

ON THE ESSENTIAL OILS OF THE ANGOPHORAS.

By HENRY G. SMITH, F.C.S.

[Read before the Royal Society of N. S. Wales, August 6, 1913.]

Introduction.

THIS genus, *Angophora*, was established by Cavanilles in 1797, the name being given by him to two species common in the neighbourhood of Sydney, viz.:—*Angophora cordifolia* and *lanceolata*. Although very closely allied to that widely distributed Australian genus—*Eucalyptus*, and in all probability its prototype, yet the number of species in the genus is very limited, only six being so far described, as against about two hundred in the former. With the exception of *A. cordifolia*, they are all fine forest trees, and so much resemble those of the cognate genus (*supra*) that they are commonly regarded as the same “family,” and this is very excusable to the unscientific mind, for the barks are almost identical and could easily be classed as “Stringybark,” or “Gum”—smooth bark. The timbers also very closely resemble those of the pale coloured woods of the *Eucalypts*. Botanically, they are only to be differentiated from the *Eucalypts* by their distinct calyx teeth and free petals.

In geographical distribution they are restricted to the east coast district of the continent, and are now classified as follows:—

<i>A. cordifolia</i> , Cav. (1797)	<i>A. lanceolata</i> , Cav. (1797)
<i>A. subvelutina</i> , F.v.M. (1858)	<i>A. melanoxyton</i> , R.T.B. (1900)
<i>A. intermedia</i> , DeCandolle (1828)	<i>A. Bakeri</i> , Dr. C. Hall (1913)

The first recorded instance of an essential oil from the leaves of any species of *Angophora*, is the notice in the work by Mr. R. T. Baker and myself “A Research on the

Eucalypts," 1902, p. 16. The leaves of *A. lanceolata* were more easily obtainable, and for this reason were used for the purpose. It was desirable, at that time, to determine whether the oil from this group of Myrtaceous trees was in agreement with that distilled from certain species of Eucalyptus. It had been found previously that the venation of the leaves of some Eucalypts, particularly those of the "Bloodwood" group, indicated the presence of pinene in their oils.¹ The terpene phellandrene is not a constituent of Eucalyptus oils from species so early in the evolution of the genus, and those Eucalypts yielding phellandrene bearing oils have quite a distinct leaf venation.

The venation of the mature lanceolate leaves of the Angophoras is similar to that of the "Bloodwood" group of Eucalypts, and the oils should, therefore, consist largely of pinene. Although the yield of oil from *A. lanceolata* is very small, yet sufficient was obtained to furnish the evidence required, and it was thus possible to show a distinct chemical connection, through their oils, between the Angophoras and the Eucalypts at the older end of that genus. The evidences in other directions, which have accumulated since that time, all tend to support the conclusions then advanced, and it may now be stated with some confidence that the Angophoras are very closely in agreement with the Eucalypts, and that Angophora is the older genus. Besides the evidence derived from the investigation of the oils, this close relation is further emphasised by the study of the kinos, or astringent exudations; and the presence of the caoutchouc on the young leaves of certain species of Angophora and Eucalyptus is also a feature of some value in this connection.

It was desirable, therefore, that an investigation of the oils of all the known species of Angophora in New South

¹ This Journal, Vol. xxxv, p. 116, 1901.

Wales should be undertaken, so that the previous conclusions might be strengthened, or otherwise.

From the results now brought forward it is apparent that the chemical changes which have become such a pronounced feature with the oils of the Eucalypts, had scarcely commenced, if at all, in the oils of the Angophoras. It is possible, however, to trace the origin of certain constituents of Eucalyptus oils, and the dextro-rotatory pinene, the geranyl-acetate, the geraniol, and the sesquiterpene, all had their origin in the oils of the Angophoras, or perhaps in some still older genus. It might be expected that certain constituents would remain persistent in some directions if the suggested relation between the genera was actual as well as apparent. That this is so is shown by the numerous pinene Eucalyptus oils, in which the dextro-rotatory form is such a distinguishing feature, and by the many Eucalyptus oils in which geranyl-acetate occurs, reaching the maximum in that of *Eucalyptus Macarthuri*.

