which have a very distinct deep groove around them, for the purpose of attaching the handle. They are not numbered.

Another photograph (Plate XV, Fig. 3), shows six magical stones, all of which are different from those described, excepting No. 3, which is the same stone depicted as No. 9 in Fig. 1. Nos. 1, 2, 3, and 4, are of the same material as No. 9 in Fig. 1. Nos. 8 and 10 are clay-slate, while the rest are grey sandstone. The three small articles on the floor of the picture are stone hatchets used by the aborigines, and are without numbers.

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

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With Plates XVI – XXIV.

[*Read before the Royal Society of N. S. Wales, December 6, 1911.*]

Melaleuca genistifolia, Sm.

Historical.—This species was described as far back as 1796, by Dr. Smith, in Trans. Linn. Soc., London, III, 277.

Bentham in his Flora Australiensis, Vol. III, p. 144, (1843, 1858) synonymises *M. lanceolata*, Otto. and *M. bracteata*, F.v.M. under it.

In our third paper on the Melaleucas published in this Journal, Vol. XLIV, it is shown both botanically and chemically that *M. bracteata* is quite distinct from *M. genistifolia*, and further it will be demonstrated in a later paper that *M. lanceolata* is all that is claimed for it as a species.

Remarks.—As Bentham's description, *loc. cit.*, may now be regarded as a composite one, and Smith's a little too brief perhaps to mark clearly the tree indicated, a description is added (*infra*) in order to definitely place the species, and to show upon what material the histological and chemical work is based. Smith after his short description in Latin *loc. cit.*, states *inter alia*:—"It is in some respects like *M. nodosa*." This evidently refers to the inflorescence, which in some instances is rather in a close cluster than a spike.

Mr. C. F. Laseron in his field notes states that at Gosford it is a small very crooked tree rather straggling in growth, growing in flat localities among other "tea trees." Diameter very rarely above 5 or 6″, timber reddish.

Description of Plant.—A shrub attaining 30 feet in height with a thick papery bark. Leaves ovate, blunt or obtuse, slightly concave, trinerved, shortly petiolate, about 3 lines long and $1\frac{1}{2}$ lines wide. Flowers in short terminal spikes or clusters. Calyx pubescent. Fruit sessile, cup or urn shaped, constricted below the rim, which is sometimes contracted, valves not exserted.

Leaf Histology.—The leaf being slightly concave, a cross section is boomerang in shape. The structure is uniform, the two parenchymas being in equal proportion. The palisade layers are of equal thickness on both sides with rather more delicate cell walls than generally obtains in the Melaleucas examined by us. The spongy parenchyma cells are circular in cross section, through the middle of which run the vascular bundles, three in this case being most prominent, these give the trinerved feature mentioned by Smith when first describing the species.

The main bundle is normally orientated, the phloem being towards the under side. A circle of sclerenchymatous fibres more numerous on the outer sides surrounds it (and similar

tissues of the other two) but occasionally a few parenchyma cells extend around it to the cuticle. The epidermal cells are small and irregularly rectangular in shape. The lysigenous oil glands are few and scattered throughout the leaf tissue. Some sections show the presence of the manganese compound in the cells.

Essential Oil.—The results obtained with the oil of this species again illustrate the fact brought forward in our last Melaleuca paper (Part III of this series), that the chemical characters of ordinary "Cajuput" oil are not representative of the group of essential oils obtainable from the Melaleucas. The constituents of the oil of each species appear to be representative and characteristic for that species wherever found growing naturally. Since our last paper we have obtained material of *M. bracteata* from Kinbombi in Queensland, hundreds of miles from the previous locality, and the oil distilled at the Museum from that material was identical in character with that described for this species (Proc. this Society, Dec. 1910).

The oil of *M. genistifolia* was distilled in Victoria in 1862 by Mr. Bosisto, but he only obtained 0·07 per cent. of oil from the leaves and branchlets, and no data are given as to the character of the oil. Our results as to yield do not agree with the above, as we obtained over half per cent. of oil from our material, which also consisted of the leaves and terminal branchlets like that which would be used commercially.

The oil of *M. genistifolia* consists very largely of dextrorotatory pinene—which has a very high rotation—and is almost devoid of cineol, less than 2 per cent. of that constituent being present in the crude oil. As the oil contains between 80 and 90 per cent. of pinene, it might have some economic value as a "turpentine" producing plant, providing the yield of oil was greater than it is.

