THE ESSENTIAL OIL FROM THE WOOD OF *ERYTHROXYLON MONOGYNUM* ROXB. PART—I

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Erythroxylon monogynum Roxb. is a small tree or shrub with dark rough brown bark, distributed in all parts of the Mysore State, Madras Presidency, Deccan and Carnatic in dry evergreen forests, Western Ghats, in dry hills of Travancore and in Ceylon (Cameron, *The Forest Trees of Mysore and Coorg*, 1894, p. 44; *Flora of British India*, 1875, 7, 414; Kirtikar and Basu, *Indian Medicinal Plants*, 1933, **1**, 415). An infusion of the wood and bark is claimed to be stomachaic, diaphoretic and stimulant diuretic (Kirtikar and Basu, *loc. cit.*). The timber is in large demand and the tree is found to be very useful in the dry evergreen forests (Gamble, *A Manual of Indian Timber*, 1922, p. 116). The fruits, leaves and the bark are also used medicinally (Watts, *The Commercial Products of India*, 1908, p. 525).

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

The oil isolated by the steam distillation had been the subject of three previous investigations:

(i) Schimmel and Co. (*Ber.*, 1904, p. 100; *J. Soc. Chem. Ind.*, 1905, **23 A**, 679) obtained an oil by steam distillation of the wood in 2·56% yield. The oil consisted wholly of a solid diterpene alcohol $C_{20}H_{32}O$; m.p. 117–18° C. and a colourless viscous liquid; b.p. 212–16° C. at 8 mm.

(ii) Shastry (*Quart. J. Mysore Forest Assoc.*, 1923, **5**, 7) obtained an oil from the Mysore variety after steam distillation in 1·15% yield. He determined the average physical constants of the oil which are reported in Table 1.

(iii) Rao, Shintre, and Simonson (*J. Ind. Inst. Sci.*, 1926, p. 145) carried out the further investigation of this oil which was supplied to them by Shastry. They found it to consist of a mixture of sesquiterpenes and sesquiterpene alcohols, exclusively. In the sesquiterpene portion they claim to have established the presence of bisabolene by preparing its trihydrochloride and trihydrobromide and also indicate the presence of cadinene simply by colour reaction. No derivative of the cadinene fraction could be prepared and the quantity of the sesquiterpene alcohols at their disposal was so small that further investigations could not be conducted. Complete absence of the diterpene alcohol, m.p. 117–18° C., isolated by Schimmel and Co. (*loc. cit.*) has been reported.

The present paper embodies the results of a fuller investigation of the oil.

THE ESSENTIAL OIL

The plant is locally called as Devadari (different from Deodar) and the English name being 'Bastard Sandal'. The wood was procured from two different places in the Mysore State, namely, Royalaput and Magadi. Both the samples were subjected to steam distillation separately. A greenish oil was obtained in 0·166% yield from the Royalaput variety and in 0·085% from the Magadi sample. It was the oil from the latter variety that was investigated fully.

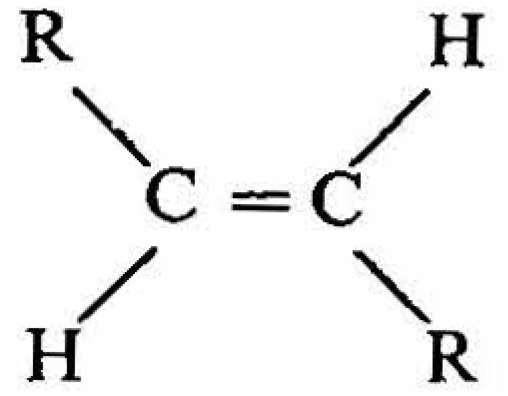
The oil had a characteristic pleasant odour and a pungent taste. Its physical and chemical constants are given in Table I and compared with the values obtained by other authors. On careful and repeated fractionation of the oil five fractions were obtained the physical properties of which are reported in Table II.

The fraction I consisting 40% of the oil was identified as α-pinene. The presence of this hydrocarbon was established by preparing nitrosylchloride and bornyl chloride. The identity of this compound was further confirmed by oxidation with potassium permanganate, and the pinonic acid thus obtained was characterised by its semicarbazone, m.p. 207° C. The mixed melting point with an authentic sample remained undepressed. The physical properties of the fraction I have been compared with the values reported for α-pinene by the other authors, in Table III.

The fractions II and III being very small in quantity could not be purified and hence were not identified. They essentially seem to consist of sesquiterpenes according to their boiling points.

