

ON THE PINENES OF THE OILS OF THE GENUS
EUCALYPTUS.—PART I.

By HENRY G. SMITH, F.C.S., Technological Museum, Sydney.

[Read before the Royal Society of N. S. Wales, October 5, 1898.]

THE following paper deals with the investigation of both dextro-rotatory and lævorotatory pinenes found existing in the oils of two new species of *Eucalyptus* growing in New South Wales.¹

The occurrence of *Eucalyptus* oils consisting almost entirely of the terpene pinene, is remarkable, and will assist to a very large extent, in enabling us to trace the origin and formation of the several constituents found existing in *Eucalyptus* oils. That a connection does exist, running through the whole series, seems probable, and it is only by carrying out investigations on oils of undoubted material, that a correct scientific knowledge can be obtained in this direction.

The group of *Eucalyptus* trees to which these two species belong is known vernacularly as the 'Stringybarks,' and both the species form part of a chemical sub-group of the botanical class of the *Eucalypts* known as the *Renantheræ*, or those having kidney-shaped anthers.

We can derive no further help from the investigation of the kinos of this group, because the exudations from all the *Eucalypts* belonging to the *Renantheræ* appear to be identical in composition; but the constituents of the oils indicate a sharp distinction. The terpene composing the oils of these two species is principally pinene; not a trace of phellandrene could be detected in them, and so we are enabled to differentiate them from the oils obtained from those trees belonging to the *Renantheræ*, such as *E. amyg-*

¹ Vide R. T. Baker, F.L.S., on two New *Eucalypts*—Proc. Linn. Soc., N.S.W., September 1898.

dalina, *E. piperita*, *E. coriacea*, etc., the oils of which consist more or less largely of the terpene phellandrene, and those that contain only a small quantity of pinene, or perhaps none at all. Although the two species from which these pinenes were obtained are types, both botanically and chemically, yet it is not to be supposed that oils containing pinene are all devoid of phellandrene, such not being the case. A variety of the Rylstone species (*E. lævopinea*)¹ was obtained from Barber's Creek, the oil of which was found to contain a small quantity of phellandrene, although consisting almost entirely of the lævorotatory pinene identical with the pinene obtained from the type species. It is worth notice that oils containing phellandrene are generally light coloured in their crude state, while those not containing phellandrene are often reddish in colour. This colour is readily removed by agitating with potash, and it is of an acid character. It is not derived from the eucalyptol(?cineol), as about the same minute quantity of eucalyptol was found in the higher boiling portions of the Rylstone oil (a red oil) as was found in that of its variety (oil almost colourless, being light yellowish with a tinge of green). We cannot at present derive much information from the colour of the crude Eucalyptus oils, although it may be found eventually to have some bearing on their constitution.

The almost entire absence of eucalyptol in the oils of certain members of this group, is also very characteristic, and it seems possible that we may eventually be able to decide how this constituent of Eucalyptus oils increases in quantity, as we go up or down the series.

This investigation was carried out on material obtained from Barber's Creek; from Currawang Creek near Braidwood; and from Nullo Mountain near Rylstone, all in this Colony.

The material from Barber's Creek, from which the dextrorotatory pinene was obtained, was botanically identical with that of the species forwarded by the Museum collector from Currawang

¹ Named *E. lævopinea* var. *minor* by Mr. Baker, loc. cit.

Creek. This species was described by my colleague Mr. R. T. Baker, (*loc. cit.*) under the name *Eucalyptus dextropinea*, a recognition to the science of chemistry for assistance rendered in the determination of species of this important and difficult genus.

