I.—ESSENTIAL OIL FROM LEAVES OF *LITSAE ZEYLANICA*, LINN.

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Litsæ Zeylanica, Linn., belongs to a large genus of about fifty-six species, of which several are indigenous to the Western ghats and other parts of Southern India, growing up to 7,000 feet in the Nilgiris and also found in Bhutan, the Khasia mountains, Java and Sumatra. It is a moderate-sized, ever-green tree whose wood is employed for furniture and house-building, as it is rarely attacked by insects and will last many years even in the ground and exposed to weather. The leaves and bark resemble those of the closely allied cinnamon species and are often used for the adulteration of the latter.

The leaves were distilled by Sastry (*Perf. and Essent. Oil Rec.*, 1923, **14**, 271) who obtained 0.6, 0.22 and 0.05 per cent. of oil from fresh, partly dried and dried leaves respectively. The constants for these oils, according to Bennett, have been given in Table I.

The leaves used for the present investigation were obtained in March and November and immediately distilled. The constants of the oils do not indicate any pronounced difference in composition due to seasonal variation. The slightly lower yield in November is probably due to the longer interval between collection and distillation.

A detailed examination of the oil has shown it to be mainly a mixture of terpenes (ocimene and α-pinene) with sesquiterpenes.

The sesquiterpenes are entirely bicyclic and belong to the cadalin group. A crystalline sesquiterpene dihydrochloride (m.p. 100-101°) was obtained, apparently a derivative of a hydrocarbon hitherto unknown, as no hydrochloride having this melting point is recorded, the only sesquiterpene dihydrochlorides melting in this region being that of (1) *dl*-cadinene (m.p. 105-106°) and (2) the tricyclic sesquiterpene heerabolene (m.p. 99-100°) isolated by Friedrichs (*Arch. Pharm.*, 1907, **245**, 208). Even if the dihydrochloride is identical with the latter, it appears certain that there is no tricyclic sesquiterpene resembling heerabolene in this oil, and it is intended to examine the compound further when a fresh supply of material becomes available.

One of the sesquiterpene fractions gave a small yield of a nitrosochloride (m. p. 165°) indicating α-caryophyllene. The quantity of sesquiterpene alcohols being small, they were not further investigated. The percentage composition of the oil is approximately as follows:— α-Pinene, 3.5; ocimene, 60.0; terpene alcohols, 1.0; bicyclic sesquiterpenes, 27.0; sesquiterpene alcohols, 3.0.

Experimental.

Two consignments of leaves and terminal branchlets were obtained, one in March and the other in the November following. The first was distilled in steam on the 5th day after collection and the second after 15 days. The distillates were pale lemon, very mobile oils, and when dried with magnesium sulphate had the constants in Table I which includes for comparison the values found by Bennett.

TABLE I.

Weight of leaves	Yield of oil per cent.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	Acid value	Sapn. value	Sapn. value after acetylation
150 lbs.	0·45	0·8376	1·4874	+0·6°	0·4	0·7	41·7
335 ..	0·39	0·8383	1·4874	+2·0	0·3	0·6	45·6
		0·890	1·4980	+1·0	0·47	22·6	81·6

Phenols and carbonyl compounds were not present in any appreciable quantity.

Distillation of the Oil.—The oil (200 g.) was washed with sodium carbonate to remove free acids and distilled at 100 mm. with a 4-pear Young's column, when the following fractions were obtained:—

TABLE II.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	Weight in gms.	Yield per cent. on original oil
1	105—110°	0·8041	1·4803	—2·2°	15·5	7·7
2	110—115	0·7995	1·4817	—1·1	83·0	41.5
3	115—120	0·8013	1·4832	—0·7	24·5	12·3
4	120—125	0·8123	1·4850	+0·2	11·0	5·5
5	130—165	0·8557	1·4902	+0·3	7·0	3·5
6	165—187	0·9111	1·4992	+1·4	49·0	24·5
	Residue				6·0	3·0

The first three fractions which contained most of the terpenes were repeatedly distilled with a 5-bulb Le-Bel column at 100 mm. and the results summarised in Table III.

TABLE III.

Terpenes.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	Weight in gms.	Yield per cent. on original oil
A	103—105°	0·8459	1·4660	—10·2°	2·5	1·3
B	105—106	0·8281	1·4723	— 8·4	5·0	2·5
C	106—107	0·8187	1·4732	— 7·6	5·0	2·5
D	107—109	0·8132	1·4760	— 7·6	3·5	1·8
E	109—112	0·8085	1·4792	— 3·4	5·5	2·8
F	112	0·8021	1·4820	— 1.8	6·5	3·3
G	112	0·7980	1·4822	— 1·4	18·5	9·3
H	112—113	0·7960	1·4828	0·0	83·2	41·6

Fractions A, B and C (α-pinene).—Fractions B and C were mixed and fractionated over sodium with a 4-pear column at 7 mm. pressure.

	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$
1	48—50°	0·8384	1·4692	—8·8°
2	50—53	0·8110	1·4772	—4·8

Fractions A and 1 readily gave a nitrosochloride which on purification melted with decomposition at 109°. Fraction 2 gave a much smaller quantity of the nitrosochloride melting at 105-107°.

