317. *The Constituents of Some Indian Essential Oils. Part XXVI. The Structures of* l-α- *and* β-*Curcumenes.*

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The two hydrocarbons present in the essential oil from the rhizomes of *Curcuma aromatica* have been further examined. *l*-α-Curcumene is now shown to have the composition $C_{15}H_{22}$ and to be a mixture of l-ζ-p-*tolyl*-β-*methyl*-Δ^{β}-*heptene* (I) and l-ζ-p-*tolyl*-β-*methyl*-Δ^{α}-*heptene* (II). The main products of the ozonolysis of the hydrocarbon were found to be l-γ-p-*tolyl*-n-*valeric acid* (IV) and l-*methyl* δ-p-*tolylpentyl ketone* (V). l-β-Curcumene has been found to be a mixture of the sesquiterpene hydrocarbons (VI) and (VII); it gave on oxidation a diketone, probably (IX), and a keto-acid (X) from which α-methylglutaric acid (XI) was obtained by oxidation with sodium hypobromite.

The separation from the essential oil occurring in the rhizomes of *Curcuma aromatica* of two hydrocarbons, *l*-α- and *l*-β-curcumene, has been described previously (Rao, Shintre, and Simonsen, *J. Indian Inst. Sci.*, 1926, **9**, *A*, 140; Rao and Simonsen, J., 1928, 2496). They were characterised by the preparation of a number of crystalline derivatives but, at the time, no evidence of their structures was obtained, although it was suggested that they were monocyclic sesquiterpenes. A further study of these hydrocarbons has now shown *l*-β-curcumene to be a monocyclic sesquiterpene, $C_{15}H_{24}$, but the analysis of *l*-α-curcumene and of some of its crystalline derivatives, together with an examination of its degradation products, has proved it to be a mixture of (I) and (II).

$$\text{(I.)}\ p\text{-}C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2 \xrightarrow{O_3} p\text{-}C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$$

$$\longrightarrow p\text{-}C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H\ \text{(IV.)}$$

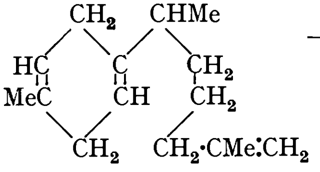
$$\underset{\text{(II.)}}{p\text{-}C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2} \xrightarrow{O_3} \underset{\text{(V.)}}{p\text{-}C_6H_4Me{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COMe}$$

It was recorded previously (*loc. cit.*, p. 2498) that on digestion with selenium α-curcumene did not yield a naphthalene hydrocarbon; it has now been found that the monohydrochloride, when heated with this reagent, gives cadalene together with an azulene. Confirmation of the structure of the carbon skeleton was obtained by oxidation of the hydrocarbon with manganese dioxide and sulphuric acid, a mixture of *p*-toluic, terephthalic and trimellitic acids being obtained. On ozonolysis *l*-α-curcumene, regenerated from the monohydrochloride, gave a mixture of acetone, formaldehyde, a lævorotatory ketone, $C_{14}H_{20}O$, b.p. 154°/15 mm., an aldehyde, $C_{12}H_{16}O$, characterised by its 2 : 4-*dinitrophenylhydrazone*, m. p. 94—95°, and a lævorotatory acid, $C_{12}H_{16}O_2$, b. p. 180°/17 mm.

On oxidation with potassium permanganate the acid gave *p*-tolyl methyl ketone and there can therefore be no doubt that it is l-γ-p-*tolyl*-n-*valeric acid* (IV). The *dl*-modification of this acid, synthesised by Rupe and Steinbach (*Ber.*, 1911, **44**, 584), yields *p*-tolyl methyl ketone on oxidation with potassium permanganate. The aldehyde was not obtained pure, but it follows that it must be represented by (III). These products, together with acetone, result from the degradation of l-ζ-p-*tolyl*-β-*methyl*-Δ^{β}-*heptene* (I), and the ketone $C_{14}H_{20}O$ must clearly be l-*methyl* δ-p-*tolylpentyl ketone* (V), being derived, together with formaldehyde, from l-ζ-p-*tolyl*-β-*methyl*-Δ^{α}-*heptene* (II). Comparative experiments on the ozonolysis of *l*-α-curcumene, regenerated from the monohydrochloride, and of the original mixture of hydrocarbons, as isolated by distillation, indicated that, whereas the former consisted of approximately equal quantities of (I) and (II), in the natural hydrocarbon (I) predominated. Experiments are in progress to confirm synthetically the structure assigned to *l*-α-curcumene.