From the results of the determinations of the oils from the leaves of *E. dextropinea*, from both Barber's Creek and Currawang Creek, localities over one hundred miles apart, it might be inferred that the oils were obtained from identical material, and the results again emphasize the fact that the same species of *Eucalyptus* gives an oil identical in composition, no matter where grown, if collected at the same time of the year. We have other evidence that this is true, and the determination of the oil, together with that of the other chemical constituents of the tree, will be of great assistance in the determination of unknown species. The genus is so prolific in chemical constituents, both crystallised and liquid, that possibly many of the difficulties experienced in the study of the Eucalypts may be effectually removed when the several products of individual trees shall have been systematically investigated by the chemist. The results brought forward in this paper are an instance in point, as the oils of the type species from the three localities possess great similarity; they all consist principally of pinene, and in colour, odour, specific gravity, etc., resemble each other most markedly, yet while the pinene from both the Barber's and Currawang Creeks material rotates the ray of light to the right, the pinene from the Rylstone *Eucalypt* rotates the ray to the left. The Rylstone material was collected under the personal supervision of Mr. Baker. We cannot admit that a tree giving an oil consisting principally of a dextrorotatory pinene having a specific rotation $= [\alpha]_D + 41.2^\circ$ is identical with one giving an oil, also consisting principally of a pinene, that is lævorotatory to even a greater degree, although the differences in some of the botanical material may not be very marked. Mr. Baker, however, informs me that the timber of *E. lævopinea* is excellent, while that of *E. dextropinea* is a comparatively worthless timber.

The late Baron von Mueller, whose knowledge of the Eucalypts of Australia was unique, recognised years ago, the possible assistance the botanist might derive in determining differences in species by the results of chemical investigation of their constituents. The reference is so important in connection with the results brought forward in this paper, that I indicate the paragraph, published by the Baron in 1879.¹

"*E. obliqua* is distinguished from *E. piperita* by . . . and perhaps by anatomic, histologic, and chemical peculiarities of the bark and wood which characteristics remain yet more comprehensively to be studied," The italics are mine.

Since that time much has been done in determining the chemical characteristics of several of the species. The results of the present research not only assisted in finally determining the species, but present possibilities of commercial value in determining the utility or otherwise of the products of the tree by the determination of its chemical constituents. According to Mr. Baker, the Rylstone specimen (*E. laevopinea*) has certain botanical affinities with those of *E. macrorhyncha*, but chemically these two trees are quite distinct, and the importance of this is apparent when it is stated that the leaves of *E. laevopinea* do not contain myrticolorin like those of *E. macrorhyncha*, nor does the oil contain eudesmol and other constituents found in the oil of *E. macrorhyncha*.

The presence of a pinene in the oil from *E. globulus* was detected some time ago. M. Cloez in 1870² published the first detailed observations relative to the oil of *E. globulus*. This research is now of historic interest from the fact that he obtained a hydrocarbon $C_{10}H_{16}$ boiling at 165° C., by distilling his so-called eucalyptol with P_2O_5 . This terpene he called eucalyptene. Afterwards Faust and Homeyer³ gave the same name to a terpene from Eucalyptus oil which according to them is a terebenthene, being readily polymerised by sulphuric acid. Later, Wallach and Gildmeister⁴

¹ Eucalyptographia, Decade III., Art. *Eucalyptus piperita*.

² Compt. rend. 1870, 687 and Journ. de Pharm. and Chimie 1870, XII. 201.

³ Ber. 7, 63, 1429. ⁴ Ann. 246, 265 - 284. Abst. Chem. Soc. 1888, 54, 1205.

stated that the hydrocarbon, eucalyptene, from *Eucalyptus globulus*, is identical with dextropinene.

In 1895 Bourchardat and Tardy¹ carried out experiments with the hydrocarbon found occurring in small quantity in the oil of *Eucalyptus globulus*, and arrived at the conclusion that it has the properties of lævorotatory terebinthene found in French oil of turpentine, but with an almost equal opposite rotation. They give its boiling point as 156 – 157° C.; its density as 0.870 at 0° C. and 0.865 at 18° C.; and its specific rotation at 15° C. as $[\alpha]_D + 39^\circ$. They give Riban's determination² for the specific rotation of lævorotatory terebinthene as -40.3° . It appears, therefore, from the results obtained by these authors on this hydrocarbon from the oil of *E. globulus*, and those obtained in this research on the same hydrocarbon from the oil from *E. dextropinea*, that these dextro-rotatory pinenes obtainable from members of two distinct groups of Eucalypts are identical, and that the dextrorotatory pinene from the whole genus Eucalyptus, is a physical isomeride of the lævorotatory pinene (terebinthene) obtained from French oil of turpentine, and possibly also of the lævorotatory pinene of the Eucalypts, although this lævo form has, so far as observed, a higher specific rotation.

