

PART XXI. THE ESSENTIAL OIL FROM THE WOOD OF 'ERYTHROXYLON MONOGYNUM', ROXB.

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The number of wood oils, the constituents of which have been studied, is somewhat limited and in view of the attention which has been directed in these laboratories to the chemistry of sandalwood oil (from *Santalum album*, L.), we welcomed the opportunity of studying the oil from the wood of *Erythroxylon monogynum*, Roxb., which is occasionally known as the 'bastard sandal' or 'red cedar'.

E. monogynum is a small tree or shrub found in considerable quantity in all parts of the Mysore State, the hilly parts of the Indian Peninsula and in Ceylon (Cameron, *The Forest Trees of Mysore and Coorg*, 1894, 44; Hooker, *Flora British India*, 1875, I, 414). The timber is in large demand and according to Gamble (*A Manual of Indian Timbers*, 1922, 116) it is one of the most useful trees in the dry evergreen forests. The fruit and leaves are edible, whilst according to Watt (*The Commercial Products of India*, 1908, 525) the leaves and bark are also used medicinally.

The oil obtained by the steam distillation of the wood does not appear to have been used technically, but in Ceylon the crude oil obtained by the destructive distillation of the wood has been used in the preservation of timber and is known locally as 'dummele'.

The oil isolated by steam-distillation of the wood has been the subject of two previous investigations. Schimmel and Co. (*Berichte*, 1904 (April), 100; *J. Soc. Chem. Ind.*, 1905, 23A, 679) obtained an oil in a yield of 2.56 per cent., from which a crystalline alcohol $C_{20}H_{32}O$, m.p. 117-118°, was separated, whilst more recently Shastry (*Quart. J. Mysore For. Assoc.*, 1923, 5, 7) has shown that the Mysore wood yields 1.15 per cent. of an oil the average constants of which are given in Table I. Mr. Shastry very kindly placed a quantity of the oil obtained by him at our disposal for further investigation.

An examination of the oil has shown it to consist of a mixture of sesquiterpenes and sesquiterpene alcohols. In the sesquiterpene fraction the presence of trisabolene was established by the preparation of the characteristic trihydrochloride and trihydrobromide, whilst the colour reactions indicated the presence of cadinene, although unfortunately we were not able to confirm the presence of this hydrocarbon by

the preparation of derivatives. The quantity of sesquiterpene alcohols obtained was very small, and we were unable to find any indication of the existence of the crystalline alcohol described by Schimmel and Co. So it is unlikely that this alcohol is present in the oil separated from wood grown in Mysore.

EXPERIMENTAL.

The oil examined was very viscid and deep reddish-brown in colour; it had the constants given in column 1 of Table I, whilst in columns 2 and 3 are given the constants observed by Schimmel and Co. and Shastry, respectively.

TABLE I.

		1	2	3
d_{30}^{30} }	...	0.9499	less than 1	$\left\{ \begin{array}{l} d_{20}^{20} \\ d_{20}^{30} \end{array} \right. \begin{array}{l} 0.918-0.927 \\ 0.918-0.927 \end{array}$
n_D^{30} }	...	1.4998	...	$\left\{ \begin{array}{l} n_D^{20} \\ n_D^{30} \end{array} \right. \begin{array}{l} 1.4855-1.498 \\ 1.4855-1.498 \end{array}$
$[\alpha]_D^{30}$ }	...	-43.9°	...	-59.0°-51.0°
Acid value	...	5.7	6.8	...
Ester value	..	22.7	1.56	5.4-12.1
Ester value after acetylation...		74.7	131.0	45.1-60.9

Prior to fractionation the oil was heated for some hours with an excess of an alcoholic solution of potassium hydroxide to hydrolyse any esters present, the alkaline solution being reserved for later investigation (p. 148). After two distillations under diminished pressure the following fractions were obtained, monocyclic terpenes being apparently completely absent.

TABLE II.

No.	B.P. 10 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
1	113-134°	0.5
2	134-136°	0.8944	1.4909	-65.5°	54.2
3	136-150°	0.3
4	150-160°	0.9414	1.4987	...	6.6
5	160-170°	0.9686	1.5034	...	6.0

The main fraction (Fraction 2) was distilled twice over sodium, when it boiled at 118–120°/8 mm. and was shown by analysis to have the formula $C_{15}H_{24}$ (Found: C, 88.2, H, 11.9; calc. C, 88.2, H, 11.8 per cent.) The purified terpene had the following constants:— d_{30}^{30} 0.8911, n_D^{30} 1.4909, $[\alpha]_D^{30}$ -71.1° . When dissolved in acetic anhydride and treated with a drop of sulphuric acid a purple coloration developed which gradually changed to indigo-blue and finally became green on warming. These colour reactions are stated to be characteristic of cadinene but, as has already been mentioned, all attempts to prepare crystalline derivatives of this hydrocarbon failed, and if present it can only be in very small amount.

On treatment of an acetic acid solution of the terpene with hydrogen chloride a liquid hydrochloride was formed which on keeping partially crystallised (2.5 grams crystalline hydrochloride from 10 grams of terpene). The hydrochloride separated from methyl alcohol in glistening leaflets, m.p. 79–80° and was shown by analysis to be a trihydrochloride (Found: Cl, 34.4; calc. Cl, 34.0 per cent.). A solution of the hydrochloride in chloroform was optically inactive. It appeared probable that the hydrochloride was bisabolene trihydrochloride which melts at the above-mentioned temperature, and confirmation was afforded by the preparation of the trihydrobromide, m.p. 84° (*Annalen*, 1909, 368, 19. Found: Br, 54.2; calc. Br, 53.7 per cent.).

In view of the very low yield of the crystalline trihydrochloride it was clear that the sesquiterpene was a mixture and it was therefore carefully refractionated using a four-pear Young still-head. Ten fractions distilling between 119° and 125°/8 mm. were obtained, and as will be seen from the constants of the extreme fractions (Table III) there was a marked difference in their physical properties.

TABLE III.

No.	B.P /8 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$
1	119–121°	0.894	1.491	-70.1°
10	123–125°	0.8853	1.4896	-49.1°

Both fractions gave on treatment with hydrogen chloride bisabolene trihydrochloride; but bisabolene was present in much larger amount in the final fraction, the yield of trihydrochloride being more than three times that obtained from the first fraction. All

attempts to prepare additional crystalline derivatives were unsuccessful and the nature of the other sesquiterpenes present could not be determined.

Fractions 4 and 5 (Table II) consisted entirely of sesquiterpene alcohols, but owing to the small quantity of material available they could not be purified and no crystalline derivatives were obtained.

The alkaline solution remaining on hydrolysis of the original oil was, after removal of the alcohol, acidified with sulphuric acid and distilled in steam. The silver salt prepared from the distillate was analysed and indicated the presence of capric acid (Found: Ag, 38.8; calc. Ag, 38.7 per cent.).

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[Accepted, 1-7-26.]