The Angophoras as a class are not promising as oil yielding plants, and from two species, *A. cordifolia* and *subvelutina*, no oil was obtained, while but traces can be distilled from the leaves of *A. intermedia*. Some of the other species, however, give fair yields of oil, more in fact than is obtainable from several species of Eucalyptus.

The following table gives the yields of oil distilled from material cut as would be done for commercial oil distillation:

<i>Angophora Bakeri</i>	0.31 per cent.
„ <i>melanoxylon</i>	0.19 „
„ <i>sp.</i>	0.13 „
„ <i>lanceolata</i> (Sydney)	0.013 „
„ <i>lanceolata</i> (Warialda)	0.005 „
„ <i>intermedia</i>	traces
„ <i>subvelutina</i>	none
„ <i>cordifolia</i>	none

In some instances, over 500 lbs. of leaves and branchlets were distilled.

To test the position of *A. intermedia*, material was obtained both from Penrith, and from near Parramatta. In the latter case no oil was obtainable, while in the former not more than 10 drops of oil were distilled from 120 lbs. of fresh material.

The investigation of the oils thus obtained shows that no marked differences in constituents can be detected between the oils of the several species of Angophora. They all consist largely of dextro-rotatory pinene with a uniformly high specific rotation; two esters of geraniol (geranyl-acetate and geranyl-valerianate), free geraniol, a high boiling constituent, most probably a sesquiterpene; with small amounts of a volatile aldehyde and a low boiling ester, the odour of which was that of amyl-acetate. Neither cineol nor phellandrene were present even in traces. The saponification number for the esters varied somewhat in the several oils, but this factor may be perhaps considered as accidental rather than discriminative, particularly as the pinene in all the oils has practically the same optical activity to the right, and does not vary much in amount.

The general characters of the oils of the Angophoras are thus in close agreement with those distilled from various species of Eucalypts. None of the species of Angophora can be considered of commercial value as oil producing trees, yet the scientific results derived from their investigation are of considerable value in helping to elucidate the problems dealing with the origin and development of the closely related genus Eucalyptus.

The Essential Oils.

ANGOPHORA BAKERI.

This species is described in the previous paper, dealing with the seedlings of the Angophoras, by Dr. Cuthbert

Hall. Although the leaves are much smaller and narrower than those of the other species, yet, the venation is similar. The oil glands in the fresh leaves are more pronounced in this species than in the others, and this is also indicated by the greater yield of oil.

Chemistry.—This material was collected in the neighbourhood of Parramatta, in the month of October, and consisted of fresh leaves and terminal branchlets, cut as for commercial oil distillation. The average yield of oil was 0·31 per cent.

The crude oil was light lemon coloured, had an indistinct odour at first, but distinctly a secondary aromatic one. The chief constituents were dextro-rotatory pinene, geraniol, geranyl-acetate, geranyl-valerianate, a small amount of a sesquiterpene, together with a little volatile aldehyde, and most probably a minute quantity of amyl-acetate. No other terpene than pinene was detected and cineol was quite absent. The botanical evidence is also against the presence of either phellandrene or cineol in the oil.

The crude oil had specific gravity at 15° C. = 0·8719; rotation $a_D = + 35^{\circ}.6$; refractive index at 22° = 1·4660; and was insoluble in 10 volumes 80 per cent. alcohol by weight.