Experimental.—The material was collected at Gosford in this State, and distilled in January, 1911. The amount of material was 214 lbs., and the oil obtained was 18 ounces, equal to 0·526 per cent. The crude oil was reddish brown in colour, due to the small quantity of iron present, but it was readily cleared to a light yellowish colour when agitated with two or three drops of phosphoric acid, well washed and dried. It had a marked turpentine odour, and cineol could hardly be detected in it.

The crude oil had the following characteristics :—

Specific gravity at 15° C. ... ... = 0·8807.
Optical rotation a_D ... ... = + 32·7°
Refractive index at 22° C. ... ... = 1·4702.
Cineol (determined by the resorcinol method in the second fraction) ... = 2 per cent.
Saponification number of ester + free acid = 6·8.
Insoluble in 10 volumes 80 per cent. alcohol.

For distillation, 100 cc. were taken. The amount of acid water and volatile aldehydes distilling below 155° C. (cor.) was very small indeed. Between 155 – 162° 79 cc. distilled; between 162 – 183° 6 cc. The thermometer then quickly rose to 250° and between that temperature and 263° 11 cc. came over. The specific gravity of the first fraction at 15° C. = 0·8661; of the second = 0·881; of the third = 0·9293. The rotation of the first fraction a_D = + 36·8°; of the second = + 19·6°. The refractive index of the first fraction at 22° C. = 1·4645; of the second = 1·4671; of the third = 1·4967.

Another distillation was undertaken with comparable results.

The first two fractions (145 cc.) were then added together and again distilled, when between 154 – 156° C. 114 cc. distilled, and between 156 – 158° 13 cc. more. The quantity of oil boiling within two degrees of temperature from

200 cc. was 114 cc., = 57 per cent. The specific gravity of the first fraction at 15° C. = 0·8638; of the second = 0·8667. The rotation of the first fraction a_D = + 39·1°, or a specific rotation $[a]_D$ = + 45·27°, of the second fraction = + 36·3°, or a specific rotation $[a]_D$ = + 41·88°. The refractive index of the first fraction at 23° C. = 1·4636; of the second fraction = 1·4638.

The nitrosochloride was readily prepared with the oil of the first fraction; it was purified by dissolving in chloroform and precipitating with methyl alcohol. It melted at 104° C. (uncorr.).

The higher boiling constituents of this oil consisted largely of the sesquiterpene, and gave the characteristic colour reactions for that substance. It also contained some ester, the saponification number being 16·7, equal to 5·8 per cent. of ester calculated as terpinyl-acetate.

Melaleuca gibbosa, Labill.

Historical.—This species was first described by Labillardière, Pl. New Holland 1799, presumably from a Tasmanian specimen, and has since been recorded from the mainland in Victoria and South Australia.

Remarks.—It stands in the happy position of having no synonyms, so that after these years its systematic status must be regarded as unchallengeable. The fruits perhaps call for a little notice, for as soon as maturity is reached they are then a little distance from each other, but gradually become immersed in woody tissue by a thickening of the rhachis. Although it appears to be a constant feature of the species, yet it may be pathological and is worthy of investigation, for perhaps here we may have a host species of either the animal or vegetable kingdom. We are indebted to Mr. E. Rodway, F.L.S., Government Botanist of Tasmania for fresh material for dissecting purposes.

Leaf Histology.—Amongst Melaleucas there are several differences which characterise the structure of the leaf texture of this species. The palisade parenchyma is not a distinct feature in a cross section, although it is more in evidence on the underside of the leaf than towards the top surface. The cells of the spongy parenchyma have circular walls in a transverse section, as against the angular shape of those of *M. leucadendron*, and this particular leaf substance is in greater proportion towards the petiole, although in other parts of the leaf it is in equal proportion to the palisade parenchyma. Near or close to the petiole, the palisade parenchyma gives place entirely to spongy parenchyma. Stomata occur mostly in the lower portion of the leaf and more especially on the inner or upper surface at that portion of the blade. Another distinguishing feature in this part is the strong development of papillose projections on the cuticle of the epidermal cells of that surface. The vascular bundles are normally orientated, the phloem facing the outer or under surface of the leaves, and are entirely surrounded by a compact or coalesced body of sclerenchymatous tissue exceeding in area that of the bundle. These were doubtfully regarded as transfusion tissue under *M. uncinata*, Part I of this series. The median bundle is finally bounded towards the cuticle by spongy mesophyll which thus makes a complete break in the continuity of the palisade parenchyma.