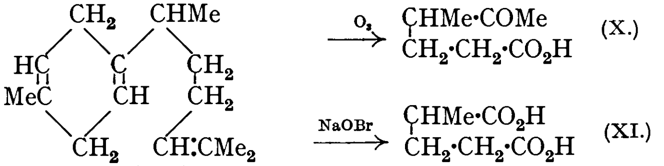
Less convincing evidence for the structure of *l*-β-curcumene, regenerated from the trihydrochloride, has been obtained, but it is clear that it is not homogeneous. On oxidation with selenium dioxide, a reagent which does not attack α-curcumene under the conditions employed, it gave a carbonyl derivative, $C_{15}H_{22}O$, and an alcohol, $C_{15}H_{24}O$. The carbonyl derivative was shown to be an aldehyde, l-β-*curcumenal*, since its *oxime* gave on digestion with acetic anhydride a *nitrile*, from which an acid was prepared characterised by its crystalline *anilide*, m. p. 87°. This suggested that the parent hydrocarbon contained the group :CMe· or $>C:CH_2$ as a part of the ring structure, the oxidation being analogous to that of α- and β-pinenes to myrtenal. On the assumption that one of the other ethylenic linkages was present as an *iso*propenyl or *iso*propylidene group in the side chain the number of possible structures for the hydrocarbon was limited, since the optical activity necessitated the presence of a centre of asymmetry and it was known from previous experiments (*loc. cit.*, p. 2505) that the hydrocarbon did not contain a conjugated system. A consideration of the various possibilities suggested that the most probable representation was (VI) or the related structure (VII). This was confirmed by a study of the products formed on ozonolysis, although these showed, as was mentioned above, that the hydrocarbon was not homogeneous. The degradation products were formaldehyde, acetone, a diketone, $C_9H_{16}O_2$, characterised by the preparation of a *di*-2 : 4-*dinitrophenylhydrazone*, m. p. 178—180°, together with small amounts of lævulic acid and the degradation products of α-curcumene.

(VI.)



$\xrightarrow{O_3}$ $HO_2C{\cdot}CH_2{\cdot}CO{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$ (VIII.)

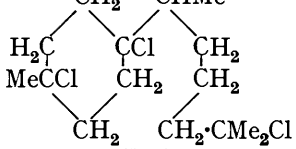
$\longrightarrow$ $Me{\cdot}CO{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$ (IX.)



$\xrightarrow{O_3}$ $CHMe{\cdot}COMe$ / $CH_2{\cdot}CH_2{\cdot}CO_2H$ (X.)

$\xrightarrow{NaOBr}$ $CHMe{\cdot}CO_2H$ / $CH_2{\cdot}CH_2{\cdot}CO_2H$ (XI.)

(VII.)



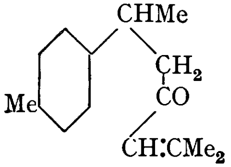
(XII.)

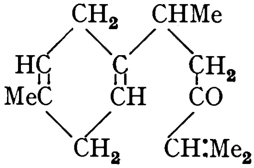
The isolation of a diketone of the composition $C_9H_{16}O_2$ (IX) clearly supported the suggested structure (VI), from which it would result by the decarboxylation of the primary oxidation product (VIII). The formation of lævulic acid suggested contamination with bisabolene and there can be no doubt that *l*-α-curcumene also was present in the hydrocarbon. The quantity of the latter hydrocarbon must have been small, since it was not found possible to prepare its characteristic nitrosate. Confirmation of its presence was, however, obtained by catalytic hydrogenation. The occurrence of bisabolene was not unexpected, since the elimination of hydrogen chloride from the trihydrochloride (XII) (on the basis of VI or VII) would naturally give some of this hydrocarbon.

