

IV.—ESSENTIAL OIL FROM LEAVES OF *CINNAMOMUM ZEYLANICUM*, BREYN.

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Cinnamomum Zeylanicum, Breyn, is an interesting example of a plant in which the leaves, bark and root yield oils differing markedly in composition. The bark is among the longest known and used spices, and the leaf oil has been a valuable commercial product on account of its eugenol content. The tree is not cultivated on any appreciable scale in India, but is found wild in the Western Ghats. *Cinnamomum Zeylanicum* exists in a number of varieties and according to E. M. Holmes (*Perf. and Essent. Oil Rec.*, 1916, 7, 41), these are difficult to classify, some botanists regarding them as distinct species. As the tree can grow from sea-level up to the highest elevation it is possible the varieties are due to local environment and soil. In view of the fact that seven or eight well-defined varieties have been observed in the moist forests of the Western Ghats (Beddome, *Flora Sylvatica for Southern India*, 1872, 262) it seemed of interest to make a chemical examination of the volatile oils obtained from them. The present paper deals with an oil distilled from a variety growing in the neighbourhood of Chamarajnagar in Mysore, which appears to be fairly common in the hilly parts of Mysore and was identified as *Cinnamomum Zeylanicum*, Breyn, by the botanist at Coimbatore. The leaves on steam distillation yielded a yellow oil which differed appreciably from the cinnamon leaf oils of commerce, the eugenol content being only 15 per cent. After fractional distillation *l*- α -pinene and *l*- β -phellandrene were identified in the terpene fraction. A tertiary alcohol was found in the fraction boiling at 140–160°/100 mm. which yielded *transterpin* on treatment with sulphuric acid. This indicates the presence of γ -terpineol, a substance only once previously recorded as existing in a natural essential oil, that of *Cupressus torulosa* (Simonsen, *Indian Forest Records*, 1923, 10, 1). The sesquiterpene fractions gave several derivatives of α -caryophyllene, the alcohol (m.p. 95–96°), nitrosochloride (171°) and nitrosate (163°) being isolated. The rotation of these fractions was low and it is probable that a considerable proportion of the inactive form of α -caryophyllene was present. Additional evidence for this was found in the fact that no solid dihydrochloride could be obtained, this derivative being a liquid in the case of inactive α -caryophyllene (Deussen, *J. pr. Chem.*, 1929, 120, 141; Chapman, *J.C.S.*, 1928, 127, 785).

The approximate percentage composition of the oil is as follows:—

Terpenes (*l*- α -pinene and *l*- β -phellandrene), 4; terpene alcohols (γ -terpineol and others), 3; eugenol, 15; sesquiterpenes (mainly α -caryophyllene), 62; sesquiterpene alcohols, 7.

Experimental.

On steam distilling 639 lbs. of the fresh leaves (moisture 46.8 per cent.) 493 g. of lemon-yellow oil was obtained, or 0.25 per cent. calculated on the

dry leaves. The oil was dried over anhydrous magnesium sulphate and was found to have the constants given in Table I, which also shows some values recorded by other observers.

TABLE I.

	Bangalore	Normal oils*	Glichitch†	Schimmel‡
d_{15}^{15}	0.9223	1.043–1.066	1.0650	1.0183
n_D^{20}	1.5070	1.530–1.540	1.5438	1.5220
α_D^{20}	-2.9°	-0°10' to +2°35'	-1.6°	+16.4°
Phenols per cent.	15	70–90	70	78

* *Bull. Imp. Inst.*, 1921, 19, 324.

† *Les Parfums de France*, 1924, 66.

‡ *Schimmel's Report*, 1892, 58.

The low density, refractive index and phenol-content indicate that the oil is not of the normal quality.

The oil (423 g.) was washed with dilute aqueous sodium carbonate to remove free acids and then with 5 per cent. potassium hydroxide to remove the phenols. The non-phenolic portion was extracted with ether, washed free from alkali and dried with anhydrous magnesium sulphate. The oil (340 g.) freed from ether was distilled at 100 mm. pressure, using a 4-pear Young still-head, the results being recorded in Table II.

TABLE II.

Fractionation of the Oil.

