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5. Essential Oils from the Queensland Flora  
Part XIV.—*Eucalyptus conglomerata*

BY

F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

6. 1- $\alpha$ - Phellandrene and its Monohydrochloride  
Part I.

BY

N. C. HANCOX, B.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

7. A New Derivative of Terpinen-4-ol

BY

N. C. HANCOX, B.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

8. Essential Oils from the Queensland Flora  
Part XV.—*Backhousia Bancroftii* and *Daphandra rapandula*

BY

F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

9. Essential Oils from the Queensland Flora  
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ESSENTIAL OILS FROM THE QUEENSLAND FLORA.

PART XIV.—EUCALYPTUS CONGLOMERATA.

*By*

F. N. LAHEY, M.Sc.,

and

T. G. H. JONES, D.Sc., A.A.C.I.

*Department of Chemistry, University of Queensland.*

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*Essential Oils from the Queensland Flora—Part XIV.—  
Eucalyptus conglomerata.*

BY F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

Department of Chemistry, University of Queensland.

[Read before the Royal Society of Queensland, 28th November, 1938.]

THE botanical characters of this Eucalypt have been described by Maiden and Blakely. As pointed out by them, it closely resembles the common stringybark, *Eucalyptus eugenioides*, except that it favours sandy, swamp country, whence its common name—Swamp Stringybark. Unlike *E. eugenioides*, however, its distribution seems to be limited to a few small areas, those recorded being at Beerwah (Queensland) and Glen Innes (New South Wales).

Mr. C. T. White, Government Botanist, drew our attention to it, growing in the swamps around Beerwah. It was found easy to distinguish it from *E. eugenioides* by smelling the crushed leaves of each, for the odour of the former is very unusual and, if anything, unpleasant, while that of the latter is the common cineol-pinene odour. The oil from the leaves of this Eucalypt has been investigated.

The yield of oil obtained from the leaves was low, ranging from .12 to .2 per cent.

The principal constituents identified in the oil are 1- $\alpha$ -phellandrene, two sesquiterpenes, a sesquiterpene alcohol, a trace of cineol, and an unidentified alcohol. Pinene was not identified, although it may have been present in amounts too small to be recognised. Of particular interest was the isolation of a white crystalline solid from the aqueous distillate from the steam distillation of the leaves. The solid appeared to be soluble in water, for it came out of solution very slowly on standing, but was rapidly thrown out on the addition of salt. The same solid was also found in the residue in the still after the first distillation of the oil. The present paper deals only with the preliminary work carried out on this solid. The work so far seems to indicate that the substance has not been described previously, and consequently a thorough investigation into its properties and constitution is necessary. This work is in progress.

#### EXPERIMENTAL.

Leaves and terminal branchlets weighing 250 lb. were subjected to steam distillation, and yielded 140 c.c. of oil. The water from the steam distillation was kept and coarse salt dissolved in it. The crude white solid which came out was filtered off. This weighed 7 grams. Three hundred and forty pounds of leaves, collected in November, 1937, yielded 305 c.c. of oil and 15 grams of crude solid from the aqueous distillate.

The two samples of oil had the following constants:—

A				B			
$d_{15.5}$	..	..	.9451	$d_{15.5}$	..	..	.9547
$[\alpha]_D$	..	..	5.7	$[\alpha]_D$	..	..	7.3
$n_D^{20}$	..	..	1.4980	$n_D^{20}$	..	..	1.4986
Ester Value	..	0		Ester Value	..	0	
Ester Value after	62.8			Ester Value after	56		
Acetylation				Acetylation			
Acid Number	..	0		Acid Number	..	0	

The oil (B) was subjected to fractional distillation at 2mm. pressure, when the following fractions were obtained:—

	$d_{15.5}$	$[\alpha]_D$	$n_D^{20}$
1. Oil collected in liquid ammonia trap	..	.8636	18.5
2. 70–80°C.	..	..	..
3. 80–92°C.	..	..	..
4. 92–112°C.	..	..	..
5. 112–128°C.	..	..	..

.. insufficient for determinations  
 .. .921 11 1.5033  
 .. .961 6.3 1.4984  
 .. (a thick green oil).

The residue in the flask solidified on cooling. After removing the adhering oil on a porous plate and purifying further by recrystallisation, the solid proved to be identical with that separated from the aqueous distillate from steam distillation.

The characteristic odour of pinene was not observed in the oil collected in the liquid ammonia trap. Furthermore, the oil failed to yield any sign of a nitrosochloride. This fraction, however, readily gave a nitrosite in good yield, which when recrystallised from acetone—water, melted at 112°C. and was identical with 1- $\alpha$ -phellandrene- $\alpha$ -nitrite.

