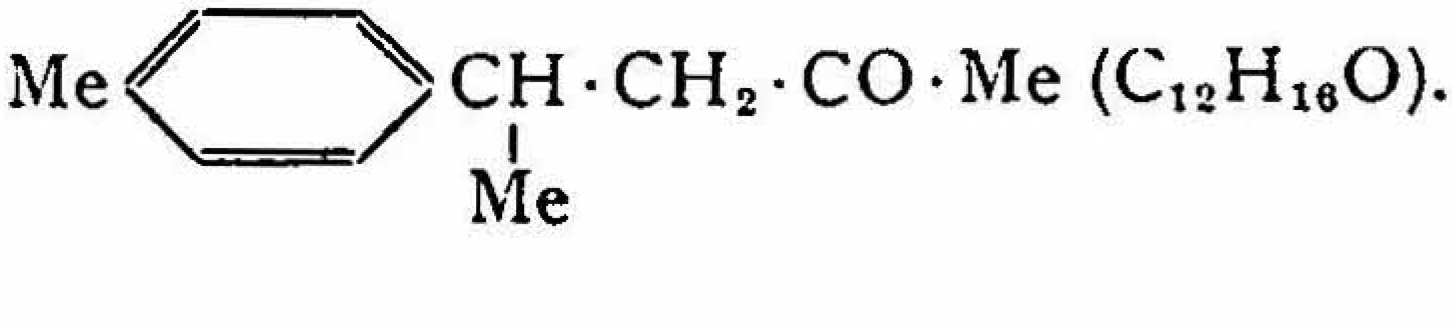
STUDIES IN INDIAN ESSENTIAL OILS.

V. ESSENTIAL OIL FROM THE RHIZOMES OF *CURCUMA LONGA*, LINN.

By N. C. Kelkar and B. Sanjiva Rao.

Curcuma longa is cultivated extensively all over India for the familiar turmeric rhizomes, over 60,000 acres being devoted to this crop. It is an indigenous plant in India and China, and is now naturalised in the Philippines, Java and Formosa. In India, it is chiefly grown in Madras, Bombay and Bengal and has been exported for many years to Great Britain, America, Germany, Persia and Turkey, where it is mainly used for colouring various food-stuffs and as a condiment. Special dyestocks have been produced in India by the careful selection of centuries of cultivation. Turmeric is a direct colour, giving a bright yellow, not removed by water but fading in sunlight. Its present importance is more as a condiment, flavouring material and in medicine.

Although the rhizome itself is an important article of trade, the oil from it is seldom distilled and is not of any commercial importance. It is, however, not without practical interest, as to it turmeric owes its aromatic taste and smell. The oil, extracted from Bengal turmeric, has been often subjected to chemical investigation (Bolley, Suida and Daube, *J. pr. Chem.*, 1868, **103**, 474; Ivanow and Gajewoskey, *Ber.*, 1872, **5**, 1103; Fluckiger, *ibid.*, 1876, **9**, 470; Kachler, *ibid.*, 1870, **3**, 713; Jackson and Menke, *Amer. Chem. J.*, 1882, **4**, 368; 1884, **6**, 81; Jackson and Warren, *ibid.*, 1896, **18**, 111; Schimmel's Report, 1890, 28; Rupe, *Ber.*, 1907, **40**, 4909; Rupe, Luksch and Steinbach, *ibid.*, 1909, **42**, 2515; Rupe and Steinbach, *ibid.*, 1910, **43**, 3465; Rupe and Wiederkehr, *Helv. Chim. Acta*, 1924, **7**, 654), but there is still considerable doubt as to its main constituents, only the presence of *d*-*a*-phellandrene having been established with certainty. The chief constituent according to Jackson and his collaborators is an alcohol turmerol to which the formula $C_{13}H_{18}O$ or $C_{14}H_{20}O$ has been assigned (Parry, *The Chemistry of Essential Oils and Artificial Perfumes*, 4th Edition, 1921, 107). The ketone curcumone discovered by Rupe in 1907 is not an original constituent of the oil but is formed by the action of alkali or acid on its main fraction. It has been recently synthesised by Rupe and Wiederkehr (*loc. cit.*) who have confirmed its structure to be

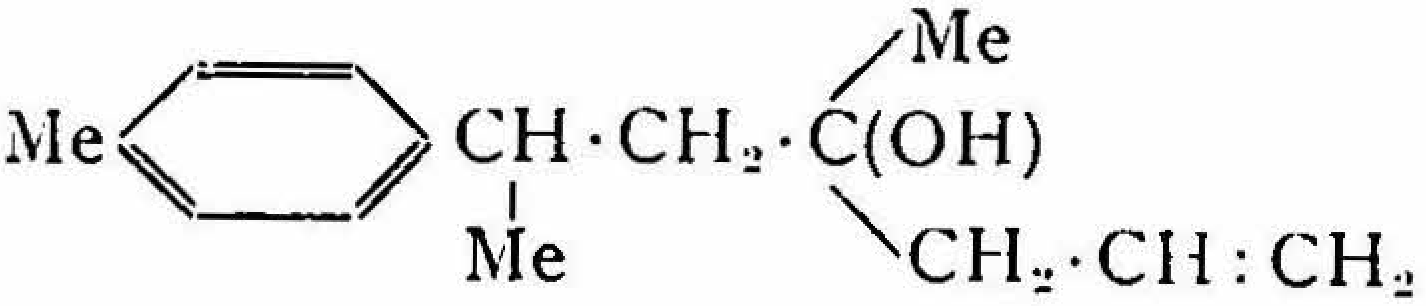


Unlike the oils examined hitherto, which were extracted from the rhizomes with a solvent and then steam-distilling the extract, the oil used in the present investigation was obtained by directly steam-distilling the powdered rhizomes. A detailed examination of the oil has revealed the presence of a number of new constituents. In the lower boiling portions of the oil, besides *d-α*-phellandrene, the presence of *d*-sabinene, cineol and borneol has been confirmed. The sesquiterpenes mainly consist of the monocyclic sesquiterpene zingiberene confirmed by the formation of the dihydrochloride (m.p. 169°), nitrosochloride (m.p. 96°), nitrosate (m.p. 86–87°) and nitrosite (m.p. 96°). Next to oil of ginger which belongs to the same natural order, turmeric oil would appear to be the most suitable source of this sesquiterpene. Its occurrence has been observed so far in only two other oils, Curcuma zedoaria (*Jour. Ind. Inst. Sci.*, 1928, **11A,** 196) and Thymus serpyllum (*ibid.*, 1932, **15A,** 83).

The main bulk of the oil consists of a mixture of sesquiterpene ketones and sesquiterpene alcohols. On treatment with hydroxylamine hydrochloride according to Stillman and Reed (*Perf. and Essent. Oil Rec.*, 1932, **23,** 278) a carbonyl value of 150 (number of milligrams of potassium hydroxide equivalent to hydroxylamine required for one gram of the oil) was obtained indicating 57·5, 58·1 or 58·6 per cent. ketone as $C_{15}H_{20}O$, $C_{15}H_{22}O$ or $C_{15}H_{24}O$ respectively. When the ketones from the turmeric oil were being investigated by the authors a preliminary note appeared by A. Pfau (*Helv. Chim. Acta*, 1932, **15,** 1481) assigning a constitution to the ketones from the oils of turmeric and cedar but no data which led to these structures being assigned have so far been published. It was, therefore, thought desirable to put the results we have obtained on record. In spite of the wide distribution of the terpene ketones, the occurrence of sesquiterpene ketones has been discovered only recently. The first members of this class to be isolated and to have their structure fully elucidated are the Ermephila ketones described lately by Simonsen and his collaborators (*J. C. S.*, 1932, **131,** 2744).