Fraction	B.P.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Weight in grams	Yield per cent. on original oil
1	100—120°	0.8420	1.4702	-30.8°	5.0	1.3
2	120—135	0.8437	1.4706	-30.5	7.0	1.8
3	135—140	0.8457	1.4718	-25.9	1.5	0.4
4	140—160	0.8570	1.4776	-19.0	7.0	1.8
5	160—170	0.8729	1.4846	-10.1	8.0	2.0
6	170—180	0.8998	1.4920	-4.9	24.0	6.0
7	180—182	0.9064	1.4982	-1.7	143.0	35.9
8	182—186	0.9117	1.4988	-1.5	24.0	6.0
9	186—200	0.9250	1.5004	-1.3	31.0	7.8
10	200—210	0.9518	1.5048	..	9.0	2.3

The first three fractions were redistilled over sodium at 100 mm. and the following fractions were obtained :—

		d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$
A	95—100°	0.8474	1.4660	-40.6°
B	100—105	0.8509	1.4698	-32.5

l- α -Pinene and *l*- β -phellandrene:—Both fractions yielded a nitrosochloride, m.p. 103—104° which on treatment with piperidine gave a nitropiperidide, m.p. 118—119° showing the presence of *l*- α -pinene.

When treated with sodium nitrite and acetic acid in petrol ether solution a fair yield of a nitrite was obtained from fraction B. It was recrystallised from acetone and melted at 101-102°; 0.1199 g. dissolved in 10 c.c. chloroform had $\alpha_D = -1.7$, $[\alpha]_D = -142^\circ$. The more soluble nitrite was obtained as an oil and could not be crystallised; *l*- β -phellandrene nitrite, according to Wallach (*Annalen*, 1904, 336, 43), melts at 102° and has $[\alpha]_D = -159.3^\circ$.

Fraction 4 (γ -terpineol).—No semicarbazone or urethane could be obtained from this fraction, nor did it react with phthalic anhydride showing that it is a tertiary alcohol. On shaking (5 c.c.) at room temperature with 1 per cent. dilute sulphuric acid (200 c.c.) for 20 hours and extracting with ether, an oil was obtained which solidified on standing. Recrystallised from ethyl acetate it melted at 156°, undepressed by admixture with authentic *transterpin*. The formation of *transterpin* indicates the presence of γ -terpineol in the original oil.

Fraction 5 was probably a mixture of terpene alcohols and sesquiterpenes.

Fractions 6, 7, and 8.—These were thrice refractionated, the final distillation under 6 mm. pressure over sodium giving the following fractions:

TABLE III.

Fraction	B.P.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Weight in grams	Yield per cent. on original oil	C.	H.
<i>a</i>	105—108°	0.8794	1.4908	..	3.5	0.9
<i>b</i>	108—110	0.8835	1.4955	—7.3°	82.0	20.6	88.1	11.9
<i>c</i>	113—115	0.8882	1.4978	—1.2	77.0	19.3	88.2	11.9
<i>d</i>	115—120	0.8968	1.5018	+6.1	17.5	4.4

Fractions a, b and c (α -caryophyllene).—On treatment with dry hydrogen chloride, neither fraction gave a solid dihydrochloride, indicating the absence of any large proportion of active α -caryophyllene.

By Bertram and Walbaum's method no solid alcohol could be obtained, but treatment with a mixture of absolute ether and sulphuric acid monohydrate (Asahina and Tsukamoto, *J. Pharm. Soc. Japan*, 1922, June) resulted in a good yield. The product crystallised from alcohol in silky needles which melted at 95-96° remaining unchanged when mixed with an authentic specimen of caryophyllene alcohol. The phenylurethane prepared in the usual manner melted at 136-137° (Found: N, 4.0; $C_{22}H_{29}O_2N$ requires N, 4.1 per cent.).

Both *b* and *c* gave good yields of a crystalline nitrosochloride, m.p. 171° and a crystalline nitrosate m.p. 162-163°. Both substances yielded when treated with benzylamine a derivative melting at 128°, confirming the presence of α -caryophyllene.

Fraction 10 (sesquiterpene alcohols).—Analysis (Found: C, 82.0; H, 11.2; $C_{15}H_{24}O$ requires C, 81.8; H, 10.9 per cent.) showed the fraction to be mainly sesquiterpene alcohol. It did not react with phthalic anhydride and therefore did not contain primary or secondary alcohols. No derivatives were obtained.

Phenols were liberated by bubbling carbon dioxide into the potassium hydroxide extract of the oil. They were extracted with ether and after removing ether, distilled under diminished pressure, the yield being 14.7 per cent. (b.p. 115–118°/8 mm. d_{30}^{20} 1.0604, d_{15}^{15} 1.0703, n_D^{15} 1.5432). Eugenol has b.p. 123°/12 mm, 118–119°/8 mm, d_{16}^{15} 1.072, n_D^{15} 1.5439 (*Ber.*, 1890, 23, 262), so the constants are in good agreement. A benzoyl derivative melting at 69–70° was obtained when the phenol was treated with benzoyl chloride in presence of potassium hydroxide. The phenylurethane prepared in the usual manner melted at 94–95°, unaltered on admixture with a pure specimen of eugenol phenylurethane.

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