The fraction IV (yield 50%) was found to be a diterpene hydrocarbon the constitution of which is not known. The physical properties, determined after several fractionations, are reported in Table IV and compared with the values of a similar diterpene hydrocarbon isolated by Lindsey *et al.*, from the essential oil of *Phyllocladus trichomanoides* (*J. Org. Chem.*, 1948, **13**, 1–9). The molecular refraction of the compound indicates the presence of four rings with one double bond. It gave a dibromide, m.p. 155–56° C., thus further confirming the presence of one double bond. A detailed investigation into the structure of the diterpene hydrocarbon will form the subject of another communication.

The fraction V, which could be isolated only in 1·8 per cent. yield, was a crystalline white solid; m.p. 118° C. It was identified as a diterpene alcohol whose constitution is not known. The molecular weight (283), determined by cryoscopic method and the analysis indicate that the compound has the molecular formula $C_{20}H_{32}O$. It was found to be unsaturated as indicated by the tests with bromine, tetranitromethane and perbenzoic acid. Xanthate tests (Feigel, *Qualitative Analysis by Spot Test*, 1947 Edition, p. 324), benzoyl, acetyl and urethane derivatives indicate the presence of either primary or secondary alcoholic group. The presence of one double bond was determined by the perbenzoic acid method. Dehydrogenation of the diterpene alcohol in presence of selenium furnished pimanthrene which was characterised by its picrate, indicating that the molecule has a phenanthrene skeleton. The infra-red spectrum of the alcohol is given in Fig. 1. The absorption at 3 $m\mu$ confirms the presence of a hydroxyl group. The band at 10·3 $m\mu$ has arisen from olefinic CH-wagging vibrations, perpendicular to the $> c = c <$ plane and indicates the presence of an ethylenic linkage of the type:



The quantity of the alcohol at our disposal being very small, a detailed investigation into the chemistry of the compound could not be carried out.

It is interesting to note that the oil investigated by us seems quite similar to the one obtained by Schimmel and Co. (*loc. cit.*) in the sense that both the oils were found to contain the solid diterpene alcohol as well as the high boiling liquid. Our sample also contains α-pinene and very small quantities of sesquiterpenes. The oil investigated by Shastry and Rao, Shintre and Simonson (*loc. cit.*) seems to be entirely different in its constituents as it neither contained the monoterpenic nor the diterpenic constituents.

EXPERIMENTAL

Wood

The wood was collected from Magadi in the Mysore State in January 1951. The stems of the plant were about one foot in diameter and had an

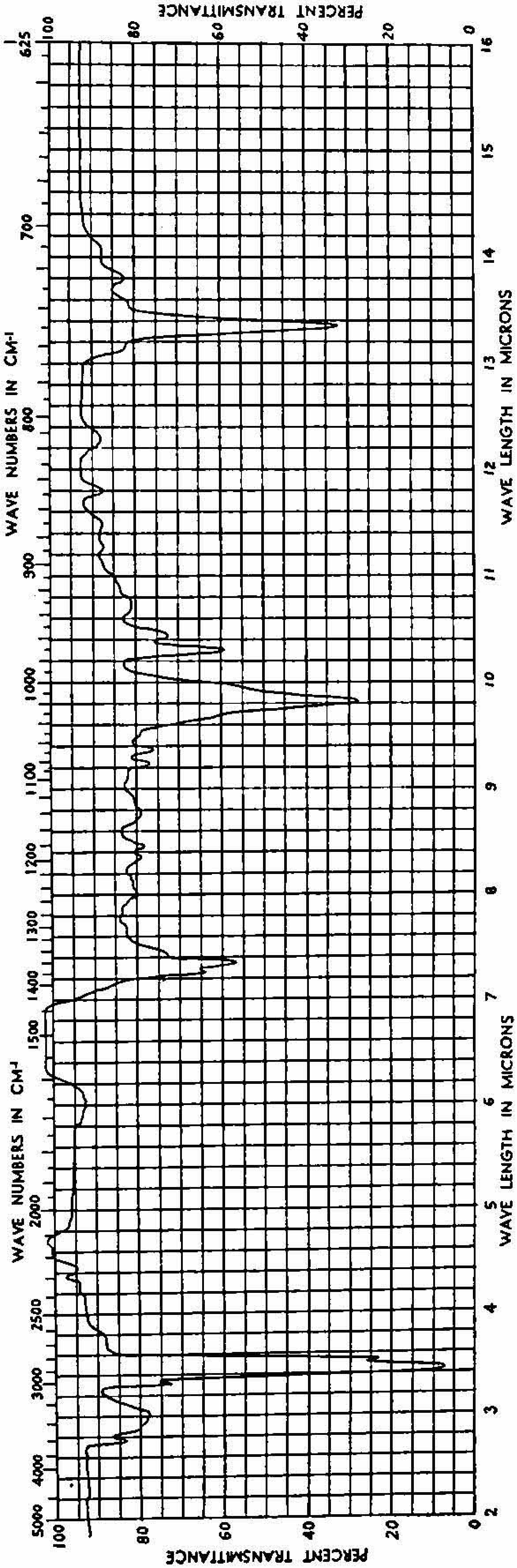

WAVE NUMBERS IN CM⁻¹
5000
4000
3000
2500
2000
1500
1400
1300
1200
1100
1000
900
800
700
625
WAVE LENGTH IN MICRONS
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
PERCENT TRANSMITTANCE
100
80
60
40
20
0

