THE CONSTITUENTS OF SOME INDIAN ESSENTIAL OILS. PART XXIV. THE ESSENTIAL OIL FROM THE RHIZOMES OF 'CURCUMA ZEDOARIA,' ROSCOE.*

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In previous communications in this series (*J. Ind. Inst. Sci.*, 1926, **9A**, 133, 140) the constituents of the essential oils derived from the rhizomes of *Kæmpferia galanga* and *Curcuma aromatica* were described, and we have now examined a third oil belonging to the *Zingiberaceæ*, namely that derived from the rhizomes of *Curcuma zedoaria*, Roscoe.

C. zedoaria grows wild in the Eastern Himalayas, and it is cultivated throughout India and Ceylon; it also grows widely in the Philippine Islands. The oil from the roots grown in the Philippines has been examined by Bacon (*Philippine J. Sci.*, 1910, **5A**, 261), who separated from it a crystalline sesquiterpene alcohol, m.p. 67°, but he does not appear to have characterised any of the remaining constituents. Earlier investigators (*Schimmel's Rep.*, Oct., 1890, 66; Haensel, *Pharm. Ztg.*, 1899, **44**, 752) established the presence in the oil, of cineole and of a crystalline substance, m.p. 142·5°, but nothing further would appear to be known of its composition. A preliminary examination of the oil was made in these laboratories in 1924 (*J. Ind. Inst. Sci.*, 1925, **8A**, 154), but no attempt was made to identify the various constituents present.

The rhizomes, which were greyish-white in appearance and, unlike *C. longa* and *C. aromatica*, seem to contain very little colouring matter, were found to yield on distillation in steam 0·94 per cent. of an oil of which approximately one-third was heavier than water. A thorough examination of this distillate has shown it to have the following composition :—*d*-α-pinene 1·5 per cent., *d*-camphene 3·5 per cent., cineole 9·6 per cent., *d*-camphor 4·2 per cent., *d*-borneol 1·5 per cent., unidentified alcohols trace, sesquiterpenes 10·0 per cent., sesquiterpene alcohols 48 per cent., residue (probably mainly sesquiterpene alcohols) 21 per cent.

The sesquiterpene fraction was found to be a mixture of substances, one of which yielded a small quantity of a crystalline nitrosate,

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m.p. 82–83°. This was probably the nitrosate of zingiberene, the nitrosate of which is stated to melt at 86°. When the sesquiterpene fraction of the oil was heated with sulphur resinification took place, but more satisfactory results were obtained with selenium (cf. Diels, *Ber.*, 1927, **60**, 2323). The naphthalene hydrocarbon, cadalene, was separated from the reaction product and characterised by the preparation of the picrate, m.p. 115°.

The bulk of the oil was a complex mixture of sesquiterpene alcohols. These did not react with phthalic anhydride, and the alcohol group was therefore probably tertiary; since attempts to prepare crystalline derivatives were unsuccessful, they were not further examined. No evidence was obtained of the presence of either of the crystalline substances (m.p. 67° and 142·5°) isolated by Bacon and Haensel.

EXPERIMENTAL.

The rhizomes, which were in the form of dry discs, were disintegrated and the grey powder was distilled in steam, when a viscid dark green oil was obtained. From 220 kg. of the rhizomes 1·55 kg. of an oil lighter than water and 0·51 kg. of an oil heavier than water were obtained (yield 0·94 per cent.). The constants of the oil dried over magnesium sulphate are given in column I of Table I, whilst in column II are given the constants of the oil distilled in 1924, and in column III those observed by Bacon (*loc. cit.*).

TABLE I.

—	No. I	No. II	No. III
d^{30}_{30}	0·9724	d^{15}_{15} 0·9863	d^{30}_{4} 0·933–0·993
n^{30}_{D}	1·5002	n^{30}_{D} 1·5024	1·4922–1·507
Acid value	1·3	2·1	...
Saponification value ...	3·0	9·8	0–2·0
Do. after acetylation.	66·6	73·8	...
Yield, per cent.	0·94	1·01	0·065–0·25

A quantity of the oil was treated with an alcoholic solution of potassium hydroxide to hydrolyse any esters present and fractionated under diminished pressure using a four-pear Young still-head, with the results summarised in Table II.

TABLE II.

No.	B.p./100 mm.	d_{30}^{30}	n_{D}^{30}	$[\alpha]_{\mathrm{D}}^{30}$	Yield, per cent.
1	55–100°	...	...	...	Trace
2	100–110°	0·9026	1·4606	+ 17·8°	2·1
3	110–120°	0·9026	1·4618	+ 15·7°	4·1
4	120–130°	0·9117	1·4628	+ 12·0°	5·6
5	130–140°	0·9200	1·4656	+ 10·5°	3·8
6	140–160°	0·9322	1·4742	+ 10·3°	9·9
7	160–180°	0·9307	1·4886	+ 3·5°	9·1
8	180–200°	0·9402	1·5034	*	14·6
9	200–230°	1·010	1·5225	*	30·8
10	230–250°	1·027	*	*	9·9
11	Residue	...	...	...	18·8

* These fractions were too deeply coloured for determination of the rotation.

Fractions 1 to 4, which were free from aldehydes and ketones, were systematically fractionated under diminished pressure, the final distillation being over sodium, when the following fractions were obtained.

TABLE III.