On the rectification of 100 cc. of the oil, a small amount of acid water with some low boiling aldehyde, and a constituent with a pear-like odour, came over below 155° C. (corr.). Between 155 – 160°, 57 per cent. distilled; and between 160 – 172°, 24 per cent. The thermometer then quickly rose to 220°, and between that temperature and 250°, 6 per cent. distilled, with some decomposition. These fractions gave the following results :—

	Sp. gr. at 15° C.	Rotation a_D	Ref. index at 19° C.
First fraction	0·8658	+ 37°·6	1·4661
Second fraction	0·8689	+ 32°·7	1·4680
Third fraction	0·8995	+ 4°·8	1·4721

72 cc. of the added first two fractions were again distilled, and before 156° C. was passed 50 cc. had distilled (= 50% of the crude oil); and 14 cc. between 156 – 157°. These two fractions gave results closely in agreement, as is seen from the following:—

	Sp. gr. at 15° C.	Rotation a_D	Ref. index at 19° C.
First fraction	0·8612	+ 37°·5	1·4658
Second fraction	0·8622	+ 36°·6	1·4663

The indications from the above are that the only low boiling terpene present in this oil is pinene, and that over 75 per cent. of the oil of this species consists of that constituent. The odour too, of the terpene was distinctly that of pinene.

The nitrosochloride was prepared with a portion of the first fraction, and this, when finally purified by precipitating by methyl alcohol from a chloroform solution, melted with decomposition at 103 – 104° C., thus confirming the identity of the pinene.

The saponification number for the esters, by boiling, together with that of the free acid, was 33·6. The secondary odour of the separated oil after saponification was that of geraniol, and the presence of geraniol in these oils was proved in that of *A. melanoxylon*. Acetic acid and valerianic acid were also both shown to be present in combination as esters in the oil of that species, and there is no reason to suppose that the esters are different in the oil of *A. Bakeri*, especially as the results of cold saponification in both oils are similar, and as the Angophora oils all resemble each other in constitution.

The saponification number of the ester as determined in the cold, with two hours' contact, was 19·2, so that this portion, calculated as geranyl-acetate, was equal to 6·7 per cent. of that ester, and the remainder calculated as geranyl-valerianate was equal to 6·1 per cent.

A portion of the crude oil was acetylated by boiling one and a half hours with acetic anhydride and anhydrous sodium acetate in the usual way. The saponification number from this was exactly 50. As no other alcohol was detected than geraniol, with the exception, perhaps, of a trace of amyl alcohol as acetate, the amount of free alcohol calculated as geraniol was 4·5 per cent.

The sesquiterpene was only present in small amount in the oil of this species.

The composition of the oil of *Angophora Bakeri* may be stated as follows:—

	Per cent.
Dextro-rotatory pinene	= 78·0
Free geraniol	= 4·5
Geranyl-acetate	= 6·7
Geranyl-valerianate	= 6·1
Water, volatile aldehydes and low-boiling esters	= 1·0
Sesquiterpene and undetermined	= 3·7
	100·0

ANGOPHORA MELANOXYLON.

This species was first described by my colleague, Mr. R. T. Baker, F.L.S., in the Proceedings of the Linnean Society of New South Wales, April, 1900.

Chemistry.—This material was collected in the month of March at Coolabah, New South Wales (430 miles west of Sydney), and forwarded to the Museum by Mr. H. T. Morgan, the Public School teacher at that place. It consisted of fresh leaves and terminal branchlets collected as would be done for commercial oil distillation.

CONTENTS.

	PAGE.
ART. I.—PRESIDENTIAL ADDRESS. By R. H. CAMBAGE, L.S., F.L.S. [With Plate I.]	1
ART. II.—Products of the Action of Concentrated Sulphuric Acid on Iron. By C. W. R. POWELL, Science Research Scholar, University of Sydney. (Communicated by Professor C. E. Fawsitt, D.SC., PH.D.)	59
ART. III.—Note on the Occurrence of Coccidiosis in House Sparrows and in Bovines in N.S.W. By J. BURTON CLELAND, M.D., CH.M., Principal Microbiologist to the Government of N. S. Wales.	70
ART. IV.—Note on the Growth of Flowering Stem of <i>Xanthorrhoea</i> <i>hastilis</i> , R.Br. By J. BURTON CLELAND, M.D., CH.M.	72
ART. V.—Note on Agar-agar Seaweed from Western Australia. By J. BURTON CLELAND, M.D., CH.M.	75
ART. VI.—Notes on Eucalyptus, (with descriptions of New Species) No. I. By J. H. MAIDEN	76
ART. VII.—Note on the Paraffins of Eucalyptus Oils. By H. G. SMITH, F.C.S.	95
ART. VIII.—The Seedlings of the <i>Angophoras</i> , and description of a New Species. By CUTHBERT HALL, M.D., CH.M. (Communi- cated by R. T. Baker). [With Plates II—IV.]	98
ART. IX.—On the Essential Oils of the <i>Angophoras</i> . By H. G. SMITH, F.C.S.	106