As phellandrene has not yet been detected in an Eucalyptus oil containing a highly dextrorotatory pinene, and as the opposite highly lævorotatory pinene has been found existing with phellandrene in several members of the Stringybark group of Eucalypts, it appears that we must arrive at the conclusion that the dextro-rotatory pinene is present in greater abundance in Eucalyptus oils of the globulus type, and that are rich in eucalyptol, particularly as those oils are usually dextrorotatory, and eucalyptol having no rotation, the activity must necessarily be due to the terpenes. Although it had been assumed that terpenes having right and left rotation were probably present in these oils, yet, no proof had previously been forthcoming that this was so, and the isolation of

¹ Compt. rend. 1895, 120, 1417 – 1420.

² Comp. rend. 78, 788; 79, 314.

the corresponding lævorotatory pinene appears now to conclusively show that such is the case, and that we have existing in the oils of the Eucalypts two pinenes, one of which is probably the physical isomeride of the other.

By obtaining the nitrosochloride I have been able to detect the presence of pinene in nearly all the oils of the class of Eucalypts to which *E. globulus* belongs, such as *E. Bridgesiana*, *E. gonio-calyx* etc., but it is only present in these oils in very small quantity, the greater portion of their constituents being terpenes other than pinene, and eucalyptol. The two species of Eucalyptus from which these present pinenes were obtained form part of a different group altogether from that to which *E. globulus* belongs. The Stringybarks are a group the investigation of whose oils has been of great assistance in extending our knowledge of the constituents of the oils of the genus.

Eucalyptol is almost entirely absent from the oils of the two species now under consideration, as it was only possible to detect its presence in the higher boiling portions, and even then it could not be detected by phosphoric acid, its presence in minute quantity being determined by iodol and also by bromine. Whether at other times of the year eucalyptol would be found to be present in greater quantity is of course a matter for future investigation.

On redistilling the oil from the Currawang Creek sample 63 per cent. was obtained between 156° and 162° C.¹ and 25 per cent. more distilled between 162° and 172° C. On distilling the oil from Barber's Creek under exactly the same conditions, 62 per cent. was obtained between 156° and 162° and 25 per cent. more between 162° and 172° C. These oils were practically identical, although the oil from the Barber's Creek sample was rather more dextrorotatory than that from Currawang Creek, but this difference might be expected, because our experiments show that the oils obtained from the trees of the same species growing together under exactly similar conditions have not the same rotation, but

¹ The temperatures given in this paper are all corrected, and stated to the nearest whole degree.

differ at times to a few degrees; constancy in optical rotation is not experienced in these oils. The oil from the Rylstone sample, rectified under exactly similar conditions, gave 60 per cent. between 157° and 164° C., and 28 per cent. more between 164° and 172° C., so that the temperature required to distil the lævoro-rotatory pinene is a little higher than that necessary to distil the dextrorotatory form.

These oils, from the type species, are red in colour, which from their general appearance might indicate the presence of eucalyptol; it was a surprise to find an almost entire absence of that constituent.

The dextrorotatory pinene.

The leaves and terminal branchlets of *Eucalyptus dextropinea*, from Currawang Creek, collected and distilled early in August 1898, gave 0.825 per cent. of oil, or 100 lbs. of leaves gave $13\frac{1}{2}$ ounces. On rectification (after discarding the first two per cent. which came over below 156° C., and which contained but a minute quantity of aldehydes) the following results were obtained:—

63 per cent.	distilled between $156 - 162^{\circ}$ C.	= first fraction
25	„ „ „	$162 - 172^{\circ}$ C. = second fraction
Specific gravity,	first fraction, at 17° C.	= 0.8655
„ „	second „ „	= 0.8710
„ „	crude oil „	= 0.8743
„	rotation, first fraction	+ 38.18°
„	„ second „	+ 36.34°

The leaves and branchlets of *E. dextropinea* from Barber's Creek, collected and distilled at end of July 1898, gave 0.850 per cent. of oil, or 100 lbs. gave $13\frac{2}{5}$ ounces. On rectification (after discarding the first two per cent. distilling below 156° C.) this sample of oil gave:—