The fraction 158–165°/11 mm. which forms nearly 60 per cent. of the oil was treated with semicarbazide, a liquid semicarbazone being formed, and then steam-distilled. The distillate consisted mainly of tertiary sesquiterpene alcohols ($C_{15}H_{24}O$ or $C_{15}H_{22}O$) and a small quantity of curcumone which was removed by again treating with semicarbazide. The presence of curcumone shows that the sesquiterpene ketones decompose to an appreciable extent on mere boiling with semicarbazide hydrochloride and sodium acetate giving curcumone. The sesquiterpene alcohols freed from the ketones were further purified by benzoylation and distilling the non-alcoholic part. The absence of reaction with phthalic anhydride showed that the alcohols were tertiary. The sesquiterpene alcohols yield curcumone by boiling with alcoholic potash under Rupe's conditions (*loc. cit.*).

Grignard (*Comp. rend.*, 1923, **176,** 1860) found that certain ethylenic tertiary alcohols decompose on distillation into ketones and that a trace of acid or alkali catalyses the reaction. He found (*ibid.*, 1926, **182,** 299) that as the temperature of distillation increased dehydration of the alcohol decreased and the ketonic decomposition increased. Thus allyl-methyl-benzyl carbinol gives 90 per cent. phenylacetone and allyl-methyl-phenyl carbinol 80 per cent. acetophenone. It was thought that curcumone is formed in a similar manner from the sesquiterpene alcohol. A tertiary alcohol $C_{15}H_{22}O$,



was synthesised from curcumone and magnesium-allyl-bromide, but the resulting alcohol, although it formed curcumone on distilling at ordinary pressure, was unaffected by boiling with strong alkali showing that it was not identical with the alcohol occurring in the oil.

Rupe discovered, as already stated, that the fraction 158–165°/11 mm. is converted into a ketone curcumone (semicarbazone m.p. 126°) by boiling with alcoholic potash. This fraction was separated into several portions by efficient fractionation but none gave any derivatives of curcumone showing that it is not an original constituent of the oil. Hintikka prepared (*Ann. Acad. Sci. Fennicae*, 1923, **19A**, 6) from a ten-year old oil by treating with sodium ethylate in alcoholic solution three specimens of curcumone and isolated two more semicarbazones (m.p. 129° and 153–154°) besides the one melting at 126°, showing that ketones other than curcumone may also be formed from turmeric oil. To examine whether ketones other than curcumone are formed by the action of alcoholic potash on the fraction 158–165°/11 mm., the latter was split up into smaller fractions, and the yield and properties of curcumone obtained from several fractions have been recorded, the higher boiling fractions giving better yields of curcumone. The fraction 152–165°/10 mm. gives about 70 per cent. yield of curcumone. The curcumone semicarbazone (m.p. 125–126°) and the benzylidene curcumone (m.p. 106°) prepared from different fractions, were identical showing that the same curcumone is formed. The difference observed by Hintikka is probably due to its being a very old sample of oil and to the changes which curcumone itself undergoes when subjected to chemical treatment.

The oxidation of the sesquiterpene ketones which form the main bulk of the oil, with dilute nitric acid, yielded *p*-toluic and terephthalic acids as observed by Jackson and Menke (*loc. cit.*) and in addition oxalic acid and an infusible acid were also formed. Owing to the small yield and the difficulty of purification, the latter has not been identified. An acid $C_{11}H_{14}O_2$ (m.p. 42·5–43°) was obtained by oxidation of these fractions with potassium permanganate in aqueous or acetone solution. The yield of the acid was doubled in the latter case. This acid was found to be identical with curcumic acid obtained by Rupe and Wiederkehr (*loc. cit.*) by oxidising curcumone with sodium hypobromite and found to have the structure  The acid $C_{11}H_{14}O_2$ (m.p. 33–34°) obtained by Rupe and Steinbach from curcumone (*Ber.*, 1910, **43**, 3465) and by Jackson and Menke (*Amer. Chem. J.*, 1884, **4**, 81) by oxidising turmerol with potassium permanganate ($C_{11}H_{14}O_2$; m.p. 34–35°) are probably impure specimens of curcumic acid. The sesquiterpene ketones occurring in the oil as well as curcumone yield the same curcumic acid, indicating that one of the ketones contains the structure 

The fraction 152–165°/10 mm. (88 per cent. ketone as $C_{15}H_{22}O$) gives about 70 per cent. yield of curcumone showing that the main bulk of the sesquiterpene ketones is converted into curcumone. The analysis of the ketone fractions and titration with bromine showed the presence of a mixture of ketones $C_{15}H_{22}O$ and $C_{15}H_{20}O$. Semicarbazones, oximes, and dinitrophenylhydrazones were all obtained as liquids. The secondary alcohol obtained by reduction of the ketones by sodium and alcohol was also found to be a mixture. No solid derivatives characterising any of the alcohols were obtained.

The oxime of the sesquiterpene ketones was only partially soluble in ether, the remainder being soluble in chloroform. Both the ether and chloroform soluble oximes contained 6·3 per cent. nitrogen, $C_{15}H_{22}NOH$ and $C_{15}H_{20}NOH$ requiring 6·0 and 6·1 per cent. respectively. The amines obtained from these oximes by reduction with sodium in alcoholic solution were different from each other, one of them giving a sparingly soluble oxalate—$C_{15}H_{21}NH_2.H_2C_2O_4$ (m.p. 130°).

The liquid semicarbazone was not hydrolysed by 2 per cent. sulphuric acid or oxalic acid in the cold but on boiling with oxalic acid, 25 per cent. of the semicarbazone decomposed giving a ketone mixture consisting of 65 per cent. curcumone and 35 per cent. of a ketone $C_{15}H_{22}O$. The larger portion (75 per cent.) of the semicarbazone was unaffected by concentrated oxalic or hydrochloric acids. The semicarbazones obtained at the laboratory temperature or by boiling on water bath were identical in their behaviour.

EXPERIMENTAL.

The crushed rhizomes (90 lbs.; moisture 9·2 per cent.) were distilled in steam yielding an oil (4·76 lbs.; 5·8 per cent.) of a lemon colour and aromatic odour. Another consignment yielded 6·3 per cent. on the dry roots. The oil was dried over anhydrous magnesium sulphate and had the constants given in Table I which also includes the values observed by previous investigators.

TABLE I.

	Bangalore	Rupe[1]	Jackson[2]	Bacon[3]
$d_{30°}^{30°}$ ..	0.9245	..	..	0.930
$d_{20°}^{20°}$ ..	0.9290	0.9388	0.9539	..
$n_D^{30°}$ ..	1.5064	..	..	1.5030
$[\alpha]_D^{30°}$ ..	−17.3°	−24.8	−24.6	+8.6
Acid value ..	0.8	..	..	..
Ester value ..	3.2	..	..	81
Acetyl value ..	26.3	..	..	..
Ketones as $C_{15}H_{22}O$ ..	58.1	..	..	..
Phenols ..	..	..	..	..