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PART II., (pp. 113-247).
CONTAINING PAPERS READ IN
AUGUST to DECEMBER.
WITH FIVE PLATES.
(Plates v, vi, vii, viii, ix.)



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The average yield of oil was 0.19 per cent. The crude oil was somewhat darker in colour than that of *A. Bakeri*, due to the larger amount of ester and free acid in the oil, the latter more readily attacking the iron of the still. The odour resembled that of *A. Bakeri*, and the aromatic secondary odour was also similar.

The chief constituents in the oil of this species were identical with those in the oil of *A. Bakeri*, although the geranyl-valerianate was a little more pronounced, as was also the sesquiterpene. Phellandrene and cineol were, of course, both absent.

The crude oil had specific gravity at 15° C. = 0.8809; rotation $a_D = + 24.9$; refractive index at 21.5 = 1.4678; and was insoluble in 10 volumes 80 per cent. alcohol.

On redistilling 100 cc. of the crude oil, a small amount of acid water, some volatile aldehydes and the constituent with a pear-like odour came over below 155° C. (corr.). Between 155 – 160°, 31 per cent. distilled; and between 160 – 193°, 41 per cent. The thermometer then rose to 225°, and between that temperature and 265°, 20 per cent. distilled, with some decomposition. These fractions gave the following results:—

	Sp. gr. at 15° C.	Rotation a_D	Ref. index at 20° C.
First fraction	=0.8638	+ 37°.6	1.4630
Second fraction	=0.8648	+ 34°.6	1.4638
Third fraction	=0.9250	too dark	1.4846

The first two fractions were again distilled when 46 per cent. of the whole oil came over to 156° (corr.) and 13 per cent. between 156 – 157°.

These two fractions gave the following results:—

	Sp. gr. at 15° C.	Rotation a_D	Ref. index at 19° C.
First fraction	=0.8615	+ 37°.9	1.4642
Second fraction	=0.8621	+ 36°.8	1.4644



The above results indicate that the only terpene in the oil is pinene, and that about 70 per cent. of that constituent was present. The nitrosochloride melted at the same temperature as that prepared with the pinene from the oil of *A. Bakeri*.

The saponification number for the esters and free acid in the crude oil by boiling was 42.5, and in the cold with two hours contact 19.8. If the ester broken down by cold saponification be considered to represent the geranyl-acetate, then the result gives 6.93 per cent. of that ester, and 9.64 per cent. geranyl-valerianate. These figures agree very well with those obtained from the ratio of the acids of the esters.

To determine these acids, the third fraction was saponified with alcoholic potash by boiling, water added, the oil separated, and the aqueous portion evaporated to small amount. This was filtered, acidified with sulphuric acid, and steam distilled until the whole of the volatile acids had come over. The distillate was exactly neutralised with barium hydrate solution; evaporated to dryness, the residue powdered and finally heated in air-oven. 0.4197 gram of the barium salt when treated with concentrated sulphuric acid and ignited, gave 0.3195 gram barium sulphate, equal to 76.12 per cent. It was thus evident that a volatile acid of higher molecular weight than acetic acid was present. That the ester containing this acid was in excess was also indicated by the amount saponified in the cold being less than half the total ester. The remainder of the barium salt was then decomposed with dilute sulphuric acid, extracted with ether, and the ether evaporated. The acids which remained gave the characteristic odour of valerianic acid. The acids were but little soluble in water, but the aqueous portion gave reactions for acetic acid. The insoluble portion when heated with a little amylic alcohol

gave an ethereal odour of apples. The reactions thus indicated the presence of acetic and valerianic as the acids of the esters. These acids were thus in combination with the barium as follows:—32·64 per cent. barium acetate, and 67·36 per cent. barium valerianate.