The presence of the isomeric hydrocarbon (VII), which should yield the keto-acid (X) on degradation, could not be recognised in the hydrocarbon regenerated from the trihydrochloride. On ozonolysis, however, of the mixture of α- and β-curcumenes, as separated from the essential oil, no difficulty was experienced in obtaining α-methylglutaric acid (XI) by the oxidation with sodium hypobromite of the acid formed on hydrolysis of the appropriate ester fraction of the acidic products from the ozonolysis. In this case there was no evidence of the formation of (VIII) and it would seem therefore that the natural hydrocarbon consists almost solely of (VII).

The occurrence in natural oils of sesquiterpenes and of sesquiterpene derivatives accompanied by related aromatic derivatives is uncommon. It is therefore of particular interest that the elegant investigations of Rupe and his collaborators (*inter al.*, Rupe, Clar, Pfau, and Plattner, *Helv. Chim. Acta*, 1934, **17**, 372; Rupe and Gassmann, *ibid.*, 1936, **19**, 569) have shown that the oil from the rhizomes of *Curcuma longa* contains the ketones *ar*-turmerone (XIII) and turmerone. The former is therefore a derivative of α-curcumene; the constitution of turmerone has not been determined, but preference is given (*loc. cit.*, p. 379) to (XIV), which makes it a derivative of β-curcumene.

(XIII.)





(XIV.)

Whilst α- and β-curcumenes form the main constituents of the lower-boiling hydrocarbon fraction of the oil from *C. aromatica*, there is present also (1—2%) a hydrocarbon which contains a conjugated system, since it reacts with maleic anhydride. The adduct has not been obtained pure. From the higher-boiling blue fractions a black picrate, m. p. 120°, was prepared identical possibly with *s*-guajazulene picrate, m. p. 122—122·5°, described by Pfau and Plattner (*Helv. Chim. Acta*, 1936, **19**, 858).

EXPERIMENTAL.

The hydrocarbon mixture was separated from the essential oil as described previously. It was found advantageous to remove the last traces of camphor by steam-distillation after the addition of alcohol.

l-*α-Curcumene*.—The hydrocarbon, regenerated from the monohydrochloride (*loc. cit.*, p. 2501), had b. p. 137°/17 mm., $d_{20°}^{20°}$ 0·8821, $n_D^{20°}$ 1·4989, $[\alpha]_{5461}$ − 34·3° (Found : C, 88·8; H, 11·2. Calc. for $C_{15}H_{22}$: C, 89·1; H, 10·9%). Titration with perphthalic acid in chloroform solution showed the presence of only one ethylenic linkage and some error must have crept into the previous results (*loc. cit.*, p. 2505) during the 478 hours for which the reaction mixture was kept. On hydrogenation in alcoholic solution with a palladium–norit catalyst absorption of hydrogen corresponding to one ethylenic linkage was extremely rapid; subsequent absorption was very slow, owing probably to hydrogenation of the aromatic nucleus. When the hydrocarbon was heated with selenium at 250° for 6 hours and at 280—310° for a further 8 hours, a deep blue oil, b. p. 150—170°/6 mm., was obtained. From this a black picrate, m. p. 120°, was prepared identical with that derived from the azulene fraction of the original oil. This azulene was formed also when *l*-α-curcumene monohydrochloride was heated with selenium under similar conditions; in addition, a sparingly soluble, yellow picrate was obtained, m. p. 115° alone and in admixture with cadalene picrate. The identity with this hydrocarbon was confirmed by the preparation of the styphnate, m. p. 139°.

l-α-Curcumene nitrosate, prepared as described previously (*loc. cit.*, p. 2500), crystallised from methyl alcohol in needles, m. p. 101°, $[\alpha]_{5461}$ − 20·3° in chloroform (*c*, 6·005). After 3 weeks the m. p. rose to 107° with a decrease in the rotatory power (− 14°; *c*, 5·256) (Found : C, 61·2; H, 7·4. Calc. for $C_{15}H_{22}O_4N_2$: C, 61·2; H, 7·5%). l-*Dihydro-α-curcumenylamine* had b. p. 153—154°/14 mm. (Found : C, 82·6; H, 11·3. $C_{15}H_{25}N$ requires C, 82·2; H, 11·4%), and its *acetyl* derivative, m. p. 109° (Found : C, 78·2; H, 10·1. $C_{17}H_{27}ON$ requires C, 78·2; H, 10·3%).