The remainder of this fraction was shaken with 50 per cent. resorcin solution. From this was recovered a trace only of cineol. No solid derivative of cineol was formed, but the unmistakable odour and the method of extraction are taken as proof of its presence.

The oil recovered after this treatment (1½ c.c.) was oxidised with permanganate, but no trace of pinonic acid was found.

The small fraction b.p. 70–80°C. at 2 mm. had a very pleasant odour and gave no reaction with 2, 4-dinitro-phenylhydrazine. Combustion results indicated the presence of an oxygenated body. As only one c.c. was available, an attempt was made to identify the probable alcohol by means of its naphthyl urethane. Although a small quantity of urethane was obtained, it was never isolated in a sufficiently pure state to be identified by its melting point.

Fractions 3, 4, and 5 gave on repeated fractionation three principal fractions, two of which contained sesquiterpenes, and the third a sesquiterpene alcohol. These fractions had the following constants:—

(a) 80–82°C. (distilled over potassium	$d_{15.5}$	.9144
	$[\alpha]_D$	–8.4
	$n_D^{20}$	1.4913
(b) 91½–92°C. (distilled over potassium)	$d_{15.5}$	.9272
	$[\alpha]_D$	+ 22.1
	$n_D^{20}$	1.4950
(c) 107–109°C. .. .. .	$d_{15.5}$	.986
	$[\alpha]_D$	+8.2

The constants of fraction (a) somewhat resembled those of aroma dendrene. Five c.c. of this oil in carbon tetrachloride were treated with ozone until absorption was complete. The oil recovered after decomposition of the ozonide with warm water had the characteristic odour associated with aromadendrone, although none of the latter crystallised out even when kept for two months in the ice-chest.

Ten c.c. of the same fraction were treated with selenium at 280°C. for two hours. A small quantity of an azulene (m.p. of picrate 120°C.) was separated by means of phosphoric acid. The main bulk of the recovered oil had density .9062 and gave combustion results indicating it to be a  $C_{15}H_{26}$  body.

Combustion results:—Found—	C 86.9	H 12.3
$C_{15}H_{26}$ requires	C 87.38	H 12.62

Similar results were obtained with the other sesquiterpene (b.p. 91½-92°C. at 2 mm.) on treatment with selenium. The recovered oil this time had  $d_{15.5}$  .9156.

Combustion results:—Found—	C 86.9	H 12.26
$C_{15}H_{26}$ requires	C 87.38	H 12.62

No trace of either cadalene or eudalene could be found in either case.

The results of combustion of fraction (c) supported the belief that it was a sesquiterpene alcohol.

Found—	C 80.8	H 11.8
$C_{15}H_{26}O$ requires	C 81.09	H 11.71

On treatment with formic acid under reflux for one hour, the alcohol was converted into a sesquiterpene with the following constants:—

$d_{15.5}$	..	..	..	..	.9208
$[\alpha]_D$	..	..	..	..—	28.2
$n_D^{20}$	..	..	..	..	1.4942

Combustion results—	C 87.7	H 11.9
$C_{15}H_{24}$ requires	C 88.23	H 11.77

*Unidentified Crystalline Solid.*—This solid was removed from the aqueous distillate derived from steam distillation by filtering at the pump. It was purified by recrystallisation from petroleum ether, from which it crystallised in white glistening needles m.p. 63-64°C. The combustion results do not conform closely with any particular formula, and the substance may therefore be a mixture of two homologues. The formula which best fits the results is  $C_{13}H_{18}O_4$ .

Molecular weight determinations by Rast's method gave values of 227 and 246, and by the depression of freezing point of benzene a value of 227 was obtained.

$C_{13}H_{18}O_4$  has molecular weight 238.

Methoxyl results of 39, 38.9, 36, and 39.4 per cent. were obtained. Three methoxyl groups are equivalent to 39.07 per cent. based on formula  $C_{13}H_{18}O_4$ .

On treatment with bromine in carbon tetrachloride the bromine was only slowly absorbed with the evolution of HBr yielding a mixture of bromides which could not be separated by recrystallisation.

On treatment with hot concentrated nitric acid, dense fumes of oxides of nitrogen were evolved. On pouring the resulting solution into water a small quantity of a reddish solid was isolated. This had m.p. 165°C. The amount of this material available was too small for analysis. It was thought that it might be identical with dinitrophenol-trimethyl-ether, a white solid which rapidly turns reddish-brown on keeping and has m.p. 165°C. This substance was synthesised, but greatly depressed the m.p. of the nitro body mentioned above.

Oxidation and other reactions which are expected to throw light on its constitution are at present being carried out, and the results of these will be published at a later date.

#### REFERENCE.

1. MAIDEN, J. H., and BLAKELY, W. F., *Crit. Rev. Gen. Eucalyptus*, Part LXXI., 5, 1929.