Fractions F, G and H (ocimene).—The physical properties of these fractions agreed fairly closely with those of the aliphatic terpene ocimene, *viz.*, b.p., 110°/100 mm., d^{30}_{30} 0·7933, n^{30}_{D} 1·4809.

Dihydro-ocimene.—Fraction II (20 c.c.) was dissolved in absolute alcohol (150 c.c.) and sodium (20 g.) gradually added, the mixture being finally heated on a boiling water bath. The reduced terpene after distillation over sodium had the following constants:—B.p., 71-72°/30 mm., d^{30}_{30} 0·7711, n^{30}_{D} 1·4458, $[R_L]_D$ 47·61 (calc. 47·45). Dihydromyrcene prepared by the reduction of myrcene, which is identical with dihydro-ocimene (*Ber.*, 1911, **44**, 2010) was found to have b.p., 70°/30 mm., d^{30}_{30} 0·7712, n^{30}_{D} 1·4465.

Dihydromyrcene tetrabromide.—The hydrocarbon (2·7 g.) from the above experiment was dissolved in a mixture of amyl alcohol (4 c.c.) and ether (8 c.c.), when bromine (6·3 g.) dissolved in amyl alcohol-ether mixture was gradually added to the well-cooled solution. There was no immediate precipitate, but after a few hours in the ice-chest a copious crop of crystals separated, which on recrystallisation from methyl alcohol melted at 87—88°, not depressed by admixture with dihydromyrcene tetrabromide.

allo-*Ocimene.*—Fraction II (20 c.c.) was boiled at 685 mm. pressure for 15 minutes and on distillation had the following constants, showing partial conversion into *allo*-ocimene: d^{30}_{30} 0·8092, n^{30}_{D} 1·5054.

Terpene alcohols.—Fraction 4 and the residue remaining after the distillation of the terpenes (Table III) were mixed and saponified with alcoholic potash. The distilled product (3 g.) gave the following constants:—B.p., 88-95°/6 mm., d^{30}_{30} 0·8578, n^{30}_{D} 1·4892, $[\alpha]^{30}_{D}$ —1·2°. No derivatives could be obtained.

Sesquiterpenes.—Fractions 4, 5 and 6 were fractionated and the product boiling at 105-135°/7 mm. was distilled under 8 mm. pressure over sodium giving the following fractions:—

TABLE IV.

Sesquiterpenes.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	$[R_L]_D$	Weight in gms.	Yield per cent. on original oil
a	108—110°	0·8969	1·4956	—3·9°	66·45	4·0	2·0
b	110—120					0·5	0·2
c	121—123	0·9012	1·4986	+1·0	66·43	33·0	16·5
d	123—125	0·9055	1·5011	+1·3	66·37	13·5	6·7
e	125—126	0·9107	1·5034	+3·1	66·22	6·5	3·2

Determination of sesquiterpenes.—Fractions *c* and *d* were mixed and fractionated into 8 fractions of which 1 and 8 had the constants given below:—

	B.P./11 mm.	d_{30}^{30}	n_{D}^{30}	$[\alpha]_{D}^{30}$	$[R_L]_D$
1	120—123°	0·8966	1·4956	—3·9°	66·46
8	128	0·9118	1·5050	+3·2	66·36

As the figures for molecular refraction of bicyclic and tricyclic sesquiterpenes are 66·15 and 64·45 respectively, the values obtained leave no doubt as to there being a mixture of only bicyclic sesquiterpenes.

Sesquiterpene dihydrochloride.—A solid hydrochloride (0·6 g.) was readily obtained when an acetic acid solution of fraction *c* (8 g.) was treated with hydrogen chloride: it crystallised from ethyl acetate in plates m.p. 100–101° (Found: Cl, 24·9; $C_{15}H_{26}Cl_2$ requires Cl, 25·6 per cent.), and was optically inactive. It may be identical with the hydrochloride obtained from *dl*-cadinene (m.p. 105–106°), or from heerabolene, which melts at 99–100° according to Friedrichs (*loc. cit.*). Heerabolene is a tricyclic sesquiterpene giving a dihydrochloride just as tricyclic copaene gives bicyclic cadinene dihydrochloride.

Fraction a (*a-caryophyllene*).—On treatment with amyl nitrite and hydrochloric acid, a nitrosochloride was obtained which on recrystallisation from alcohol melted at 165°. Attempts to prepare the caryophyllene alcohol were not successful.

Dehydrogenation with selenium (*cadalin*).—Fractions *c*, *d*, *e* were each separately heated with selenium powder at 260° during 24 hours. The product obtained by distillation over sodium gave in all cases excellent yields of cadalin picrate, m.p. 115° (mixed melting point 115°), showing that the sesquiterpenes belong to the cadalin group.

Sesquiterpene alcohols.—The fraction boiling above 135°/6 mm. had the following constants:—B. p. 135–145°/6 mm., d_{30}^{30} 0·9376, n_{D}^{30} 1·5026, $[\alpha]_{D}^{30}+4{\cdot}8^{\circ}$. A small quantity treated with sodium reacted vigorously, but the quantity of product was too small for further investigation.

Acids.—The sodium carbonate washings and the alkali liquor from saponification of esters were together treated with sulphuric acid and the volatile acids distilled in a current of steam. The silver salt was prepared after neutralisation with ammonia solution (Found: Ag, 51·1; silver *iso*valerate requires Ag, 51·7 per cent.).