Essential Oil.—The oil of this species consists largely of dextro-rotatory pinene, cineol, a small quantity of ester, and a sesquiterpene. It belongs to the pinene-cineol group of Melaleuca oils, and resembles somewhat in general characters the oil of *M. nodosa*, although it is richer in cineol than the oil of that species. The yield of oil is somewhat small, so that *M. gibbosa* cannot be considered of value as an oil producing tree.

Experimental.—The material was collected at Little Swanport, on the east coast of Tasmania, and distilled in June, 1908. The leaves and terminal branchlets were alone used, and 316 lbs. of material gave 8 ounces of oil, equal to 0·158 per cent. The crude oil was of a dark lemon yellow colour, and had an odour resembling the cineol-pinene oils of the Melaleucas, as for instance that of *M. thymifolia*. The crude oil had the following characters:—

Specific gravity at 15° C. ... ... = 0·9138.
Optical rotation a_D ... ... = + 4·5°
Refractive index at 20° C. ... ... = 1·4703.
Cineol (determined by the resorcinol method) = 61·5%
Saponification number of ester + free acid = 9·9.
Insoluble in 10 vols. 70 per cent., but soluble in 1 vol. 80 per cent. alcohol.

This comparative insolubility is evidently due to the presence of the pinene and the sesquiterpene.

For distillation 100 cc. were taken. The usual small amount of acid water, and volatile aldehydes, were first obtained, and these reminded strongly of valeric aldehyde. Between 165–173° (corr.) 28 cc. distilled, and between 173–195° 52 cc. came over. The thermometer then quickly rose to 245° and between that temperature and 265° 16 cc. distilled. The specific gravity of the first fraction at 15° C. = 0·8963; of the second = 0·9045; of the third = 0·9252. The rotation of the first fraction a_D = + 6·8°, of the second = + 3·9°. The refractive index of the first fraction at 20° C. = 1·4621; of the second = 1·4630; of the third = 1·4954. The cineol in the first fraction was removed by resorcinol, the residue again rectified, and the portion distilling below 158° C. utilised for the preparation of the nitrosochloride. This substance was readily formed; it was purified by dissolving in chloroform and precipitating with methyl alcohol. It melted at 104° C. The active

terpene in the oil of this species is therefore dextro-rotatory pinene, and the limonenes appear to be absent.

The high boiling fraction consisted largely of the sesquiterpene, which is so pronounced a constituent in the oil of *M. pauciflora*, and the characteristic colour reactions were readily obtained with it. It also contained a fair quantity of ester, the saponification number being 20·7. The odour of the separated oil, after saponification, reminded of terpineol, and the acid was determined as acetic, so that the ester is probably terpinyl-acetate, and the fraction thus contained 7·24 per cent. of that substance.

Melaleuca pauciflora, Turcz.

Historical.—This species was described by Turczaninoff in Bull. Mosc. in 1847, and so far its systematic position or rank has not been challenged, nor has it any appendages in the form of synonyms.

Remarks.—This Melaleuca is characterised by leaf features found to occur only in one other species of the genus, viz., *M. hypericifolia*, which latter species has, however, other specific differences sufficient to warrant a systematic differentiation. The inflorescence of the two also shows marked distinctiveness. The leaves of this species have the peculiarity of incurving unless pressed as soon as gathered.

Leaf Histology.—As this plant has a convex leaf a transverse section gives a vinculum figure. The leaf is channelled above so that two convex surfaces form the upper cuticle, which is characterised below by a very much thicker development of palisade parenchyma than the upper surface, as shown in the plate. The spongy parenchyma is fairly limited in area, the cells being circular in cross section. Stomata occur on both surfaces, and are rather more numerous than obtains in other species of

Melaleuca examined, and what might be expected, more so in the channel of the midrib. Bundles occur through the median line of the spongy parenchyma, the central vascular bundle,—the midrib, of course, being the largest. It is normally orientated and entirely surrounded by a thin layer of sclerenchyma fibres. The medullary rays being well defined, the cells increasing outwards in size.