No	B.p./100 mm.	d_{30}^{30}	n_{D}^{30}	$[\alpha]_{\mathrm{D}}^{30}$
i	96—98°	0·8821	1·4601	+ 25·3°
ii	98—100°	0·8849	1·4608	+ 26·0°
iii	100—101°	0·8892	1·4608	+ 20·0°
iv	102—106°	0·8985	1·4595	+ 10·3°
v	106—107°	0·9061	1·4563	+ 3·0°
vi	107—110°	0·9095	1·4565	+ 1·8°

Fractions i, ii, and iii were redistilled at the ordinary pressure and yielded two main fractions (*a*) 152–156°/684 mm., d_{30}^{30} 0·8787, n_{D}^{30} 1·4598, and (*b*) 156–162°/684 mm., d_{30}^{30} 0·8849, n_{D}^{30} 1·4605. These two fractions consisted of a mixture of *d*-α-pinene and *d*-camphene. The former hydrocarbon was identified by the preparation of the nitrosochloride, m.p. 104–105°, which yielded on treatment with benzylamine a nitrolbenzylamine, m.p. 122–123°, whilst the latter was characterised by conversion into *d-iso*borneol, m.p. 208°, the m.p. of which was not depressed on admixture with an authentic specimen. Fraction iv was a mixture of *d*-camphene and 1 : 8-cineole. The presence of the hydrocarbon was confirmed by the formation from it of *d-iso*borneol, whilst the cineole was characterised by the preparation of its compounds with phosphoric acid and hydrobromic acid. The percentage of cineole in this fraction as determined by the method of Baker and Smith was 71·5 per cent. Fractions v and vi consisted of nearly pure cineole ; limonene and dipentene could not be detected.

Fractions 5 and 6 (*Table II*).—These two fractions on careful fractionation yielded a crystalline solid (5·7 per cent.) which melted at 186–188°. When the solid (5 gms.) was heated with an excess of phthalic anhydride at 130° for some hours, *d*-camphor (3·7 gms.) was separated. This had m.p. 173–174° and $[\alpha]_D^{30}$ + 43·7° in alcohol solution. Its identity was confirmed by the preparation of the semicarbazone, m.p. 235–237°. The acid phthalate, from which the camphor had been removed, had m.p. 164°, and on hydrolysis gave an alcohol which after crystallisation from light petroleum had m.p. 203-204°, $[\alpha]_D^{30}$ + 38·6° in alcohol solution. The presence of *d*-borneol was confirmed by the preparation of the phenylurethane, m.p. 138°.

The oil (1·5 per cent.), from which the mixture of *d*-camphor and *d*-borneol had been separated, gave on treatment with phthalic anhydride in benzene solution a small quantity of an acid phthalate, m.p. 130–132°, which yielded a silver salt, m. p. 90–93°. These constants do not appear to be identical with those of the corresponding derivatives of any known primary alcohol, but, owing to the small amount of material available, no further examination was possible.

Sesquiterpenes and sesquiterpene alcohols.—Fractions 7–10 (Table II) were repeatedly distilled under diminished pressure when ultimately the following fractions were obtained :—

TABLE IV.

No.	B.p./100 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield, per cent.
a	160–161°	0·9014	1·4942	—8·2°	0·5
b	170–180°	0·9111	1·4958	—6·8°	13·1
c	180–185°	0·9234	1·5027	*	0·6
d	185–190°	0·9398	1·5068	*	0·7
e	190–200°	0·9813	1·5150	*	6·9
f	200–210°	1·0104	1·5218	*	9·6
g	210–220°	1·021	1·5358	*	9·9
h	220–230°	1·029	1·5442	*	7·3
i	230–240°	1·034	...	*	12·1

* These fractions were too deeply coloured for the determination of the rotation.

Fractions (*a*) and (*b*) on redistillation over sodium were separated into three main fractions.

TABLE V.

No.	B.p./9 mm.	d_{30}^{30}	n_{D}^{30}	$[\alpha]_{D}^{30}$	$[R_L]_D$	Yield, per cent.
x	112–114°	0·8903	1·4902	−7·7°	...	0·7
y	116–118°	0·8898	1·4922	−8·4°	66·6	2·6
z	120–121°	0·8947	1·4960	− 8·8°	66·0	6·6

Fractions (*x*) and (*y*) were analysed (Found: for (*x*) C, 87·9; H, 11·9; for (*y*) C, 87·9; H, 11·8; $C_{15}H_{24}$ requires C, 88·2; H, 11·8 per cent.). None of the fractions yielded crystalline hydrochlorides or nitrosites, but from fraction (*z*) a small quantity of a crystalline (see above) nitrosate, m.p. 82–83°, was separated; as already mentioned, this was probably the nitrosate of the monocyclic sesquiterpene zingiberene. Unfortunately it was not possible to confirm the presence of this hydrocarbon.

When fractions (*y*) and (*z*) were treated with selenium under the conditions used by Diels (*loc. cit.*) a hydrocarbon, b.p. 135–140°/10 mm., n_D^{30} 1·5334, was obtained. There can be little doubt that this hydrocarbon consisted essentially of cadalene, since it yielded a picrate melting as stated by Ruzicka (*Helv. Chim. Acta*, 1921, **4**, 508) at 115° (Found: C, 58·9; H, 5·1; N, 9·9. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9; N, 9·8 per cent.).

Fractions (*c*) to (*i*) consisted essentially of sesquiterpene alcohols, as is indicated by the analyses of fractions (*c*) and (*d*) (Found: for (*c*) C, 84·4; H, 10·8; for (*d*) C, 81·6; H, 10·9. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9 per cent.).

Attempts to prepare crystalline derivatives of these alcohols or to dehydrogenate them with sulphur were not successful.

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