62 per cent.	distilling between $156^{\circ} - 162^{\circ}$ C.	= first fraction
25	„ „ „	$162^{\circ} - 172^{\circ}$ C. = second fraction
Specific gravity,	first fraction, at 17° C.	= 0.8676
„ „	second „ „	= 0.8744
„ „	crude oil „	= 0.8763
„	rotation, first fraction,	= + 39.59°
„	„ second „	= + 37.06°

From the above results it was apparent that the two samples might be considered identical oils, only varying to the same extent as is usually found with oils of the same species of *Eucalyptus*, at the same time of the year ; the further investigation was, therefore, continued on the oil from the Barber's Creek sample alone. On again rectifying the first fraction of the oil from Barber's Creek (that portion boiling between 156° – 162° C.) the following results were obtained :—

28 per cent.	distilled between	156° – 157° C.	= first fraction
30	„ „ „	157° – 158° C.	= second fraction
23	„ „ „	158° – 160° C.	= third fraction
Remainder not distilled.			

Specific gravity,	first fraction	at 18° C.	= 0.8632
„	second „	„	= 0.8644
„	third „	„	= 0.8660
„	rotation, first fraction,	= $+40.43^{\circ}$	
„	second „	= $+40.08^{\circ}$	
„	third „	= $+39.03^{\circ}$	

The third and final rectification, taking the fraction 156° – 158° C., gave 50 per cent. of an oil boiling between 156° – 157° C. This gave results as follows :—

Specific gravity	at $\frac{4}{4}^{\circ}$ C.	= 0.8750
„	„ $\frac{1.8}{16}^{\circ}$ C.	= 0.8629

Specific rotation, using the specific gravity obtained at 18° C. = $+41.2^{\circ}$

The boiling point of this dextrorotatory pinene may be stated at 156° C. and to have a specific rotation for sodium light $+41.2^{\circ}$.

A sample of commercial dextrorotatory oil of turpentine containing the pinene Australene was rectified in the same apparatus and under exactly similar conditions, and using the same correction; 35 per cent. distilled between 156° – 157° C. This fraction had a specific gravity at 20° C. = 0.8624 and a specific rotation $+13.8^{\circ}$.

The levorotatory pinene.

The leaves and branchlets of *Eucalyptus levopinea*, collected by my colleague, Mr. R. T. Baker, at Rylstone in Aug. 1898, distilled

a few days afterwards, gave 0.66 per cent. of oil,¹ or 100 lbs. gave 10½ ounces. On rectification (after discarding two per cent. that came over below 157° C.) the following results were obtained:—

60	per cent.	distilled between 157° – 164° C.	= first fraction
28	„ „ „	164° – 172° C.	= second fraction
Specific gravity, first fraction, at 18° C. = 0.8676			
„	„	second „	„ = 0.8725
„	„	crude oil	„ = 0.8732
„	rotation,	first fraction,	– 46.74°
„	„	second „	– 44.3°

On again rectifying the first fraction (that portion distilling between 157° – 164° C.) the following results were obtained:—

42	per cent.	distilled between 157° – 160° C.	= first fraction
35	„ „ „	160° – 164° C.	= second fraction
Remainder not distilled.			

Specific gravity first fraction at 19° C. = 0.8630

„ „ second „ „ = 0.8641

„ rotation, first fraction – 47.86

„ „ second „ – 47.38

The third and final rectification, again taking the first fraction, gave 50 per cent. of an oil boiling between 157° – 158° C. This gave results as follows:—

Specific gravity at $\frac{4}{4}$ ° C. = 0.8755

„ „ $\frac{19}{16}$ ° C. = 0.8626

Specific rotation taking density at 19° C. – 48.63.

The boiling point of this lævorotatory pinene may be stated to be 157° C. and the specific rotation for sodium light – 48.63°. This lævorotatory pinene thus boils at one degree higher temperature than the dextrorotatory form, and has a higher reverse rotation.

The same apparatus was used for the whole of the redistillations, and the results were obtained under exactly similar conditions, and upon the same quantity of oil. The redistillations were not

¹ This Eucalypt is known locally as “Silver Top Stringybark.”

carried out under reduced pressure, so that they are strictly comparative. The temperatures given are those of the oil at the time the specific gravities were taken, and all are given against water at 16° C., except of course the determination of the pinenes at 4° C. The rotations were taken in a 200 mm. tube, the specific rotations being calculated from $\frac{a}{l \cdot d}$ the temperatures of (*d*) being those stated in the paper.