Essential Oil.—The oil of this species is another instance of the differences in the characters and constituents of those obtainable from the various species of Melaleuca, as it has little resemblance to that of ordinary "cajuput." There appears to be an entire absence of pinene in this oil, the terpene present being limonene and probably dipentene. The principal constituent is a high boiling one, and no less than 67 per cent. of the total oil came over between 260–276° (corr.). This high boiling fraction consisted principally of a sesquiterpene, and as it occurs in the oil of this species in such large quantity it should be possible to work out its chemical characteristics and combinations, and so determine whether it is new to science. It is dextro-rotatory, and the optical rotation of the purest sample so far obtained, was $a_D = + 8{\cdot}5°$. Its specific gravity is somewhat high = 0·9364 at 15° C., and its refractive index at 21° C. = 1·5004. It boils between 260 – 270° C. It has marked colour reactions when two drops of oil are dissolved in 10 cc. solvent, and shaken with one or two drops of sulphuric acid.

(*a*) If the solvent is glacial acetic acid the colour is pink at once, soon changing to crimson, and then to purplish-brown on long standing.

(*b*) If the solvent is acetic anhydride the colour is bright green at once, soon becoming darker green, and deep blue on long standing.

(*c*) If the vapours of bromine are passed over a film of the oil on a watch glass, the colour is bright blue and violet at once, changing to green on standing.

(*d*) If the vapours of bromine are allowed to fall down a test tube on to a solution of two drops in glacial acetic acid, a violet colour at once forms, changing to indigo-blue on standing.

This sesquiterpene appears to be present in the high boiling portions of the oils of many species of Melaleuca, and the above colour reactions are readily obtained with them.

The amount of cineol in the crude oil is but small, it was determined by the resorcinol method in the first fraction, and calculated for the crude oil. The whole of the cineol was removed from the first fraction by the aid of 50 per cent. resorcinol, and the separated terpenes again rectified. Nothing distilled below 175° C. (corr.), so that pinene cannot be present but in traces. The greater portion of the terpenes distilled between 175 – 178° C., and gave other indications for limonene or dipentene.

The ester in this oil is probably terpinyl-acetate, as the acid was determined as acetic, and the odour of the separated oil, after saponification, reminded strongly of terpineol. Free terpineol is probably also present, as on boiling the oil with acetic anhydride and anhydrous sodium acetate in the usual way, over 5 per cent. of an alcohol was shown to be present.

The high boiling fraction when agitated with acetic anhydride did not easily dissolve, so that it was possible to remove largely the ester and the free alcohol from the sesquiterpene by the method of agitation.

Experimental.—The material was collected at Gosford, in this State, and distilled in January, 1911. 208 lbs. of material (leaves and terminal branchlets) gave 10 ounces of oil, equal to 0·3 per cent. The crude oil was of a dark amber colour, somewhat viscous and greasy in appearance —similar in this respect to the oil of *M. bracteata*—and

left a permanent stain on paper. It had a somewhat pleasant odour, probably due to the terpineol present. The crude oil had the following characteristics:—

Specific gravity at 15° C. ... ... = 0·9302.
Optical rotation a_D ... ... = + 3·3°
Refractive index at 24° C. ... ... = 1·4921.
Cineol (determined by the resorcinol method) = 8·7%
Saponification number of ester + free acid = 8·25.
Scarcely soluble in 10 volumes 80 per cent. alcohol.

For distillation 100 cc. were taken. A few drops only of acid water and volatile aldehydes came over below 177°C. (corr.). Between 177 – 218° 29 cc. distilled. The thermometer then quickly rose to 260°, and between that temperature and 276° 67 cc. came over. The specific gravity of the first fraction at 15° C. = 0·8801; of the second = 0·9382. The rotation of the first fraction a_D = + 3·4°; of the second = + 7·8°. The refractive index of the first fraction at 24° C. = 1·4767; of the second = 1·4991. After the removal of the cineol in the first fraction by resorcinol, the portion of the terpenes distilling between 175 – 178° C. had specific gravity at 15° C. = 0·8572; rotation a_D = + 4·9°; refractive index at 22° C. = 1·4769. The fraction had the odour of limonene. When tested for the tetrabromide a few crystals formed, but they were difficult to separate, neither phellandrene nor sylvestene were present, and all the indications go to show that the terpene in this oil is limonene, or dipentene.

The saponification number for the ester in the large high boiling fraction was 9·2, equal to 2·16 per cent. of terpinyl-acetate in the crude oil. A portion was then esterised in the usual manner when the S.N. had risen to 36·6, representing 5·05 per cent. of free alcohol as terpineol in the crude oil. Methyl eugenol and the ester of cinnamic acid appeared to be both absent in the oil of this species.