The ketones were estimated by the oximation process of Stillman and Reed (*loc. cit.*). The latter consists in estimating the excess of hydroxylamine left after oximation of the ketone, by titrating with hydrochloric acid using bromo-phenol blue as indicator.

Free acids.—The oil (1600 g.) was dissolved in ether (3000 c.c.) and the solution shaken with 2 per cent. sodium carbonate solution (600 c.c.). The alkaline layer was removed, acidified with dilute sulphuric acid and distilled in steam. The oil that separated had a fatty smell and was dried and titrated against standard alkali (0.2135 g. required 22·5 c.c. NaOH (0·087 N), equivalent 108·9) which indicated a mixture of valeric and caproic acids.

Acids present as esters.—The oil (500 g.) recovered from the last experiment was boiled with alcoholic potassium hydroxide (3 per cent.), poured into water and extracted with ether. The alkaline solution was evaporated to a small bulk, acidified with dilute sulphuric acid and distilled in steam. The silver salt was prepared from the distillate after neutralisation with ammonia (Found: Ag, 51·3; silver valerate requires Ag, 51·7 per cent.).

Distillation of the oil.—The oil (1000 g.) which weighed 993 g. after treatment with 2 per cent. sodium carbonate, was distilled under

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[1] *Ber.*, 1909, **42**, 2516.

[2] *Loc. cit.*

[3] *Philippine J. Sci.*, 1910, **5A**, 262.

diminished pressure (20 mm.) with a 4-pear Young's column, the following fractions being obtained:—

TABLE II.

Fraction	B.P.	$d^{30°}_{30°}$	$n^{30°}_{D}$	$[\alpha]^{30°}_{D}$	Weight in g.	Yield per cent. on original oil
1	60– 80°	0·8559	1·4682	+75·7°	16·0	1·6
2	80– 85	0·8612	1·4731	+66·5	5·0	0·5
3	85– 90	0·8714	1·4758	+54·7	4·0	0·4
4	90–100	0·8802	1·4769	+27·7	2·0	0·2
5	100–110	0·8841	1·4774	+22·9	1·5	0·2
6	110–125	0·8911	1·4784	+14·8	1·5	0·2
7	125–140	0·8975	1·4802	– 7·5	4·0	0·4
8	140–145	0·9041	1·4836	–29·1	46·0	4·6
9	145–150	0·9075	1·4982	–42·4	37·0	3·7
10	150–155	0·9164	1·5013	–32·3	152·0	15·2
11	155–160	0·9287	1·5037	–29·0	103·0	10·3
12	160–165	0·9344	1·5072	–26·1	131·0	13·1
13	165–170	0·9430	1·5097	–22·5	143·0	14·3
14	170–175	0·9469	1·5111	–18·3	144·0	14·4
15	175–180	0·9481	1·5141	–10·7	178·0	17·8

In the accompanying graph in Fig. 1 curves are drawn by plotting the physical constants, *viz.*, boiling points, specific gravities, refractive indices and rotations against the percentage yield of the oil. The yield of the lower boiling constituents is comparatively small, for all the curves rise abruptly until they reach about 11 per cent. yield and then gradually deflect towards the abscissæ. The optical rotation curve contains four or five zones.

Fraction 1 (*d–sabinene and d–α–phellandrene*).— No semicarbazone or urethane could be obtained from this fraction. It was distilled over sodium twice and had then the following constants: d^{30}_{30} 0·8522; n^{30}_{D} 1·4668; $[\alpha]^{30}_{D}$ +80·4°. On oxidation with alkaline permanganate a small quantity of *d*–sabinenic acid was obtained melting at 55–56° which was unaltered when mixed with an authentic specimen.

The fraction also yielded an appreciable quantity of a nitrite when treated with sodium nitrite and acetic acid in petrol ether solution. It was recrystallized from aqueous acetone and melted at 112–113°, 0·1038 g. dissolved in 10 c.c. chloroform had $\alpha_D = -1\cdot3°$; $[\alpha]_D = -125°$; *d–α*–phellandrene nitrite, according to Wallach, melts at 113° and has $[\alpha]_D = -138°$.

Fractions 2–6.—They were mixed and refractionated twice with a Young column at 20 mm. when the following fractions were obtained:

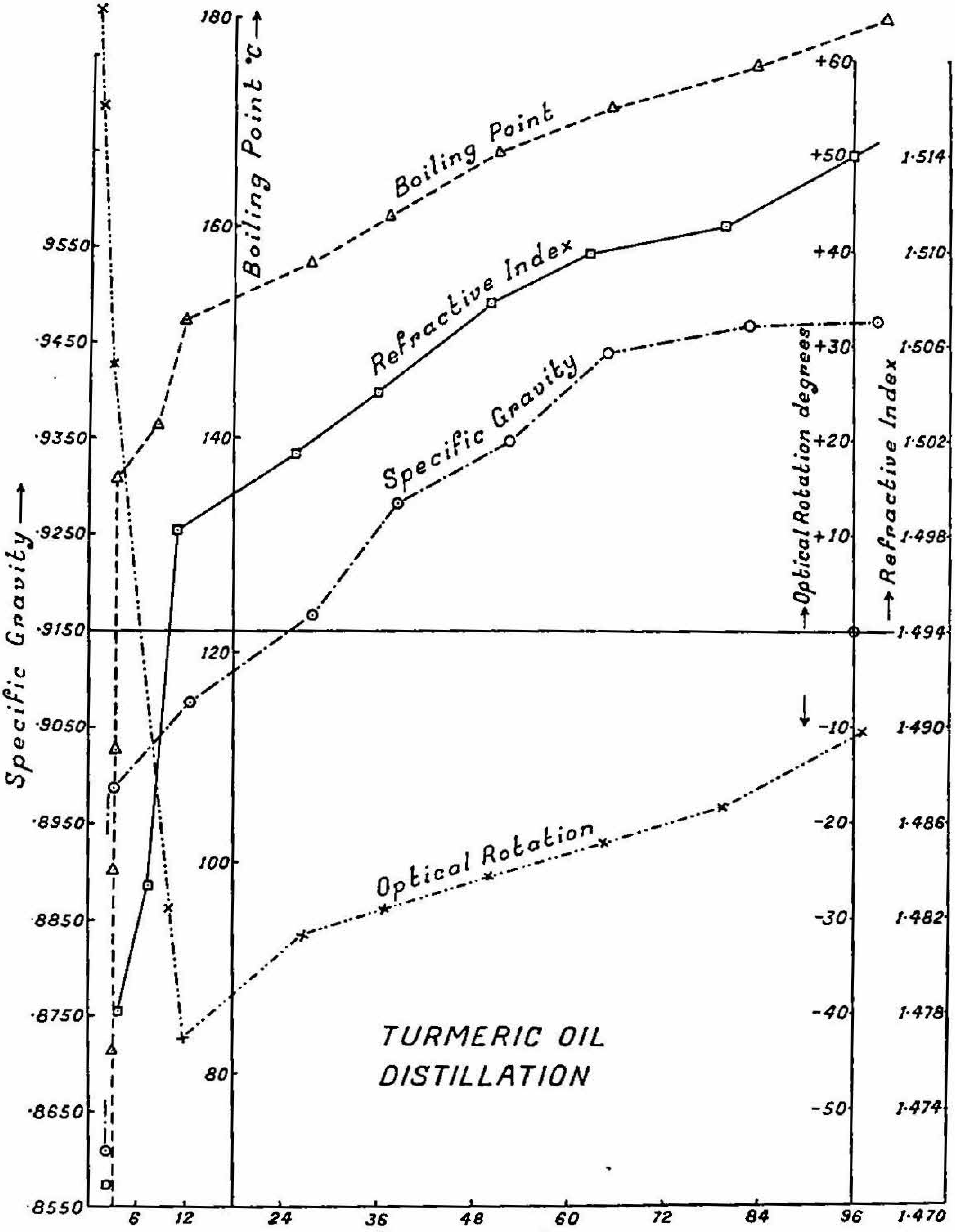


Fig. 1.

