion and this when purified from acetic-ether melted at 118-119 thus indicating dipentene as well as lævo-limonene.

There were thus shown to be present in this oil about 5 per cent. cineol, about 6 per cent. pinene, and about 4 per cent. limonene, the remainder consisting largely of the aliphatic sesquiterpene alcohol, while the presence of the corresponding sesquiterpene was also indicated. A portion of the crude oil was boiled two hours with acetic anhydride and sodium acetate in the usual way, and the acetylated oil determined. 1.5371 gram. required 0.1764 gram. KOH giving 115 as the saponification number. This represents 45.6 per cent. of a sesquiterpene alcohol. Thus nearly half the crude oil of this sample consisted of the alcohol characteristic of this species of Melaleuca.

We are indebted to Dr. B. Daydon Jackson, F.L.S., of the London Linnean Society, and Dr. M. Treub of Java, for assistance and material. Also to Mr. J. H. Maiden, F.L.S., and Prof. A. J. Ewart, D.Sc., for kindly permitting us to examine material in the Sydney and Melbourne Herbaria respectively.



Baker, Richard T. and Smith, Henry George. 1913. "On the Australian Melaleucas and their essential oils, Part V." *Journal and proceedings of the Royal Society of New South Wales* 47, 193–214. <u>https://doi.org/10.5962/p.359640</u>

View This Item Online: https://doi.org/10.5962/p.359640 Permalink: https://www.biodiversitylibrary.org/partpdf/359640

Holding Institution Smithsonian Libraries and Archives

Sponsored by Biodiversity Heritage Library

Copyright & Reuse

Copyright Status: Not in copyright. The BHL knows of no copyright restrictions on this item.

This document was created from content at the **Biodiversity Heritage Library**, the world's largest open access digital library for biodiversity literature and archives. Visit BHL at https://www.biodiversitylibrary.org.