Material of this species was also received from Port Macquarie, in this State, and distilled November 1910. In general appearance and characters it resembled the oil from the Gosford sample, and was even more viscid. The specific gravity at 15° C. = 0·9552, which is higher than that of the sample from Gosford. The refractive index at 24° C. = 1·4923. The saponification number of ester + free acid = 8·1. The rotation was not sharp, but it was between two and three degrees to the right.

Explanation of Plates.

Plate XVI.

Melaleuca genistifolia.

Figs. 1 and 2. Flowering twigs.
,, 3. Individual flower.
,, 4. Individual bundle of stamens.
,, 5. Individual leaf.
,, 6. Individual early fruit.
,, 7. Individual fruit with contracted rim.
,, 8. Cluster of fruits. 1, 2, and 3, natural size.

Plate XVII.

Fig. 1. A cross section through the centre of a complete leaf, showing the general disposition of the parenchymatous tissue, oil glands and vascular bundles. × 110

Fig. 2. A cross section through half a leaf, towards the upper portion. × 110.

Plate XVIII.

Fig. 3. A transverse section through little more than half a leaf. The midrib on the extreme right is surrounded by sclerenchymatous fibres shown black in the plate; a smaller bundle is on the extreme left towards the edge of the leaf. Other rudimentary bundles are seen in the median line but not surrounded by fibres as in the case of the other two. A few oil glands are seen. × 140.

Plate XIX.

Fig. 4. This is a higher magnification of the midrib or main bundle in Fig. 3. The dark cells are sclerenchymatous tissue, and this is now seen to much greater advantage here than in that figure. The larger crescent shaped cluster is towards the underside of the leaf, the concave face butting on to the phloem with its cell walls scarcely discernible. The xylem cells succeeding these upwards have thicker cell walls and are quite distinct. The larger cells in the outer field are those of the spongy parenchyma. × 450.

Plate XX.

Fig. 5. This is another section of a leaf cut without bleaching out the cell contents, consequently the presence of manganese compound is marked by the dark substance in the lumen of the spongy parenchyma. Three oil glands are shown. The chloroplastids are distinctly seen in each cell. × 140.

Melaleuca gibbosa.

Fig. 6. A transverse section of just a little more than half a leaf, the midrib or central vascular bundle being on the left of the picture, to the left of which is a large oil gland. × 140.

Plate XXI.

Fig. 7. A slightly larger section of a portion of a leaf between the midrib and edge, and showing chloroplastids in the cells of the palisade parenchyma. The upper surface of the leaf has the papillose projection of the cuticle. × 150.

Fig. 8. Similar to figure 7, but a large oil gland is to the right of the main bundle in this case, thus showing how irregularly the oil glands are distributed throughout the leaf. × 140.

Plate XXII.

Fig. 9. A cross section through more than half a leaf, towards the petiole. × 110.

Plate XXIII.

Fig. 10. A cross section through the centre of a leaf towards the petiole, showing how the palisade parenchyma is displaced by

the spongy parenchyma in the upper portion of the leaf over the central vascular bundle, and beyond. Only one whole oil gland comes into the field of vision. × 140.

Plate XXIV.

Fig. 11. A cross section through the central bundle of a leaf and surrounding tissue cut from the upper portion of the leaf. Here the palisade parenchyma is in its normal position, and the mass of sclerenchymatous fibres surrounding the central bundle are distinctly seen. This section also shows clearly the papillose projections of the cells of the cuticle on the ventral surface, and these are the first so far met with in Melaleucas. In a few of the spongy parenchyma cells calcium oxalate crystals can be seen. × 225.

Melaleuca pauciflora.

Fig. 12. A cross section through a two-thirds portion of a leaf. The bundle is normally orientated, the channel denoting the upper or ventral surface, towards which it will be noticed that the palisade parenchyma is more strongly developed than on the dorsal surface. The oil glands it will also be seen are not numerous. Here also as in *M. gibbosa* the spongy parenchymatous cells bound the central bundle on the dorsal side. Several bundles occur on the median plane of the leaf texture, two at the extremities of the picture being cut obliquely. Four crystal sacs occur in the palisade parenchyma of the upper surface towards the right, and in two, rhomboidal crystals are well outlined. × 110.