TABLE III.

Fraction	B. P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	Weight in g.	Yield per cent on original oil
A	– 70°	0·8746	1·4687	+46·2°	3·0	0·3
B	70–115	0·8991	1·4795	–13·9	3·0	0·3
C	115–130	0·9005	1·4659	–27·3	4·0	0·4

They all had a marked camphoraceous odour. Each of them yielded a yellowish white precipitate on triturating a well-cooled solution in petrol ether with concentrated phosphoric acid showing the presence of cineol.

Fraction C (*Borneol*).—Since from the constants an alcohol was suspected, the fraction (1 g.) was treated with an excess of phenyl isocyanate, when on standing a crystalline urethane was deposited. It was freed from diphenylurea with light petroleum and was recrystallized from dilute alcohol when needles melting at 137–138° were obtained. The identity of this substance with the phenylurethane of borneol was proved by the method of mixed melting point.

Fractions 7–11 were repeatedly refractionated at 5 mm. and fractions which appeared to be mainly sesquiterpenes were mixed and distilled over sodium when the fractions given in Table IV were obtained.

TABLE IV.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	$[R_L]_D$	Weight in g.	Yield per cent. on original oil	Carbon	Hydrogen
D	115–117°	0·8677	1·4935	–38·4	68·4	15·0	1·5	88·15	11·71
E	117–121	0·8691	1·4937	–59·2	68·4	85·0	8·5		
F	121–123	0·8695	1·4938	–47·4	68·4	50·0	5·0		
G	124–127	0·8734	1·4941	–26·5	68·0	30·0	3·0		
H	127–131	0·8742	1·4942	–22·0	68·0	15·0	1·5		

Fractions D–H (*Zingiberene*).—The physical constants of these fractions do not vary very widely and the differences are probably due to other sesquiterpenes and perhaps traces of sesquiterpene ketones, since the values of $[R_L]_D$ are very constant. Fractions D, F and H gave a nitrosochloride with amyl nitrite and hydrochloric acid melting at 96° (mixed m. p. 95–96°) after crystallisation from a mixture of ethyl acetate and alcohol.

Zingiberene dihydrochloride.—Fraction E (10 g.) was dissolved in glacial acetic acid (50 c.c.) and through the well-cooled solution, a brisk current of dry hydrogen chloride was passed until the solution was saturated. On pouring into water, isozingiberene dihydrochloride (4·3 g.) was obtained melting at 168–169° after recrystallisation from ethyl acetate (Found: Cl, 25·8; $C_{15}H_{26}Cl_2$ requires Cl, 25·6 per cent.).

Zingiberene nitrosate.—Fraction E (5 g.) yielded (1·2 g.) nitrosate melting at 86–87° after recrystallisation from ethyl acetate (Found: C, 60·71; H, 8·02; N. 9·3; $C_{15}H_{24}N_2O_4$ requires C, 60·81; H, 8·11; N, 9.46 per cent.).

Zingiberene nitrosite.—Fraction E (5 c.c.) dissolved in petroleum ether (40 c.c.) was mixed with a saturated solution of sodium nitrite and glacial acetic acid (4 c.c.) gradually added and allowed to stand. The crystals which separated melted at 96–97° after crystallising from methyl alcohol. The physical constants and the formation of these derivatives left no doubt as to the sesquiterpene fractions being mainly composed of zingiberene.

The residue (140 g. ; Table IV) with fractions 12–15 (Table II) were mixed and fractionated at 12 mm. twelve times using a 16″ Widmer column, mixing together fractions having the same physical properties, the fractions in Table V being obtained.

TABLE V.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{5780}$	$[\alpha]^{30}_{5461}$	$\frac{[\alpha]^{30}_{5461}}{[\alpha]^{30}_{5780}}$	Weight in g.	Yield per cent. on original oil
a	150–152°	0·9226	1·5024	−26·8°	−33·2°	1·24	90	9·0
b	152–154	0·9250	1·5029	−28·4	−35·8	1·26	82	8·2
c	154–156	0·9317	1·5047	−29·4	−35·7	1·21	20	2·0
d	156–157	0·9358	1·5065	−28·3	−32·1	1·13	15	1·5
e	158–159	0·9378	1·5074	−30·4	−34·2	1·13	24	2·4
f	159–160	0·9445	1·5094	−27·3	−30·7	1·12	21	2·1
g	160–161	0·9448	1·5101	−26·3	−29·9	1·13	27	2·7
h	160–161	0·9448	1·5105	−26·1	−29·3	1·12	25	2·5
i	160–161	0·9448	1·5109	−24·2	−27·3	1·12	36	3·6
j	160–161	0·9458	1·5116	−19·5	−21·4	1·10	27	2·7
k	160–161	0·9461	1·5122	−16·8	−18·4	1·10	51	5·1
l	160–161	0·9466	1·5125	−12·2	−13·5	1·10	11	1·1
m	161–162	0·9469	1·5130	− 8·5	− 8·8	1·03	48	4·8
n	161–162	0·9477	1·5130	− 4·7	− 4·5	0·96	11	1·1
o	162–163	0·9477	1·5135	− 2·6	− 2·1	0·81	12	1·2
p	163–164	0·9479	1·5138	− 0·1	+1·0	..	16	1·6
q	164	0·9499	1·5150	+3·9	+5·3	1·36	25	2·5
r	164	0·9499	1·5150	+7·8	+9·8	1·26	18	1·8

In the adjoining graph in Fig. 2 which shows the relation between physical constants and percentage composition, it is obvious that in spite of repeated distillation, the fractions are still very complex mixtures. It does not seem possible to isolate any pure constituents by fractionation alone. The results obtained by the combustion of some of the fractions are as follows :

Fraction	*a*	*e*	*m*	*o*	*q*	$C_{15}H_{24}O$	$C_{15}H_{22}O$	$C_{15}H_{20}O$
Carbon per cent.	84·1	82·3	82·9	82·8	83·1	81·8	82·6	83·3
Hydrogen per cent.	10·1	10·3	10·2	10·1	9·9	10·9	10·1	9·2
Molecular wt. (by freezing point of benzene)			216		212			