FIG. 1.

aromatic smell when freshly cut. The wood was chipped and disintegrated into powder in March 1951.

Essential Oil

The wood (583 lb.) was steam distilled from a large copper still when a light green oil (225 g.; 0·085%) was obtained. The oil was obtained as a mobile liquid, and after drying over anhydrous sodium sulphate, the physical and chemical constants were determined which are reported in the Table I.

TABLE I

	Present sample	Rao, Shintre and Simonsen (*loc. cit.*)	Shastry (*loc. cit.*)	Schimmel and Co. (*loc. cit.*)
d ..	0·9333 $d^{26°}_{26°}$	0·9499 $d^{30°}_{30°}$	0·918−0·927 $d^{28°}_{28°}$	Less than 1
n_D ..	1·494 $n^{26°}_D$	1·4998 $n^{30°}_D$	1·4955−1·498 $n^{20°}_D$	..
$[\alpha]_D$ ..	+18·9°$[\alpha]^{26°}_D$	−43·9°	−(59·0°−51·0°)$[\alpha]_D$	..
Acid value ..	6·6	5·7	..	6·8
Ester value ..	10·79	22·7	5·4−12·1	1·56
Acetyl value ..	60·17	74·7	45·1−60·9	131

Fractionation

The oil was carefully and repeatedly fractionated from a towers column of the total condensation take off type. The column was packed with fine glass helices and was worked at the reflux ratio of 1 : 10. Five fractions were isolated whose physical properties are reported in the following Table II.

TABLE II

Fraction	b.p.	Weight (g.)	Yield (per cent.)	d	n	$[\alpha]_D$
I	73° C./45 mm.	90	40	0·8562 $d^{28°}_{28°}$	1·4625 $n^{20°}_D$	+41·8°$[\alpha]^{28°}_D$
II	80–90° C./3 mm.	2·25	1	0·8859 $d^{26°}_{26°}$	1·4775 $n^{20°}_D$	..
III	90–100° C./3 mm.	2·25	1	0·9473 $d^{26°}_{26°}$	1·492 $n^{20°}_D$	..
IV	149–50° C./1·5 mm.	94·5	42	0·9647 $d^{28°}_{28°}$	1·5155 $n^{28°}_D$	+18°$[\alpha]^{28°}_D$
V	Solid	4·1	1·8	..	..	..
Residue	..	31	14	..	..	..

Identification of α-pinene

Physical Constants.—The physical constants of fraction I were found to be closely related with α-pinene and are reported in the following Table III. The values reported by other authors are given for comparison.

TABLE III

α-Pinene	b.p.	d	$[\alpha]_D$	n
Fraction I ..	73° C./45 mm.	0·8562 $d^{28°}_{28°}$	+41·8$[\alpha]^{27°}_D$	1·4625 $n^{29°}_D$
Fuguitt *et al.*[1] ..	52·2° C./20 mm.	0·8542 $d^{25°}_{4°}$	+34·07$[\alpha]^{25°}_D$	1·4631 $n^{25°}_D$
Dupont and Deselbres[2]	156° C./760 mm.	0·8620 $d^{15°}$	+48·85$[\alpha]_D$	1·465 $n^{12°}_D$
Wallach[3] .	155–56° C./760 mm.	0·8580 $d^{20°}$	*dl*	1·4655 $n^{21°}_D$

[1] Fuguitt *et al.*, *J. Am. Chem. Soc.*, 1942, 64, 2978.

[2] Dupont and Deselbres, *Bull. Soc. Chem.*, 1923, IV, 33, 1252.

[3] Wallach, *Annalen*, 1890, 258, 344.

Nitrosyl chloride of α-pinene.—Nitrosyl chloride was prepared as usual from the fraction I and crystallised from a mixture of methyl alcohol and chloroform; m.p. 108–9° C. The mixed m.p. with an authentic sample remained undepressed (Found: N, 6·91. $C_{10}H_{10}NOCl$ requires N, 6·95%).