Conversion of l-*Dihydro-α-curcumenylamine into* l-*α-Curcumene*.—To a solution of the base (4·5 g.) in water (20 c.c.) and acetic acid (2 c.c.) a concentrated aqueous solution of sodium nitrite

(1·6 g.) was gradually added. After 2 hours the mixture was heated on the water-bath until the evolution of nitrogen was complete; aqueous sodium hydroxide (NaOH, 3 g.) was then added, and the heating continued for 15 minutes. The oil was extracted with ether, and the extract washed with dilute hydrochloric acid (to remove unchanged base) and aqueous sodium carbonate, dried, and evaporated. Distillation of the oil showed it to be a mixture of hydrocarbon and alcohol. For complete conversion into the hydrocarbon the mixture (11 g. from three experiments) was digested with potassium hydrogen sulphate (5 g.) at 190—200° for 3 hours. The oil, recovered by steam-distillation and extraction with ether, had b. p. 130—140°/11 mm. and gave after two distillations over sodium l-α-curcumene, b. p. 130°/13 mm., $d_{20^\circ}^{20^\circ}$ 0·8775, $n_D^{25^\circ}$ 1·5001, $[\alpha]_{5461}$ — 41·47° (Found: C, 89·2; H, 11·0%). The identity was confirmed by the preparation of the nitrosate.

Oxidation of l-α-*Curcumene*.—(1) *With manganese dioxide*. The hydrocarbon was oxidised with manganese dioxide and sulphuric acid under the conditions used by Ruzicka, Schinz, and Meyer (*Helv. Chim. Acta*, 1923, **6**, 1077). In the resulting mixture of acids, separated by the fractionation of their methyl esters, *p*-toluic acid, m. p. 180° (anilide, m. p. 147°), terephthalic acid (methyl ester, m. p. 140°), and trimellitic acid, m. p. 233°, were identified.

(2) *With ozone*. A solution of the hydrocarbon (6 c.c.) in methyl acetate (40 c.c.) was ozonised at 0° until ozone passed freely through the solution, the issuing gases being passed through water (A). After removal of the solvent under diminished pressure, water (10 c.c.) was added, and the ozonide decomposed by heating on the water-bath under conditions permitting the trapping of any readily volatile carbonyl derivative in an aqueous solution of *p*-nitrophenylhydrazine acetate (B). After heating for 1 hour on the water-bath, the solution was boiled for ½ hour, cooled, and extracted with ligroin (b. p. 60—80°). The ligroin solution was washed with aqueous sodium hydroxide (C), and the solvent removed, leaving an oil (D). The aqueous solution (A) gave with dimedone a precipitate identified as the formaldehyde derivative, m. p. 181° both alone and in admixture. From (B) the yellow precipitate (0·5 g.) was collected and crystallised from dilute alcohol, from which it separated in needles, m. p. 148° both alone and in admixture with acetone-*p*-nitrophenylhydrazone. The oil (D), dissolved in alcohol, was added gradually to a suspension of silver oxide (from $AgNO_3$, 12 g.) in dilute aqueous sodium hydroxide, and the mixture heated on the water-bath for 5 hours. The neutral oil was removed in steam, and the filtered alkaline solution added to (C). The volatile oil (7 g. from 18 c.c. of hydrocarbon), isolated by ether, was mixed with an excess of semicarbazide acetate, and the semicarbazone collected and washed with ether to remove oily impurities. The *semicarbazone* (5·4 g.) crystallised from methyl alcohol in prismatic needles, m. p. 138—139° after sintering at 134° (Found: C, 69·3; H, 9·0. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8%). For the isolation of the ketone the semicarbazone (12 g.) was mixed with dilute sulphuric acid (10%; 50 c.c.) and distilled in steam. l-*Methyl* γ-p-*tolylpentyl ketone*, isolated from the steam-distillate by ether, was a viscid oil with a somewhat unpleasant odour, b. p. 154°/15 mm., $d_{20^\circ}^{20^\circ}$ 0·9454, $n_D^{20^\circ}$ 1·5016, $[\alpha]_{5461}$ — 30·8° (Found: C, 82·3; H, 9·5. $C_{14}H_{20}O$ requires C, 82·4; H, 9·8%). With Fuson's reagent it gave iodoform.