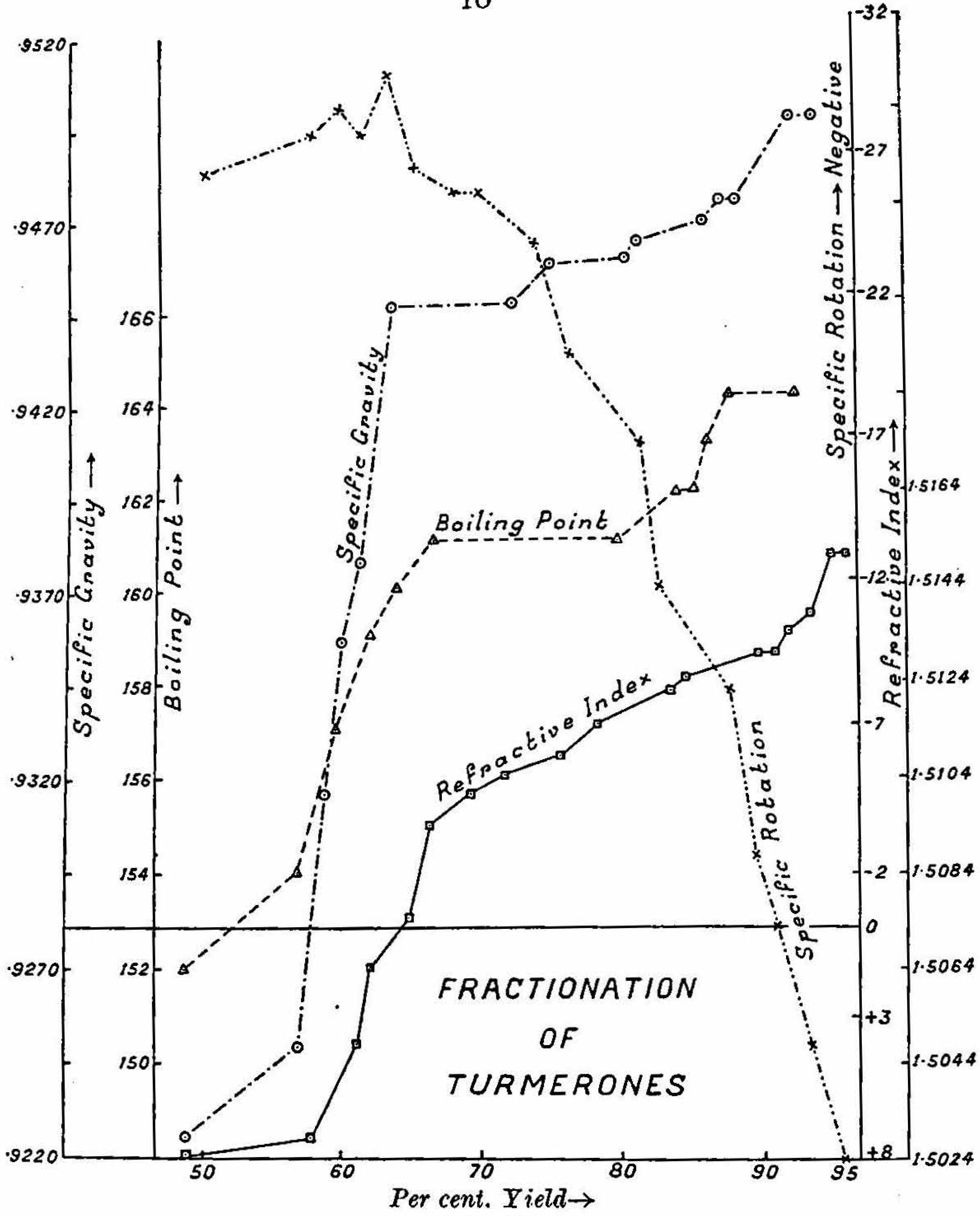


Fig. 2.

The values indicate that the fractions are mainly mixtures of $C_{15}H_{22}O$ and $C_{15}H_{20}O$ compounds. The solution of the fraction *q* (1·042 g.) in carbon tetrachloride required bromine (1·1544 g.) dissolved in the same solvent, the excess bromine added being estimated by titration with sodium thiosulphate. From this one finds a molecule of $C_{15}H_{22}O$ or $C_{15}H_{20}O$ takes up 3 atoms of bromine showing that the fraction is probably a mixture of two substances having one and two double bonds. The main bulk of the oil 158-165°/11 mm. fraction also absorbed about the same amount of bromine.

The fractions *a* and *q* were found to have acetyl values of 10·5 and nil corresponding to 4·1 per cent. alcohol as $C_{15}H_{24}O$ in (*a*). That it was not wholly an alcohol was also confirmed by treating a known weight of the fractions with magnesium methyl iodide dissolved in phenetol and measuring the amount of methane evolved (Hibbert and Sudborough, *J.C.S.*, 1904, **85,** 933). Fraction *m* (0·1365 g.) gave methane (6·3 c.c.) at 31°C and 685 mm. or 2·8 per cent. alcohol as $C_{15}H_{24}O$. Fractions *o* and *q* showed still smaller proportion of the alcohol. On treatment of fractions *a*, *m* and *q* with phthalic anhydride at 130°, no phthalic ester was isolated showing that the alcohols are tertiary.

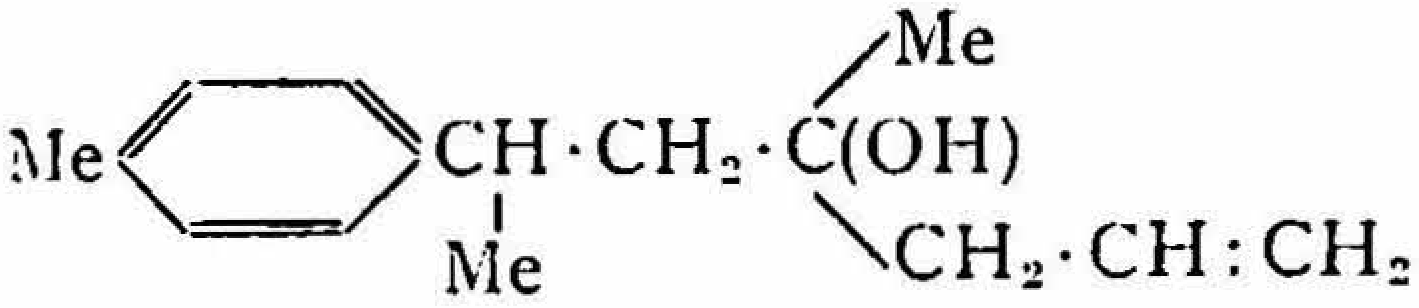
The higher boiling fractions were found to be richer in the carbonyl compounds by Stillman and Reed's method. The fractions *c*, *h* and *m* gave 181·2, 214·0 and 233·4 as carbonyl values corresponding to 71, 84 and 94 per cent. as $C_{15}H_{22}O$. There was no coloration with fuchsine reagent nor did any fraction reduce silver nitrate showing the absence of any aldehyde.