The oil separated after saponification was steam distilled and in the portion which came over, the odour of geraniol was most prominent; the distilled water also had an odour strongly resembling that of rose water. When mildly oxidised with bichromate of potassium in sulphuric acid, the aldehyde citral was readily formed. It thus appears that geraniol is the only alcohol in these esters, and that it is in combination with both acids in the oils of the Angophoras.

A portion of the crude oil was acetylated in the usual way and the saponification of this gave results indicating that 5·1 per cent. of free geraniol was present in the oil of this species.

From the above determinations the composition of the oil of *A. melanoxyton* may be stated as follows:—

	Per cent.
Pinene = 72·0
Free geraniol = 5·1
Geranyl acetate = 6·9
Geranyl valerianate = 9·6
Water, volatile aldehydes and low-boiling ester	= 1·0
Sesquiterpene and undetermined = 5·4
	100·0

Power and Kleber¹ show geraniol to be present in the oil of *Sassafras* leaves in combination with both acetic and valerianic acids.

ANGOPHORA SPECIES.

This species, which grows in the neighbourhood of Bingara, New South Wales, (370 miles north of Sydney), is

¹ Pharm. Review, XIV, p. 103.

considered by my colleague, Mr. R. T. Baker, to be new to science, and it is his intention to describe it before the Linnean Society of this State. As the oil is similar in constitution to those of the other species of *Angophora*, it may be described here.

Chemistry.—The material was forwarded by the Museum collector from Myall Creek, near Bingara, 370 miles north of Sydney. It was cut as for commercial oil distillation.

The average yield of oil was 0.13 per cent. The crude oil was, in odour and appearance, identical with that of *A. Bakeri*. The chief constituents were also identical with those of that species, with the exception that the pinene was present in greater quantity, and the ester in correspondingly less amount. Phellandrene and cineol were, of course, both absent.

The crude oil had specific gravity at 15° C. = 0.8703; rotation $a_D = + 36°.3$; refractive index at 20° = 1.4669; and was insoluble in 10 volumes 80 per cent. alcohol.

On the rectification of 100 cc., the usual amount of acid water and volatile aldehydes, together with the constituent of pear-like odour, came over below 155° C. (corr.). Between 155–157°, 60 per cent. distilled, and between 157–165°, 21 per cent. came over. These fractions gave the following results:—

	Sp. gr. at 15° C.	Rotation a_D	Ref. index at 17° C.
First fraction	0.8645	+ 37°.9	1.4665
Second fraction	0.8679	+ 37°.3	1.4669

These two mixed fractions were again rectified and the large portion distilling at 156° separated. This had specific gravity at 15° = 0.8618; rotation $a_D + 38°.1$; and refractive index at 18° = 1.4655. The nitrosochloride melted at the same temperature as those from the pinenes of the other species. The indications are, therefore, that over 80 per

cent. of the oil of this species of *Angophora* consists of pinene.

The saponification number for the esters and free acids was 18·9, thus showing that the esters were present in somewhat less amount than in the oils of either *A. Bakeri* or *A. melanoxylon*.

ANGOPHORA LANCEOLATA.

This species was described by Cavanilles in 1797. It is a common tree in the neighbourhood of Sydney, and grows principally on the Hawkesbury Sandstone formation. This kind of acid soil is the one it naturally selects by choice, and throughout its wide distribution it still clings to the sandstone. In the district around Warialda, where the low hills are capped with sandstone, this tree is also found growing. It is the only *Angophora* with a smooth bark; all the others have thick, semi-fibrous, soft barks.