In one experiment the oil, prior to treatment with silver oxide, was mixed with an alcoholic solution of 2 : 4-dinitrophenylhydrazine sulphate; a red oil separated on keeping. The alcohol was decanted, and the oil washed with dilute sulphuric acid and extracted with ligroin (b. p. 60—80°). The ligroin solution deposited γ-p-*tolylvaleraldehyde*-2 : 4-*dinitrophenylhydrazone* as a yellow solid, which, after further crystallisation from ligroin, was obtained in golden leaflets, m. p. 94—95° (Found: C, 61·2; H, 5·8; N, 16·1. $C_{18}H_{20}O_4N_4$ requires C, 60·7; H, 5·6; N, 15·7%). A further quantity of the hydrazone was obtained by dilution of the original alcoholic solution.

The alkaline solution (C) was acidified, the acid extracted with ether, and the solvent evaporated from the dried extract. l-γ-p-*Tolyl*-n-*valeric acid* was a viscid oil, b. p. 180°/17 mm., $[\alpha]_{5461}$ — 13·82° in alcohol (*c*, 13·243) (Found: C, 75·1; H, 8·2. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). The p-*phenylphenacyl* ester crystallised from methyl alcohol in leaflets, m. p. 73—74° (Found: C, 80·7; H, 6·6. $C_{26}H_{26}O_3$ requires C, 80·8; H, 6·7%).

Oxidation of l-γ-p-*Tolyl*-n-*valeric Acid*.—To a solution of the acid (3 g.) in aqueous sodium carbonate, aqueous potassium permanganate (4%) was added gradually. The oxidation was slow and was complete after the addition of 240 c.c. Distillation in steam gave an oil, from which a semicarbazone was prepared crystallising from methyl alcohol in prisms, m. p. 204° both alone and in admixture with *p*-tolyl methyl ketone semicarbazone (Found: N, 21·7. Calc. for $C_{10}H_{13}ON_3$: N, 22·0%).

l-β-*Curcumene*.—The hydrocarbon, regenerated from the trihydrochloride as described previously (*loc. cit.*, p. 2504), had b. p. 142°/19 mm., $d_{25^\circ}^{25^\circ}$ 0·8670, $n_D^{20^\circ}$ 1·491, $[\alpha]_{5461}$ − 48·2° (Found : C, 88·0; H, 11·7. Calc. for $C_{15}H_{24}$: C, 88·2; H, 11·8%).* On catalytic hydrogenation absorption of hydrogen corresponding to two ethylenic linkages was rapid (*ca.* 2 hours), but subsequently it became very slow and reached approximately 80% of the quantity required for three ethylenic linkages only after 15 hours. β-Curcumene was readily oxidised by chromic acid to terephthalic acid.