On mixing equal volumes of the two pinenes, the rotation in the 200 mm. tube was -6.2° showing that the dextrorotatory pinene had neutralised exactly the same amount of rotation of the lævorotatory form.

By referring to the results it will be seen that the specific gravities of the several fractions of the two oils, their rates of distillation and the percentage amounts distilling below 172° C. are fairly concordant, with the exception that the oil from *E. lævopinea* boils at a slightly higher temperature than that from *E. dextropinea*. The real difference between these Eucalyptus pinenes is their extreme opposite rotation, and while the specific rotation of the dextrorotatory Eucalyptus pinene is twice as great as that observed in the pinene (australene) from dextrorotatory oil of turpentine, the specific rotation of the lævorotatory Eucalyptus pinene is greater than that of the pinene (terebinthene) from lævorotatory oil of turpentine.

The Eucalyptus pinenes are identical in appearance, being colourless, mobile liquids, having an odour with a slight resemblance to ordinary oil of turpentine; the dextropinene has more markedly the odour of ordinary oil of turpentine than has the lævorotatory form.

The nitrosochlorides.

One volume of the pinene was added to one volume of amyl nitrite and the mixture dissolved in two volumes of glacial acetic acid; this was cooled in a freezing mixture of ice and salt, and concentrated hydrochloric acid and glacial acetic acid, in equal parts, slowly added while the blue colour remained; it was then

allowed to crystallise in the freezing mixture. The crystals from both forms were identical in every respect and melted quite sharply at 103° C. The product from the dextropinene was heated with alcoholic soda and the nitrosoterpene thus formed, when crystallised from alcohol, melted at 128° – 129° C.

The hydrates.

About four or five volumes of the pinenes were agitated for two or three days with one volume of nitric acid (sp. gr. 1.25) added to half its quantity of alcohol; the solutions were then allowed to slowly evaporate in open vessels. After some days fine crystals were formed in some quantity with both forms. These were rhombic crystals, and when purified by recrystallisation from alcohol, melted at 116° – 117° C. with elimination of water. On melting these terpene hydrates and taking the melting point of the terpenes thus formed, it was found that they both melted at 102° – 103° C. and that they both sublimed in crystals. The terpene hydrate from either form was soluble in boiling water, in alcohol and in ether; both behaved chemically in exactly the same manner in every respect.

A vapour density determination gave almost the identical figures required for the molecule $C_{10}H_{16}$.

The monohydrochloride was prepared from the dextropinene, this had the odour and appearance of ordinary camphor and melted at 123° – 124° C.

Crystalline tetrabromides could not be obtained by ordinary methods.

Polymerisation of the Oil.

A portion of the crude oil, *E. dextropinea* from Barber's Creek was treated with a very small quantity of sulphuric acid; much heat was generated, and the oil was much darkened. After the action was thought to be complete the product was well washed, dried, and distilled. It was then found that polymerisation had taken place, the boiling point of the oil being raised considerably. In the original crude oil from Barber's Creek there was obtained

on redistillation, no less than 77 per cent. below 165° C., (see table), whereas in the polymerised oil only 7 per cent. was obtained below 165° C., or tabulating the results :—

160° C.	to	162° C.	=	3	per cent.
162	„	165	=	7	„
165	„	167	=	25	„
167	„	172	=	58	„
172	„	178	=	64	„

The fraction obtained between 165° C. and 178° C. was found to have been reduced in rotatory power by about half. Originally the rotation for the whole fraction on the first distillation was $+66.5^{\circ}$ in a 200 mm. tube. After polymerisation of the oil the rotation in the same tube was $+32.3^{\circ}$. Evidently the polymerisation had not been complete.

From the results of the above determinations it is apparent that these Eucalyptus pinenes are chemically identical with terebenthene and australene, and only differ from them by having greater rotation. We thus arrive at the conclusion that the pinenes from the oils of the Eucalypts (N.O. Myrtaceæ), appear identical with those obtained from Pinus (N.O. Coniferæ).

