

## THE ESSENTIAL OIL OF A PHYSIOLOGICAL FORM OF *EUCALYPTUS CITRIODORA* HOOK.

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Following the announcement of the occurrence of a physiological form of *Eucalyptus citriodora* by two of the authors (Penfold and Morrison, 1948), the investigation described hereunder was undertaken.

The results obtained have confirmed those obtained in the preliminary experiments that the chief constituent of the oil of *E. citriodora* (Type), namely citronellal, has been largely replaced in the new form by an equivalent amount of citronellol and its esters. The amount of foliage available for investigation has been insufficient for a determination of the minor constituents, but these will be dealt with in a subsequent communication. The principal components so far identified are citronellol and its acetic and citronellic acid esters, and citronellal.

Also under investigation are oils from individual trees containing percentages of aldehyde varying from 40 to 50 per cent., percentages which indicate an intermediate position between the form described in this paper and the "Type" oil.

It is worthy of note that the trees, whose foliage yielded essential oils containing only about 10 per cent. citronellal, were observed in their natural habitat growing in close environmental association with trees of normal oil composition (65–85 per cent. citronellal) referred to in this paper as the "Type".

All the trees examined were found to be morphologically indistinguishable from one another, but for purposes of identification, the physiological form described in this paper will be referred to as *Variety "A"*.

### THE ESSENTIAL OIL.

The essential oils obtained by steam distillation of the foliage of eight individual forest trees were almost water white in colour. All possessed a pleasant odour of citronellol modified by that of its esters. The odour differed markedly from the sharp aldehydic odour of citronellal, which is characteristic of the oil of the type species. The yields and range of physico-chemical characteristics, together with those of the "Type" oil for comparison, are shown in Table 1.



TABLE I.  
*Eucalyptus citriodora* Hook., Variety "A".  
Eight Trees from Cordalba, Queensland.

Tree No.	Date Received.	Yield, % on Sample as Received.	$d_{15}^{15^\circ}$	$n_D^{20^\circ}$	$\alpha_D^{20^\circ}$	Sol-ubility in 70% w/w alc. Vol.	Ester No. 1½ hrs. Hot Sap.	Ester No. after Acetyl-ation.	Alde- hyde Content. %	Remarks.
1	12/ 7/48	1.4	0.8855	1.4569	+2.55°	—	120.00	231	0.9	Air dry, leaf only.
2	30/ 7/48	0.8	0.8876	1.4608	+2.1°	—	149.5	228	6.1	Fresh leaves and terminal branchlets.
3	2/11/48	2.0	0.8825	1.4570	+1.5°	1.25	86.5	271	11.0	Do.
4	11/ 1/49	1.8	0.8830	1.4544	+0.7°	1.3	116.0	265	14.0	Fresh leaf only.
5	11/ 1/49	1.6	0.8864	1.4556	+0.8°	1.3	127.0	249	12.0	Do.
6	23/ 1/50	3.0	0.8872	1.4507	+1.01°	1.4	191.4	258	6.0	Air dry, leaf only.
7	23/ 1/50	1.5	0.8736	1.4541	−0.90°	1.7	149.5*	270	11.0	Do.
8	13/ 6/50	3.4	0.8853	1.4521	−0.7°	1.5	163.0	277	14.0	Do.
Type oil		0.5 to 0.75%	0.8640 to 0.8770	1.4511 to 1.4570	+3° to −3°	1.3 to 1.5	12 to 60	230 to 292	65 to 85%	Fresh leaves and terminal branchlets.

## EXPERIMENTAL.

The oil from tree No. 8 was selected for examination. The aldehyde content was determined by the hydroxylamine method of the Essential Oil Sub-Committee of the Society of Public Analysts (1932). The ester number after acetylation was equivalent to 96.2% of acetylatable substances (calculated as  $C_{10}H_{18}O$ ) in the original oil.

Forty millilitres of the crude oil were fractionally distilled at 10 mm., the fractions obtained having the characteristics shown in Table II

TABLE II.

Fraction No.	B.p.	Vol., ml.	$d_{15}^{15^\circ}$	$n_D^{20^\circ}$	$\alpha_D^{20^\circ}$
1	70– 96°	6	0.8666	1.4544	−5.6°
2	95–106°	6	0.8772	1.4536	−4.4°
3	107–109°	24	0.8839	1.4504	+0.64°
Residue	—	3			

*Determination of Citronellal.*

Fraction 1 yielded a semicarbazone, m.p. 84° from petroleum ether, and a yellow 2:4-dinitrophenylhydrazone, m.p. 80° from ethanol, both alone and in admixture with authentic specimens of these derivatives. Fraction 1 thus appears to consist principally of citronellal.

*Determination of Citronellol.*

A portion (20.5 ml.) of the crude oil was saponified with 0.5N alcoholic potassium hydroxide (250 ml.) at room temperature for two days. After dilution with water, 18 ml. of oil were recovered from the solution of potassium salts of the acids derived from the esters. The oil (15 ml.) after drying with anhydrous  $Na_2SO_4$ , was heated for two hours on the steam bath, under a reflux with phthalic anhydride (15 g.) and benzene (15 ml.). The cold reaction mixture was



neutralized with aqueous potassium hydroxide and freed from unchanged oil by extraction with ether. After removal of ether the alcohol was recovered by steam-distillation with excess of sodium hydroxide. Ten millilitres of a colourless oil of pleasant rose-odour were obtained having  $d_{15}^{15^\circ}$  0.8620,  $n_D^{20^\circ}$  1.4556,  $\alpha_D$  +1.71°. These constants correspond closely with those of citronellol. Supporting evidence for the presence of this alcohol was obtained by the preparation of the allophanate, m.p. 106–107°, and the silver salt of the acid phthalate, m.p. 126°. (Mixed melting points showed no depression.) Hence the primary alcohol, free, and combined as ester, consists entirely of citronellol.

*Determination of Acids (Citronellic and Acetic) Combined with Citronellol.*

The solution of potassium salts of the acids derived from the esters was evaporated to a small volume and extracted with ether to remove traces of oil. After removal of residual ether, the solution was acidified with dilute sulphuric acid. About 1.5 ml. of an oily acid separated which was converted directly to its silver salt.

0.1003 g. silver salt yielded 0.0393 g. silver = 39.18% Ag.

Silver citronellate requires 38.99% Ag.

A further specimen of the oily acid was isolated, and had  $b_{10}$  140–153°,  $d_{15}^{15^\circ}$  0.9431,  $n_D^{20^\circ}$  1.4591,  $\alpha_D$  +1.0°.

The benzylthiuronium ester was prepared, m.p. 146–147°, both alone and in admixture with an authentic specimen. This acid is therefore citronellic acid.

The aqueous solution from the separation of the oily acid was steam distilled, the distillate being collected in three fractions. After neutralization with ammonia, each fraction was evaporated to a small volume and the silver salt of the acid prepared.

Fraction 1. 0.1004 g. Ag salt gave 0.0651 g. Ag = 64.84% Ag.

„ 2. 0.2608 g. Ag salt gave 0.1692 g. Ag = 64.88% Ag.

„ 3. 0.1966 g. Ag salt gave 0.1275 g. Ag = 64.85% Ag.

Silver acetate requires 64.67% Ag.

From a mixture of the silver salts of each of the foregoing fractions an anilide was prepared, m.p. 114°, undepressed in admixture with an authentic specimen of acetanilide. This acid is therefore acetic acid.

No evidence was obtained for the presence of formic, butyric or valeric acids.

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