Ozonolysis of l-β-*Curcumene.*—The hydrocarbon (5 c.c.) in methyl acetate (50 c.c.) was ozonised as described above for α-curcumene, the products being separated in a similar manner. Formaldehyde (dimedone derivative) and acetone (*p*-nitrophenylhydrazone) were identified. The neutral oil (from 20 c.c. of the hydrocarbon), after distillation in steam, was distilled at 20 mm., yielding three fractions : (a) b. p. — 100°, (b) b. p. 145—155°, (c) b. p. 155—165°. From fraction (a) a *di*-2 : 4-*dinitrophenylhydrazone* was prepared which crystallised from *cyclo*hexyl acetate in orange needles, m. p. 178—180° (Found : C, 49·1; H, 4·7; N, 21·3. $C_{21}H_{24}O_8N_8$ requires C, 48·8; H, 4·6; N, 21·7%). From fractions (b) and (c) the semicarbazone of *l*-methyl γ-*p*-tolylpentyl ketone, m. p. 138—139°, and the 2 : 4-dinitrophenylhydrazone of γ-*p*-tolylvaleraldehyde, m. p. 94—95°, were obtained in small yield. The acid products of the ozonolysis (9 g.) were esterified with diazomethane, and the resulting ester fractionated at 20 mm., yielding three main fractions : (i) b. p. — 120°, (ii) b. p. 120—140°, and (iii) b. p. 150—170°. From a portion of fraction (i) a 2 : 4-dinitrophenylhydrazone was prepared which crystallised from methyl alcohol in yellow needles, m. p. 147°, both alone and in admixture with methyl lævulate 2 : 4-dinitrophenylhydrazone (Found : C, 46·6; H, 4·4. Calc. for $C_{12}H_{14}O_6N_4$: C, 46·4; H, 4·5%). The remainder of the ester was hydrolysed with methyl-alcoholic potassium hydroxide solution, and the acid, isolated in the usual manner, identified as lævulic acid by the preparation of the 2 : 4-dinitrophenylhydrazone, m. p. 205—206° both alone and in admixture. Fraction (ii) (3 g.) showed ketonic properties, but no crystalline derivatives could be prepared from either the ester or the acid obtained therefrom by hydrolysis. The acid gave bromoform on oxidation with sodium hypobromite, but the dicarboxylic acid could not be obtained solid. From fraction (iii) γ-*p*-tolyl-*n*-valeric acid was isolated and identified by the preparation of its *p*-phenylphenacyl ester.

Ozonolysis of the Mixture of l-α- *and* l-β-*Curcumene.*—The mixture of hydrocarbons (25 c.c.), as isolated from the essential oil, was ozonised as described above. Very little formaldehyde was obtained and acetone was present in considerable quantity. The neutral oxidation products (3·3 g.) consisted almost solely of the substituted valeraldehyde together with a small quantity of the pentyl ketone. The acidic products (20 g.) were esterified with diazomethane, the lower-boiling fraction (3 g.), b. p. 100—140°/23 mm., hydrolysed with methyl-alcoholic potassium hydroxide solution, and the resulting acid oxidised with aqueous sodium hypobromite. The dicarboxylic acid (1·2 g.), isolated by ether, crystallised and after draining on porous porcelain had m. p. 70°, raised to 76—77° by one crystallisation from chloroform–ligroin (Found : C, 49·2; H, 7·0. Calc. for $C_6H_{10}O_4$: C, 49·3; H, 6·9%). The identity with α-methylglutaric acid was confirmed by the preparation of the di-*p*-toluidide, m. p. 174°. The aqueous solution from which the glutaric acid had been extracted was further extracted with ether in a constant extraction apparatus; a small quantity of succinic acid, m. p. 184—185° both alone and in admixture, was separated.

Oxidation of the Curcumenes with Selenium Dioxide.—The mixture of hydrocarbons (20 g.) was gradually added to a solution of selenium dioxide (13 g.) in alcohol (100 c.c.) and after 1 hour was heated at 40—50° for 3 hours; the solution was then filtered from selenium and poured into water. The oil was extracted with ether, the extract dried over potassium carbonate, and the solvent removed. Distillation of the residual oil under diminished pressure (5 mm.) readily gave three fractions somewhat difficult to free from contamination with selenium : (i) b. p. 120—140° (8 g.); (ii) b. p. 155—160° (8 g.); (iii) b. p. 160—170° (1 g.). The last two fractions were deep blue owing to the presence of an azulene. Fraction (i), after distillation over sodium, had b. p. 119—122°/5 mm. (7 g.) and consisted essentially of *l*-α-curcumene. It was recovered practically unchanged after further treatment with selenium dioxide. The identity was confirmed by the preparation of the nitrosate. Fraction (ii) on redistillation had b. p. 159—160°/5 mm., $d_{30^\circ}^{30^\circ}$ 0·9595, $n_D^{30^\circ}$ 1·5202. On oximation (Stillman and Reed, *Perf. Essent. Oil Rec.*, 1932, **23**, 278) it was found to contain 66% of a carbonyl derivative. It gave with semicarbazide acetate the semicarbazone, m. p. 159°, described below. From the deep blue oil, b. p. 138—143°/5 mm.,

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* The constants for this hydrocarbon recorded previously are incorrect. A reference to the original notes shows the following to be the correct values: $d_{30^\circ}^{30^\circ}$ 0·8625, $n_D^{30^\circ}$ 1·4888, $[\alpha]_D$ − 37·5°.