Bornyl chloride.—Bornyl chloride was prepared from the fraction I, by passing dry hydrochloric acid gas in a chloroform solution of the hydrocarbon; m.p. 120° C. The mixed m.p. with a genuine sample remained undepressed. The hydrochloride possessed a distinct smell of camphor.

Potassium permanganate oxidation.—Fraction I (20 g.) was subjected to potassium permanganate oxidation according to the procedure adopted by Thurber and Roll (Guenther, *The Essential Oils*, Vol. II, p. 58). Pinonic acid thus obtained was identified by its semicarbazone which on twice crystallising from dilute methyl alcohol melted at 207° C. Mixed m.p. with an authentic sample remained undepressed.

Fraction IV

The physical constants of this fraction have been reported in the following Table IV and compared with the values of a diterpene hydrocarbon obtained by Lindsey *et al.*, from *Phyllocladus trichomanoides* (*loc. cit.*).

TABLE IV

	b.p.	d	n	$[\alpha]_D$	$[R_1]_D$
Diterpene obtained by Lindsey, etc. (*loc. cit.*)	156–57°/1 mm.	0·9640 $d_{25°}^{25°}$	1·5168 $n_D^{25°}$	+22·6$[\alpha]_D$	85·36
Diterpene (present sample)	149–50/1·5 mm.	0·9647 $d_{28°}^{28°}$	1·5155 $n_D^{28°}$	+18$[\alpha]_D^{27°}$	85·33

Dibromide.—Fraction IV (1·1 g.) dissolved in anhydrous ether (10 c.c.) was treated with bromine under ice cooling until a pale yellow colour of bromine persisted. After 2 hours of standing in an ice-bath, ether was removed and the pasty residue after keeping in a crystallising dish for a week yielded some crystals which were separated by pressing on a porous plate and crystallised from alcohol; m.p. 155–56° C. The molecular weight of the dibromide was determined by the cryoscopic method. (Found : Br, 37·68%; Mol. wt. 417·2. $C_{20}H_{32}Br_2$ requires Br, 37·03%; Mol. wt. 432).

Fraction V (m.p. 118°)

Molecular weight and analysis.—Molecular weight of the substance was determined by cryoscopic method (Found: Mol. wt. 283·4. $C_{20}H_{32}O$ requires Mol. wt. 288) (Found: C, 83·45; H, 11·19. $C_{20}H_{32}O$ requires C, 83·33; H, 11·11%).

Unsaturation.—The substance decolorised bromine in carbon tetrachloride solution and developed a deep yellow colour with tetranitromethane.

Determination of double bond.—The presence of one double bond was estimated by perbenzoic acid method. The value obtained after one hour was 1·038 and after 76 hours 1·11.

Benzoyl derivative.—To the substance (0·1 g.) dissolved in pyridine (1·5 c.c.) a little more than the equivalent amount of benzoyl chloride was added when a white precipitate immediately separated out. The mixture was warmed over water-bath for 15 min. and after diluting with water the solid was filtered. The derivative was crystallised in colourless plates from petroleum ether; m.p. 110° C. (Found: C, 81·56; H, 8·92. $C_{27}H_{36}O_2$ requires C, 82·64; H, 9·18%.)

Acetyl derivative.—The substance (1 part), acetic anhydride (2 parts) and sodium acetate (1 part) were heated together gently for an hour on a sand-bath. The mixture was cooled and water (5 parts) added through the condenser. The contents were warmed on the water-bath for 15 minutes to destroy the excess of acetic anhydride. A solid acetyl derivative separated on cooling which was filtered, washed with water and crystallised from alcohol in long colourless plates; m.p. 76° C. (Found: C, 79·25; H, 10·1. $C_{22}H_{34}O_2$ requires C, 80·00; H, 10·3%).

Urethane derivative.—On warming gently a mixture of the substance and naphthyl-isocyanate (a little less than the equimolar quantity) for half an hour, a solid separated on cooling which was crystallised several times from petroleum ether in pinkish crystalline urethane derivative; m.p. 138° C. (Found: N, 3·16; $C_{31}H_{39}NO_2$ requires N, 3·06%).

Infra-red spectrum.—The infra-red spectrum was determined by a spectrophotometer of the double beam type with a sodium chloride prism and a 10 per cent. solution of the compound in carbon disulphide was used.

Dehydrogenation.—The substance (0·5 g.) was dehydrogenated with selenium at 300–50° C. and a picrate forming material was isolated by chromatographing the dehydrogenated product (petroleum ether used as solvent). Picrate; m.p. 128° C. Pimanthrene picrate; m.p. 128 (Berth, *J. Soc. Chem. Ind.*, 1933, **52**, 338).

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