Essential Oils from the Queensland Flora—Part XVI.—Eucalyptus microcorys.

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Since the extensive investigations of Baker and Smith¹ on the essential oils of the Australian Eucalypts, very little work has been done on these important oils. Meanwhile great advance has been made in terpene chemistry and chemical technique and it was thought that oils from some of the more abundant species of Eucalypts could, with advantage, be subjected to a more thorough investigation.

The essential oil of *Eucalyptus microcorys* was chosen as it grows abundantly in southern Queensland, where it is cut for its timber known as Tallow wood.

The essential oil was a light-yellow mobile oil, smelling strongly of cineol.

Baker and Smith² recorded the presence of pinene, cineol, volatile aldehydes and sesquiterpenes. We have confirmed these observations and also have shown the presence of isoamyl isovalerate, borneol, bornyl acetate, and butyrate, and have proved the volatile aldehyde present to be isovaleric aldehyde. Also a small quantity of a carbonyl compound was isolated but not identified.

EXPERIMENTAL.

Two samples of leaves of *Eucalyptus microcorys*, one from Enoggera. Brisbane, and the other from Yandina, yielded .71 and .73 per cent. of oil respectively.

The physical constants of the two oils were very similar and also agreed very closely with those given by Baker and Smith (loc. cit.).

		Sample A.	Sample B.	Constants by Baker and Smith.
$d_{15\cdot 5}^{15\cdot 5}$		·9069	·8953	·895
$[\alpha]_{\mathrm{D}}$	• •	+17.9	+18.6	+18.3
$n_{\overline{D}}^{20}$		1.4690	1.4671	1.4690
Ester value		23.8	22.5	19.6
Acetyl value		60.4	62.7	
Cineol content		46 %	43.9%	49 %

Sample B was extracted in turn with sodium carbonate and sodium hydroxide solutions. These extracts yielded very small amounts of an acid and a phenol which were not further examined.

The residual oil after drying was submitted to fractional distillation at two millimetres pressure when the following fractions were obtained:—

		$d_{15\cdot 5}^{15\cdot 5}$	$n\frac{20}{D}$	[a] _D
(1). Collected	in			
liquid amr	nonia			
trap		·8772	1.4595	+32
(2). 30–40°C .		·894	1.4600	+16
(3). 40–44°C.		·8908	1.4400	- 2.8
(4). 44–56°C.		·9548	1.4720	28
(5). 56-60°C.		·9739	1.4810	-17
(6). 60-80°C.		·9484	1.4926	+24

Fraction (1) was shaken with saturated sodium bisulphite solution. A solid compound separated which, on decomposing with caustic soda solution, gave a volatile aldehyde identified as isovaleric aldehyde by the preparation of its 2:4 dinitro-phenyl-hydrazone, m.p. and mixed m.p. 123° C.

The residual oil of this fraction mixed with fraction (2) was extracted three times with resorcin solution. The cineol recovered from the resorcin compound had

$d_{15\cdot 5}^{15\cdot 5}$		 	·9316
$[\alpha]_{D}$	• •	 • •	·45
$n_{\overline{D}}^{20}$			1.4554

It readily formed an o-cresol compound m.p. 55°C.

The oil freed from cineol had the following constants: --

$d_{15\cdot 5}^{15\cdot 5}$				·8638
$[a]_{D}$				45.8
$n_{\overline{D}}^{20}$	• •	•••	•••	1.4648

This was d-a-pinene for on oxidation with permanganate a good yield of pinonic acid was obtained, identified by its semicarbazone m.p. 204°C.

Fraction (3) contained an ester and consequently was hydrolysed with alcoholic KOH. From the aqueous alkaline solution on acidification and steam distillation was obtained an acid which formed a silver salt giving 51.68 per cent. silver on ignition. Silver isovalerate contains 51.65 per cent. silver.

The alcohol from the ester was extracted by means of phthalic anhydride. It distilled at 130-140°C. and formed a naphthyl urethane m.p. 67°C. identical with the naphthyl urethane of isoamyl alcohol.

From a consideration of the constants of fractions (4) and (5) it was thought that these would contain the mixture of carbonyl compounds, cuminal, phellandral and cryptal, originally known as aromadendral. Consequently fractions (4) and (5) were combined and submitted to extraction by the method of Macbeth³.

The extraction with normal sodium sulphite yielded one cc. of a carbonyl compound which, after purifying by a second extraction, had

b.p.			60°C.	at 1mm.
$d_{15\cdot 5}^{1\overline{5}\cdot 5}$	•••	• •		·978
$[a]_{\mathrm{D}}$	• •		•••	-45
$n_{\overline{D}}^{20}$			• •	1.488

It yielded a 2:4 dinitro-phenyl-hydrazone m.p. 176°C. and so appeared to be different from any constituent of aromadendral. This carbonyl compound was not identified as very little was available for experiments. Extraction with sodium bisulphite failed to remove anything.

The oil remaining after these extractions had a strong camphoraceous odour. It failed to yield a positive test with 2:4 dinitro-phenylhydrazine. By careful fractionation, a fraction was obtained with:

b.p.	 • •	57–62°C. at 2 mm
$d_{15\cdot 5}^{15\cdot 5}$	 	·9629
$[\alpha]_{\mathbf{D}}$	 	-22
Ester value	• •	=41

This fraction was heated with phthalic anhydride in dry benzene for 8 hours. The alcohol recovered from the acid-phthalate in the usual way partially solidified. The solid was filtered and dried on a porous plate. After recrystallising from petroleum ether it melted at 199°C. Lack of material prevented further purification but by mixed melting point determinations it was shown to be borneol.

The recovered oil was hydrolysed with alcoholic KOH. From the aqueous solution on acidification and steam distillation, a solution of acids was obtained. The silver salts of these acids were formed and analysed.

First crystals gave 55.39 per cent. Ag.

Silver butyrate requires 55.36 per cent. Ag.

Second crystals gave 59.28 per cent. Ag.

It appears as though both butyric and acetic acids are present as esters.

The oil containing the alcoholic portion of the ester was extracted with phthalic anhydride resulting in the isolation of borneol, and a mobile alcohol which was not identified.

The remainder of the oil consisted of sesquiterpenes which gave the usual colour reaction with bromine vapour and glacial acetic acid. These were not further examined.

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