Sesquiterpene alcohols.—The fraction of the oil (500 g.) boiling above 150°/10 mm. with semicarbazide hydrochloride (300 g.) and sodium acetate (300 g.) was boiled in alcoholic solution and allowed to stand for 48 hours and then distilled in steam. An oil (53 g.) was recovered as distillate. This was treated again with semicarbazide and then by distillation in steam an oily distillate (43 g.) was obtained. The latter gave no more semicarbazone and had the following properties: b.p. 102–107°/3 mm., d^{30}_{30} 0·9491; n^{30}_{D} 1·4980; $[\alpha]^{30}_{D}$–15·2°. To separate the hydrocarbons and other non-alcoholic bodies, the product was benzoylated by Schotten-Baumann's process and the non-benzoylated portion was distilled at 1 mm. The alcohol obtained on decomposing the benzoyl derivative with alkali had the following constants: b.p. 108-110°/3 mm.; d^{30}_{30} 0·9565; n^{30}_{D} 1·4982; $[\alpha]^{30}_{D}$ –14·6°; C, 81·96; H, 10·3; $C_{15}H_{24}O$ requires C, 81·8; H, 10·9 per cent. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1 per cent. The crude sesquiterpene alcohol was also purified by the boric acid method (*Chem. Ztg.*, 1928, **52,** 898). The crude alcohol (15 g.) was heated with acetic anhydride (15 g.) and boric acid (5 g.) for 5 hours at 120°. The acetic anhydride was distilled at 100 mm. and the sesquiterpenes at 3 mm. The ester was washed with dry ether and decomposed with alkali. The liberated alcohol, on distillation, had the following constants: b.p. 108–112°/3 mm.; d^{30}_{30} 0·9548; n^{30}_{D} 1·4993; $[\alpha]^{30}_{D}$ –12·8°.

The purified alcohol did not react with phthalic anhydride at 130° and was therefore a tertiary alcohol. By Hibbert and Sudborough's method 0·1467 g. yielded 17·3 c.c. methane at 23·5° and 683 mm. showing 7·5 per cent. hydroxyl while $C_{15}H_{24}O$ and $C_{15}H_{22}O$ require 7·7 and 7·8 per cent. hydroxyl respectively. This confirmed that it was not mixed up with ketone and was mainly alcoholic, unlike any of the fractions in Table V.

Curcumone from the sesquiterpene alcohol.—The alcohol (3 g.), 30 per cent. potash (10 c.c.) and ethyl alcohol (10 c.c.) were boiled together for an hour. The reaction product was purified by distillation and gave a benzylidene derivative melting at 105° (mixed melting point with benzylidene curcumone 105°).

Synthesis of an alcohol $C_{15}H_{22}O$.—It appeared possible that an ethylenic tertiary alcohol of the Grignard type (see p. 9) will decompose into curcumone on treatment with alkali. The alcohol



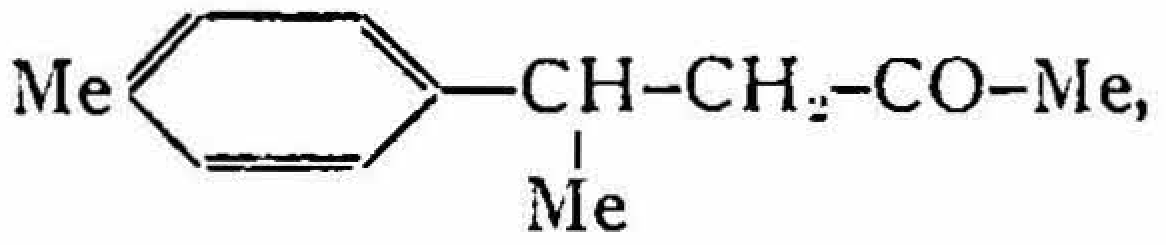
was prepared by the action of magnesium-allyl-bromide on curcumone. The magnesium-allyl-bromide was obtained in excellent yield by Gilman's process (*Bull. Soc. Chim.*, 1928, **43,** 1323; Meisenheimer, *Ber.*, 1921, **54,** 1655) from allyl-bromide (12 g.), magnesium (4·6 g.) and ether (200 c.c.). It was decanted from excess of magnesium into a second flask cooled by an ice-bath and curcumone (10 g.) dissolved in dry ether (100 c.c.) added gradually left overnight and finally boiled for an hour. Ice-water was then added, acidified with dilute sulphuric acid and the liberated alcohol extracted with ether.

A better yield of the tertiary alcohol was obtained by the following process. A solution of allyl-bromide (30 g.) and curcumone (30 g.) in ether (100 c.c.) was added gradually during 2 hours to magnesium (12 g.) suspended in ether (50 c.c.). After about 10 c.c. was added a violent reaction occurred so that cooling with ice was necessary. At the end of the reaction, the mixture was heated for an hour, decomposed with ice and dilute sulphuric acid. The product on distillation gave the following fractions:

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	Weight in g.
I	110–140°	0·9376	1·5030	9
II	140–145	0·9511	1·5051	12

On distilling fraction II (5 g.) at ordinary pressure there was decomposition but the distillate gave a semicarbazone (m.p. 125°) identical with that from curcumone. Fraction II (5 g.) was suspended in water (50 c.c.) and 4 per cent. potassium permanganate (110 c.c.) added drop by drop, the solution being maintained between 0 and 5°. The acid formed was recovered and after three days in the ice-chest a few needles appeared (m.p. 39–42°). Fraction II (5 g.), 30 per cent. aqueous potash (8 c.c.) and ethyl alcohol (10 c.c.) were boiled together for two hours on the waterbath. The reaction product distilled at 145–155°/ 7 mm. No derivatives of curcumone could be obtained, showing that the synthetic alcohol is not identical with the sesquiterpene alcohol occurring in the oil. Two more alcohols with the double bond in different positions in the side chain are being synthesised.

Curcumone.—It has been pointed out by Rupe (*loc. cit.*) that the main fraction of the oil boiling above 158°/11 mm. is converted into a ketone curcumone by boiling with an equal volume of 30 per cent. alcoholic potash for three hours. Rupe identified curcumone by its semicarbazone (m.p. 126°) and its benzylidene derivative (m.p. 106°) and confirmed its structure to be



, by its synthesis in 1924.

A few of the fractions (Table V) were separately boiled with alcoholic potash for two hours and from the reaction product, semicarbazones and benzylidene derivatives were prepared. The yields of these derivatives from each fraction (5 g.) prepared under similar conditions have been tabulated below:

Fraction ..	*a*	*c*	*e*	*i*	*o*	*r*
Semicarbazone in g. ..	0·2	0·6	1·2	3·8	4·4	4·9
Benzylidene curcumone in g. ..	0·2	0·7	1·8	3·1	5·5	5·6

The semicarbazones obtained from different fractions had the same melting point (125–126°) and were found to be identical with that from curcumone. No semicarbazones melting at 129° or 153° as found by Hintikka (*loc. cit.*) could be isolated. The benzylidene curcumone (m.p. 105-106°) from different fractions was also identical. It is concluded that the higher fractions are richer in the substances yielding curcumone.

To prepare a large quantity of curcumone the fraction 152–165°/10 mm. (200 g., d^{30}_{30} 0·9450, n^{30}_{D} 1·5115, $[\alpha]^{30}$ −18·8°) was boiled with 30 per cent. aqueous potash (180 g.) and ethyl alcohol (225 c.c.) for 6 hours.

The crude curcumone on fractionating twice at 7 mm. gave the following results:

TABLE VI.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30°}_{5780}$	$[R_L]_D$	Weight in g.
w	108–112°	0·9430	1·4874	−56·7°		9
x	112–115	0·9426	1·4932	−65·7	54·3	102
y	115	0·9429	1·4949	−56·3	54·5	41
z	115–125	0·9457	1·4980	−15·4		10

Nearly 70 per cent. of the initial fraction is converted into curcumone. The four fractions yielded a semicarbazone identical with that from curcumone. The curcumone is formed not only from the sesquiterpene alcohol which is only about 9 per cent. but also from the sesquiterpene ketones which form the bulk of the oil.

