

## PART XX. THE ESSENTIAL OIL FROM THE RHIZOMES OF 'CURCUMA AROMATICA', SALISB.

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The plant *Curcuma aromatica*, Salisb., like *Kaempferia galanga*, the essential oil from the rhizomes of which forms the subject of the preceding communication, belongs to the natural order *Zingiberaceæ* and is commonly known as wild turmeric. It occurs wild throughout India and is frequently cultivated especially in Mysore, Travancore, and Cochin. The rhizomes, which are light yellow in colour, are common articles of commerce in many parts of India. At one time the roots were exported for use as a dyeing material and at the present time a form of arrowroot is prepared from them in Travancore. According to Dymock (*Pharm. Ind.*, 1893, 3, 396) the roots are also used medicinally. The essential oil does not appear to have been examined.

On steam-distillation of the disintegrated roots an oil is obtained in a yield of 6.1 per cent. The oil is greenish brown in colour and has a pleasant camphoraceous smell. Examination has shown it to consist to the extent of over 65 per cent. of what appears to be a new laevorotatory monocyclic sesquiterpene for which the name *l-curcumene* is proposed. The hydrocarbon has been characterised by the preparation of the *trihydrochloride* (m.p. 84–85°), the *trihydrobromide* (m.p. 73–74°) and the *nitrosate* (m.p. 100.4°).

In a valuable series of communications Ruzicka (*Helv. Chim. Acta*, 1921, 4, 505 and subsequent papers) has applied Vesterberg's (*Ber.*, 1903, 36, 4200) sulphur method to elucidating the constitution of monocyclic and bicyclic sesquiterpenes, and has shown that in all cases one of the two naphthalene hydrocarbons, cadalene (3:8-dimethyl-5-isopropyl-naphthalene) or eudalene (1-methyl-7-isopropyl-naphthalene) results. When *l-curcumene* is treated with sulphur, although vigorous evolution of hydrogen sulphide takes place, no naphthalene derivative appears to be formed. This new monocyclic sesquiterpene behaves therefore abnormally, and we hope in a future communication to discuss its constitution.

In addition to *l-curcumene* the oil has been found to contain *d*-camphene, *d*-camphor and two sesquiterpene alcohols which are

probably tertiary and which do not yield any crystalline derivatives. The oil also contained either free or in combination a small quantity of *p*-methoxycinnamic acid.

The composition of the oil is approximately as follows :—

<i>d</i> -Camphene	....	....	....	0.8	per cent.
<i>d</i> -Camphor	....	....	....	2.5	" " <sup>1</sup>
Sesquiterpenes (mainly <i>l</i> -curcumene)	...	...	...	65.5	" "
Sesquiterpene alcohols	....	....	....	22.0	" "
Acids	....	....	....	0.7	" "
Unidentified	....	....	....	8.5	" "

### EXPERIMENTAL.

Prior to examination the oil was thoroughly dried over anhydrous magnesium sulphate, when it was found to have the following constants :— $d_{30}^{30}$  0.9139,  $n_D^{30}$  1.5001,  $[\alpha]_D^{30}$  -12.5°, acid value 0.9, ester value 2.03, ester value after acetylation 58.66. After treatment with an alcoholic solution of potassium hydroxide to hydrolyse the esters present the oil was distilled under diminished pressure, the results being recorded in Table I.

TABLE I.

No.	B.P./100 mm.	$d_{30}^{30}$	$n_D^{30}$	$[\alpha]_D^{30}$	Yield per cent
1	70-140°	0.8988	1.4709	30.8°	3.0
2	140-170°	0.8898	1.4951	- 17.9°	60.7
3	170-185°	0.9131	1.5022	..	3.7
4	185-200°	0.9576	1.5166	...	24.2
	Residue and loss	...	...	...	8.4

These four fractions were subjected to a prolonged systematic fractionation when ultimately eleven fractions were obtained.

<sup>1</sup> This was the yield of camphor separated from the appropriate fraction after draining on porous porcelain. The other fractions of the oil contained considerable quantities of the ketone but there does not appear to be any satisfactory method for estimating camphor in essential oils, the ordinary methods for the estimation of ketones, such as Kleber's phenylhydrazine method, giving very low results. The value must therefore be regarded as only approximate.

TABLE II.