Chemistry.—Material of this species for oil distillation was collected at the Military Reserve, Mosman, Sydney, in the month of June. The yield of oil was very small, equalling only 0·013 per cent. It was a somewhat thick oil and with such a small amount it was difficult to separate. The specific gravity of the crude oil at 15° C. = 0·927; and the refractive index = 1·4946; the oil was insoluble in 10 volumes 80 per cent. alcohol. These results indicate a considerable amount of the sesquiterpene. The saponification number of the esters and free acid by boiling was 24·2; and in the cold with two hours contact 10·1. The secondary odour of the separated saponified oil was that of geraniol, so that judging from the results with the other oils, it may be considered that the geranyl-acetate equalled 3·53 per cent., and the geranyl-valerianate 5·99 per cent.

The available oil was then distilled, and 4 cc. obtained, boiling between 157 - 163° C. (corr.). This had a pinene

odour; specific gravity at $15^{\circ} = 0.8661$; rotation $a_D = +33.8$; and refractive index at $16^{\circ} = 1.4697$. The indications are, therefore, for pinene similar in physical properties to that distilled from other species of *Angophora*, and although the rotation is somewhat less, yet, this is due largely to incomplete rectification, owing to the want of sufficient material.

Material of this species was also procured from Warialda, New South Wales (460 miles north of Sydney). It was forwarded by the Museum Collector in the month of April. The amount of oil was very small, equalling only 0.005 per cent. As such a small quantity of oil was available nothing further was done with it, but it resembled strongly the oil of this species recorded above.

As already stated no oil was obtained from either *A. cordifolia* or *subvelutina*, and only traces from *A. intermedia*.

Summary of Results.

The general results obtained with the crude oils of the three chief oil bearing species of *Angophora* are here tabulated for means of ready reference.

	Rotation a_D	Sp. gr. at 15°	Ref. index.	S.N. of esters.
<i>A. Bakeri</i>	+ 35.6	0.8719	1.4660 at 22°	33.6
<i>A. melanoxylon</i>	+ 24.9	0.8809	1.4678 at $21^{\circ}.5$	42.5
<i>A. sp.</i>	+ 36.3	0.8703	1.4669 at 20°	18.9

All these oils are insoluble in 10 volumes 80 per cent. alcohol by weight. The differences are but slight when the increased amount of ester in the oil of *A. melanoxylon* and the less amount in the oil of the unnamed species are considered.

Little is yet known of the influence which different times of the year may exert on the oils of the *Angophoras*, although it is not expected that this would influence the results to any great extent.

The finally rectified pinenes of all the species agree very closely in general characters, and this is well shown when the results are tabulated:—

	Rotation a_D	Sp. g. at 15°	Ref. index.	Sp. rota. $[a]_D$
<i>A. Bakeri</i>	+ 37°·5	0·8612	1·4658 at 18°	+ 43°·54
<i>A. melanoxylon</i>	+ 37°·9	0·8615	1·4642 at 19°	+ 43°·99
<i>A. sp.</i>	+ 38°·1	0·8618	1·4655 at 18°	+ 44°·21
<i>A. lanceolata</i>	+ 33°·8	0·8661	1·4697 at 16°	...

The higher specific gravity, refractive index, and lower rotation of the pinene from *A. lanceolata* is accounted for by the difficulty in sufficiently rectifying the small amount of oil available. There seems, however, no reason to suppose that the physical properties of the fully rectified pinene from this species, would differ from that of the other species.

The essential oils from the oil-yielding species of *Angophora* are thus seen to be very similar in chemical constituents and in general characters.

I am indebted to my colleague, Mr. R. T. Baker, F.L.S., for the botanical information contained in this paper, and for the authenticity of the material worked upon.



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