Sesquiterpene ketones.—It has been shown that the main bulk of the oil (b.p. 158–164° 11mm.) consists of sesquiterpene ketones (88 per cent. as $C_{15}H_{22}O$). To remove the alcohols present in the ketone mixture, the fraction (100 g.) was treated with benzoylchloride (50 g.) and 10 per cent. caustic soda (200 c.c.) and shaken for four hours. The reaction product was distilled in steam. The semicarbazone, oxime, phenylhydrazone and *p*-nitrophenylhydrazone were all liquids.

Sesquiterpene ketone semicarbazone.—The oil (100 g.) was mixed with semicarbazide hydrochloride (45 g.) and sodium acetate (40 g.) in dilute alcoholic solution and allowed to stand for seventy-two hours. It was poured into water and the reaction product (118 g.) was distilled in steam. The residue (74 g.) consisted of the mixture of ketone semicarbazones [the ketone $C_{15}H_{22}O$ (59 g.) should yield semicarbazone 75 g.]. When the mixture of oil and semicarbazide was heated for four hours on the water-bath, instead of keeping at the ordinary temperature a solid (m.p. 245°) separated which was found to be hydrazodicarbonamide. The semicarbazone from which the unattacked ketone had been removed with steam had N, 13·3; $C_{16}H_{25}ON_3$ requires N, 15·3, the analytical value for nitrogen is thus too low.

Hydrolysis of the semicarbazones.—The liquid mixture of semicarbazones could not be readily hydrolysed. Both oxalic acid and 2 per cent. sulphuric acid failed to decompose the semicarbazone in the cold. Boiling with phthalic anhydride was also ineffective. The liquid semicarbazone (60 g.) was distilled in steam in presence of oxalic acid (40 g.). An oil (15 g.) was recovered from the distillate having the following properties: b. p. 110–160°/ 7 mm., d_{30}^{30} 0·9477, n_D^{30} 1·5040, $[\alpha]_D^{30}$ +10·4°. On fractionation at 7 mm. through a packed column (1 ft.), the following fractions were obtained:

TABLE VII.

Fraction	B.P.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Weight in g.
K	108–110°	0·9437	1·5000	− 6·0°	1·3
L	110	0·9444	1·5010	+ 0·2	1·5
M	110–112	0·9467	1·5020	+ 7·2	4·3
N	112–145	..	..	..	0·2
P	145–150	0·9544	1·5120	+26·2	3·5

Fractions, K, L *and* M (*Curcumone*).—The constants are in agreement with those for curcumone. The three fractions gave excellent yields of a benzylidene derivative (m.p. 105–106°) and a semicarbazone (m.p. 125°) both identical with those from curcumone. The original ketone liberated from the semicarbazone has apparently undergone decomposition into curcumone as soon as it was liberated in presence of oxalic acid.

Fraction P.—Analysis, C, 82·74; H, 10·12; $C_{15}H_{22}O$ requires C, 82·56; H, 10·09. No benzylidene derivative was obtained showing absence of curcumone. The semicarbazone, oxime and dinitrophenylhydrazone were all liquids. The ketone (1 g.) was boiled with 30 per cent. alcoholic potash (10 c.c.) for an hour. The recovered product gave a benzylidene derivative (m.p. 106°) and a semicarbazone (m.p. 124–125°) showing conversion of the ketone into curcumone. On oxidation of the ketone (2·5 g.) with permanganate (8 g.) in acetone solution an acid (0·4 g.) melting at 42-43° was isolated and found to be identical with curcumic acid by mixed melting point.

The major portion of the semicarbazone of the sesquiterpene ketones was however unattacked by oxalic acid. Both boiling concentrated oxalic acid and alcoholic hydrochloric acid did not decompose the residual semicarbazone. It was recovered by extracting with ether (12 g.), chloroform (6 g.) and alcohol (26 g.).

Reduction of ketone mixture by sodium and alcohol.—To find if the ketones contain conjugated double bonds, the fraction *q* (25 g.) was reduced with sodium and alcohol. After first reduction the specific gravity at 30° fell from 0·9444 to 0·9260 and after four more reductions no further change in properties was observed, the final product giving the following fractions on distillation at 3 mm.

B.P.	d_{30}^{30}	n_D^{30}	Per cent. bromine absorbed.
103–105°	0·9129	1·4870	47·8
105–110	0·9181	1·4885	44·5
110–112	0·9192	1·4880	..

The product is a mixture of a saturated and an unsaturated body which could not be separated by distillation. The secondary alcohol $C_{15}H_{28}O$ formed during reduction, was separated by means of the phthalic ester and had the following constants: b. p. 135–140°/10 mm., d_{30}^{30} 0·9156, n_D^{30} 1·4854, $[\alpha]_D^{30}$ –5·0; C, 80·5; H, 12·8; $C_{15}H_{28}O$ requires C, 80·4; H, 12·5 per cent.).

Oxime.—The fraction 158–165°/10 mm. (100 g., 88 per cent. turmerone as $C_{15}H_{22}O$) hydroxylamine hydrochloride (70 g.) and sodium carbonate (27 g.) in alcoholic solution was boiled together for 3 hours and distilled in steam. The residue (36·5 g.) was extracted with ether and then with chloroform (65·0 g.). Ether soluble oxime contained N, 6·6 per cent. and the chloroform soluble oxime N, 6·6 per cent.; $C_{15}H_{24}NOH$ requires N, 6·0; $C_{15}H_{22}NOH$ requires N, 6·07;

$C_{15}H_{20}NOH$, N, 6·06. The higher content of nitrogen is perhaps due to traces of nitrogen oxides (Nef. *Annalen*, 1900, **310**, 330).

Reduction of ether soluble oxime by sodium and alcohol.—The oxime (10 g.) was dissolved in absolute alcohol (100 c.c.) and sodium (10 g.) added as rapidly as possible. When all the sodium had dissolved, the base was distilled in steam, dissolved in ether and the ethereal extract repeatedly washed with dilute hydrochloric acid. The well-cooled solution of the hydrochloride was made alkaline with sodium hydroxide solution and the resulting oil (3·5 g.) isolated by extraction with ether. The crude base was mixed with excess of an aqueous solution of oxalic acid and the sparingly soluble oxalate which separated was collected; it was obtained as a fine crystalline powder m.p. 130° (Found: C, 66·6; H, 8·7. $C_{15}H_{21}NH_2.H_2C_2O_4$ requires C, 66·4; H, 8·1; N, 4·56 per cent.). No other crystalline derivatives of the base could be obtained.

Reduction of chloroform soluble oxime.—The oxime (10 g.) in absolute alcohol (100 c.c.) was treated with sodium (10 g.). The resulting amine (3·5 g.) gave no crystalline derivative and had the following properties: b.p. 85–95°, d^{30}_{30} 0·9263, n^{30}_{D} 1·4924.

Oxidation of sesquiterpene ketones by dilute nitric acid.—Fraction *q* (20 c.c.) was mixed with dilute nitric acid (1 : 2; 50 c.c.) and gradually heated under reflux for 8 hours. There was a vigorous reaction at 85° and after it subsided, the temperature was raised to 130° when the acid boiled briskly. On gradual addition of more acid (50 c.c.) the brown pasty mass which had been formed, gradually disappeared and a small quantity of white powder was deposited. This was soluble in alkali, with difficulty in sodium bicarbonate and was re-precipitated by acids. It was infusible even at 400°.