No.	B.P./10 mm.	$d_{30}^{30}$	$n_D^{30}$	$[\alpha]_D^{30}$	Yield per cent.
1	45-65°	0.8634	1.46	49.4°	0.5
2	65-75°	0.8892	1.4671	39.7°	0.5
3	75-85°	...	...	..	1.25
4	85-105°	0.8998	1.4822	...	0.3
5	105-125°	0.8979	1.4897	- 11.1°	1.7
6	125-131°	0.8857	1.4939	- 16.8°	23.7
7	131-133°	0.8863	1.4947	- 16.5°	35.5
8	133-150°	0.9131	1.4998	. <sup>1</sup>	3.1
9	150-153°	0.9272	1.5051	... <sup>1</sup>	8.9
10	153-158°	0.9667	1.5198	... <sup>1</sup>	13.4
11	158-161°	0.9691	1.5246	.. <sup>1</sup>	2.5

*Fractions 1 and 2, d-Camphene.*—The two fractions were redistilled at the ordinary pressure using a four-pear Young still-head, when a terpene fraction with the following constants was separated:—b.p. 152-155°/687 mm.,  $d_{30}^{30}$  0.8597,  $n_D^{30}$  1.4569,  $[\alpha]_D^{30}$  50.6°. These constants indicated the presence of *d*-camphene and this was established by the preparation of the hydrochloride, m.p. 149-150°, the identity being confirmed by the method of mixed melting point. No *a*-pinene could be detected in this fraction of the oil.

*Fraction 3, d-Camphor.*—This fraction, which partially solidified in the condenser during distillation, had a strong camphoraceous smell and crystallised almost completely on keeping. The solid was collected and purified by crystallisation from alcohol, when it was found to melt at 175°, and this melting point was not depressed on admixture with a specimen of *d*-camphor from another source. The rotation was found to be 43.6° which is in agreement with that recorded for *d*-camphor, namely, 44°. The identity was further confirmed by the preparation of the oxime which melted at 118°.

*Fractions 4 and 5.*—These two fractions were found to be a mixture of *d*-camphor and sesquiterpenes; the alcohol-content (C<sub>10</sub>H<sub>16</sub>O) as determined by acetylation was less than three per cent.

<sup>1</sup> Owing to the green colour of these fractions the rotation could not be determined.

*Fractions 6 and 7, l-Curcumene.*—Fractions 6 and 7 which formed the bulk of the distillate, consisted essentially of *l*-curcumene. The hydrocarbon was purified by repeated distillation over sodium, when it boiled at 127–129°/6 mm. and had the following constant:— $d_{30}^{30}$  0.8760,  $n_D^{30}$  1.4929,  $[\alpha]_D^{30}$  -21.5°,  $[R_L]_D$  67.67, calc. 67.76 (Found: C, 88.1; H, 11.9;  $C_{15}H_{24}$  requires C, 88.2; H, 11.8 per cent.).

*l-Curcumene* is a faintly yellow oil with a slight and not unpleasant smell. When dissolved in acetic anhydride and treated with a drop of sulphuric acid a bright pink colour develops which becomes dark red on warming.

*l-Curcumene trihydrochloride* was readily obtained when an acetic acid solution of the hydrocarbon was treated with hydrogen chloride. It separated from methyl alcohol in hexagonal plates, m.p. 84–85° (Found: Cl, 33.6;  $C_{15}H_{27}Cl_3$  requires Cl, 34.1 per cent.). It is dextrorotatory, having  $[\alpha]_D^{30}$  26.04° in chloroform.

*l-Curcumene trihydrobromide* crystallised from methyl alcohol in needles, m.p. 73–74°.

*l-Curcumene nitrosate* was obtained in poor yield when amyl nitrite and nitric acid were added to an acetic acid solution of the hydrocarbon. It crystallised from light petroleum in rectangular prisms, m.p. 100.4° (Found: N, 9.5;  $C_{15}H_{24}O_4N_2$  requires N, 9.5 per cent.).

*Fraction 8* consisted of a mixture of sesquiterpenes and sesquiterpene alcohols.

*Fractions 9, 10 and 11*, were refractionated, when two main fractions were obtained; (i) b.p. 142–144°/7 mm.,  $d_{30}^{30}$  0.9586,  $n_D^{30}$  1.5135 (Found: C, 81.9; H, 10.3;  $C_{15}H_{24}O$  requires C, 81.8; H, 10.9 per cent.); (ii) b.p. 152–154°/7 mm.,  $d_{30}^{30}$  0.9701,  $n_D^{30}$  1.5208 (Found: C, 81.5; H, 10.4 per cent.).

Both fractions were coloured (i) being light green whilst (ii) was deep blue when freshly distilled, the colour however changing to a brownish green on keeping. Since the molecular refractive index was 69.0, both fractions appear to be monocyclic. All attempts to prepare crystalline derivatives by treatment with phthalic anhydride and

*p*-nitrobenzoyl chloride were unsuccessful and from their marked stability to dehydrating agents it may be concluded that they are tertiary alcohols.

*Free and Combined Acids.*—The alkaline solution separated from the treatment of the original oil with an alcoholic solution of potassium hydroxide (p. 141) was, after removal of the alcohol, acidified with sulphuric acid and distilled in steam. An analysis of the silver salts of the volatile acids indicated the presence of caprylic acid (Found: Ag, 42.9; calc. Ag, 43.0 per cent.). The residual liquid from the steam-distillation on keeping deposited a crystalline solid which was collected and purified by crystallisation from hot water, when it was found to melt at 170° and was identified as *p*-methoxycinnamic acid by the method of mixed melting point.