As the Eucalyptus pinenes lend themselves so readily to polymerisation by acid, and as the crude oils from all the Eucalypts contain organic acids in some form, it is probable that certain constituents found in Eucalyptus oils are the result of a process of natural polymerisation of these pinenes in the oil cells of the leaf. It may be that eventually structural differences in the molecule may be determined between the Eucalyptus pinenes and those obtained from the Coniferæ, as indicated by the natural alteration products. Further research may decide this, but it does not appear that we shall receive much assistance from the preparation from these pinenes of known chemical compounds, because they, so far, have proved themselves identical with those obtained from the pinenes from the Coniferæ.

It may be well for the purpose of identification to retain specific names for these *Eucalyptus* pinenes, and as *Eucalyptene* stands for the dextropinene, I suggest the name *Eudesmene* for the lævotatory pinene.

The discovery of *Eucalyptus* oils consisting principally of pinenes prevents the determination of sophistication of *Eucalyptus* oils with commercial oil of turpentine ; if its presence was proved there is no reason why it should not have been obtained directly from *Eucalyptus* leaves, and need not have been the effect of adulteration. The necessity of determining the constituents of *Eucalyptus* oils to be used medicinally is thus again emphasized.

I wish to express my thanks to my colleague Mr. R. T. Baker, for botanical assistance in the preparation of this paper.

Table I., Results of the Oils of Both Species.

Crude Oil.		First Rectification.			Second Rectification.					Third Rectification—Pinenes.			
Percentage Yield.	Specific gravity, Crude Oil.	[a] _D first fraction.	Specific gravity, second fraction.	[a] _D second fraction.	Specific gravity, first fraction.	[a] _D first fraction.	Specific gravity, second fraction.	[a] _D second fraction.	Specific gravity, third fraction.	[a] _D third fraction.	Specific gravity, $\frac{4}{4}$ ° C.	Specific gravity, $\frac{1.8}{1.6}$ ° C.	[a] _D at 18° C.
0.825	0.8743 at 17°C.	+ 38.18°	0.8710 at 17°C.	+ 36.34°	...	...	...	...	...	...	...	...	...
				<i>Eucalyptus dextropinea</i> , Currawang Creek.									
0.850	0.8763 at 17°C.	+ 39.59°	0.8744 at 17°C.	+ 37.06°	0.8632 at 18°C.	+ 40.43° at 18°C.	0.8644 at 18°C.	+ 40.08°	0.866 at 18°C.	+ 39.03°	0.875	0.8629	+ 41.2°
				<i>Eucalyptus dextropinea</i> , Barber's Creek.									
				<i>Eucalyptus laevopinea</i> , Rylstone.									
0.66	0.8732 at 18°C.	- 46.74°	0.8725 at 18°C.	- 44.3° at 19°C.	0.863 at 19°C.	- 47.86° at 19°C.	0.8641 at 19°C.	- 47.38°	...	...	0.8755	0.8626 at 19°C.	- 48.63° at 19°C.

Table II. gives the results of the redistillations of the crude oils of the two species of Eucalypts. Temperatures are corrected to the nearest whole degree. The results are percentages obtained from one temperature to another. The (*a*) denotes the commencement of the second fraction, the (*b*) that of the third fraction.

Below 156° C.	157	158	159	160	161	162	163	164	165	166	167	172	183	204
2	7	14	23	37	48	65	71(a)	75	79	83	85	90	93(b)	96
					<i>Eucalyptus dextropinea</i> , Currawang Creek.									
2	7	13	22	34	46	64	70(a)	74	77	80	83	89	92(b)	96
					<i>Eucalyptus dextropinea</i> , Barber's Creek.									
					<i>Eucalyptus laevopinea</i> , Rylstone.									
Below 157° C. 2%		...	...	10	22	41	54	62	69(a)	74	79	90	93(b)	96



Smith, Henry George. 1898. "On the pinenes of the oils of the genus Eucalyptus, Part I." *Journal and proceedings of the Royal Society of New South Wales* 32, 195–208. <https://doi.org/10.5962/p.359297>.

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DOI: <https://doi.org/10.5962/p.359297>

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