The filtrate on concentration and cooling deposited white needles. On triturating with 50 per cent. alcohol, the insoluble portion which separated was purified by sublimation and was confirmed to be terephthalic acid (Equiv. wt., 166; C, 57·7; H, 3·7. $C_8H_6O_4$ requires C, 57·8; H, 3·6 per cent.). The dimethyl ester prepared by refluxing acid (0·5 g.), sulphuric acid (0·5 g.) and methyl alcohol (20 c.c.) melted at 139–140° (mixed m.p. 140°).

The alcohol soluble portion melted at 180° and was found to be *p*-toluic acid (mixed m.p. 180°). The amide melted at 160° (mixed m.p. with *p*-toluamide 159–160°).

On further concentration of the original mother liquor, another crystalline substance was deposited which proved to be oxalic acid.

Oxidation of the ketones by potassium permanganate (curcumic acid).—The oil from fraction *m* (10 g.) was suspended in water (100 c.c.) and to the well-cooled liquid, 4 per cent. $KMnO_4$ solution (500 c.c.)

was gradually added, using mechanical stirring. The neutral bodies were small. The acid portion was purified by distillation in steam. The product (0·7 c.c.) gradually solidified in the ice-chest, needle-shaped crystals (0·38 g.) being obtained. It was recrystallised from methyl alcohol twice when it melted at 42·5–43°. The acid (0·1013 g.) required alkali (7·5 c.c. of ·0755 N) the equivalent being 177·6. It is identical with curcumic acid obtained by Rupe by oxidation of curcumone with sodium hypobromite.

The same acid was obtained in double the yield by oxidising in acetone solution, powdered potassium permanganate (18 g.) being gradually added.

Dehydrogenation with sulphur and selenium.—Fraction *p* (10 g.) heated with sulphur at 180–220° gave a product with the following properties after distillation over sodium, b.p. 140–145°/14 mm. d^{30}_{30} 0·8975, n^{30}_{D} 1·5546, $[\alpha]^{30}_{D}$ + 30·8°. No picrate was formed.

Treatment with selenium powder, instead of sulphur and heating at 240–250°, a low boiling hydrocarbon was obtained, b.p. 55–120°/11 mm., d^{30}_{30} 0·8706, n^{30}_{D} 1·4927. Neither cadalin nor eudalin was formed.

Changes in optical rotation of different fractions of turmeric oil.—During the investigation of the oil, a peculiar phenomenon was observed. The whole oil does not show any pronounced change in the optical rotation but the fractions showed considerable difference in the rotations on keeping. The change in the earlier fractions is from dextro to lævo and in the later lævo to dextro, the two effects nearly balancing each other.

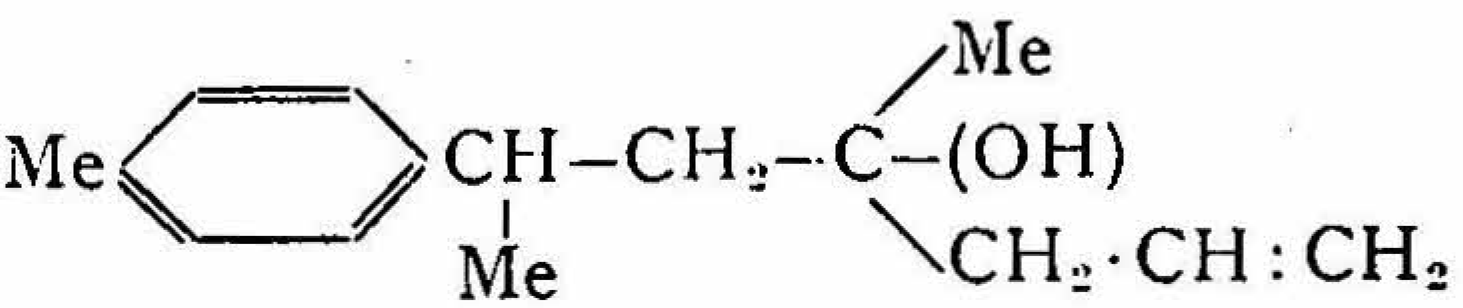
SUMMARY.

1. In addition to *d*–α–phellandrene (1 per cent.) whose occurrence in the turmeric oil was known, *d*–sabinene (0·6 per cent.), cineol (1 per cent.), borneol (0·5 per cent.) and zingiberene (25 per cent.) have been found in the oil.

2. Next to oil of ginger, turmeric oil would appear to be the most suitable source of zingiberene.

3. No alcohol of the formulæ $C_{13}H_{18}O$ or $C_{14}H_{20}O$ appears to be present in the oil. A tertiary alcohol $C_{15}H_{24}O$ or $C_{15}H_{22}O$ which yields curcumone on boiling with alkali is present (9 per cent.).

4. A tertiary alcohol



has been synthesised and its properties studied. It does not yield curcumone on boiling with potash and is hence not identical with the alcohol occurring in the oil.

5. A mixture of sesquiterpene ketones, turmerones $C_{15}H_{22}O$ or $C_{15}H_{20}O$ (58 per cent.) is present in the oil. The semicarbazone, oxime and dinitrophenylhydrazone were all obtained as liquids.

6. The oxidation of the mixture of ketones (turmerones) with potassium permanganate yielded curcumic acid, m.p. 42–43°, identical with that obtained by oxidation of curcumone. On boiling with dilute nitric acid, the ketones gave *p*–toluic, terephthalic and oxalic acids. A small quantity of an infusible acid not identified was also obtained.

7. The secondary alcohol $C_{15}H_{28}O$ formed by reduction of the ketones did not yield any solid derivatives. On oxidation with chromic acid, a ketone $C_{15}H_{26}O$ was obtained which gave a liquid semicarbazone and oxime.

8. No naphthalene hydrocarbon was obtained from turmerones or the secondary alcohols obtained from them by dehydrogenation with sulphur or selenium.

9. Curcumone is not an original constituent of the oil but is formed by the action of alkali on the sesquiterpene ketones and alcohols present in the oil. No other ketones of the type found by Hintikka are formed in this reaction.

10. Appreciable quantities of curcumone were formed from the turmerones by mere boiling with semicarbazide hydrochloride and sodium acetate in alcoholic solution.

11. The mixed semicarbazones of turmerones were only partially (20 per cent.) decomposed by oxalic acid. The ketones obtained consisted mainly of curcumone and about 25 per cent. of another ketone $C_{15}H_{22}O$. The residual semicarbazone could not be decomposed even with alcoholic hydrochloric acid or sulphuric acid.

12. The ketone $C_{15}H_{22}O$ obtained by decomposition of the semicarbazone with oxalic acid gave curcumic acid on oxidation with potassium permanganate.

13. Two oximes were obtained from the turmerone fraction, one soluble in ether and the other soluble in chloroform.

14. The ether soluble oxime gave on reduction with sodium and alcohol an amine $C_{15}H_{23}NH_2$ characterised by a sparingly soluble oxalate $C_{15}H_{23}NH_2 \cdot (COOH)_2$ m.p. 130°. The amine from the chloroform soluble oxime did not give any solid derivatives.

The authors desire to express their best thanks to Mr. M. S. Kotnis for assistance in some experiments.

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[Accepted 30–10–1933.]