$d_{30^\circ}^{30^\circ}$ 0·9536, $n_D^{30^\circ}$ 1·5124, $[\alpha]_D$ − 35°, remaining after the removal of the aldehyde as semicarbazone, an azulene was isolated by treatment with phosphoric acid (Ruzicka and Hagensmitt, *Helv. Chim. Acta*, 1931, **14**, 1104); it formed a black picrate, m. p. 120° (Found : N, 10·0. Calc. for $C_{15}H_{20},C_6H_3O_7N_3$: N, 9·8%).

β-*Curcumenal and* β-*Curcumenol.*—To a solution of selenium dioxide (5 g.) in alcohol (80 c.c.), l-β-curcumene (10 g.) was added, and the mixture kept at 40—50° for 2 hours. The product (8·5 g.), b. p. 159—160°/4 mm., isolated in the usual manner, was treated with semicarbazide acetate and the semicarbazone (6·5 g.), which formed very rapidly, was collected. The residual oil, b. p. 150—153°/6 mm., was heated with phthalic anhydride in benzene solution for 3 hours, and the liquid hydrogen phthalate hydrolysed with ethyl-alcoholic potassium hydroxide; *l*-β-curcumenol, b. p. 175°/17 mm., $d_{30^\circ}^{30^\circ}$ 0·9563, $n_D^{30^\circ}$ 1·5164, $[\alpha]_D$ − 39°, was then obtained as a colourless viscid oil. The analytical figures were unsatisfactory. The p-*xenylurethane* crystallised from ligroin (b. p. 40—60°) in needles, m. p. 79—80° (Found : C, 81·1; H, 7·6. $C_{28}H_{33}O_2N$ requires C, 81·0; H, 8·0%). Oxidation of an acetic acid solution of the alcohol with chromic acid gave β-curcumenal in a practically quantitative yield.

The crude *semicarbazone* (see above), m. p. 153°, crystallised from alcohol in narrow rectangular plates, m. p. 159°, $[\alpha]_D$ − 77·8° in chloroform (*c*, 4·5) (Found : C, 70·0; H, 8·6; N, 15·7. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·1; N, 15·4%). l-β-*Curcumenal*, obtained from the semicarbazone (39 g.) by digestion on the water-bath for 2 hours with oxalic acid (30 g.) in acetone (200 c.c.), was purified by distillation in steam. The yield of aldehyde (8 g.) was very poor and much unchanged semicarbazone was recovered. The aldehyde had b. p. 149—150°/3 mm., 175°/17 mm., $d_{30^\circ}^{30^\circ}$ 0·9644, $n_D^{30^\circ}$ 1·5331, $[\alpha]_{5461}$ − 74·1° (Found : C, 82·5; H, 9·9. $C_{15}H_{22}O$ requires C, 82·6; H, 10·1%); it was somewhat unstable and after digestion with water it no longer gave crystalline derivatives. The 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol in orange needles, m. p. 139°, $[\alpha]_D$ − 145·4° in chloroform (*c*, 3·4) (Found : N, 14·2. $C_{21}H_{26}O_4N_4$ requires N, 14·1%). The *nitroguanylhydrazone* separated from alcohol in lustrous plates, m. p. 151°, $[\alpha]_D$ − 86·1° in chloroform (*c*, 3·1) (Found : N, 21·7. $C_{16}H_{25}O_2N_5$ requires N, 21·9%). The *oxime*, prepared by digestion of an alcoholic solution of the aldehyde with hydroxylamine hydrochloride and sodium bicarbonate for 2 hours, was a viscid oil, b. p. 170—175°/4 mm., $d_{30^\circ}^{30^\circ}$ 0·9851, $n_D^{30^\circ}$ 1·5324, $[\alpha]_D$ − 67° (Found : N, 6·3. $C_{15}H_{23}ON$ requires N, 6·0%). β-*Curcumenonitrile*, b. p. 178—182°/17 mm., was formed when the oxime (3·4 g.) was heated on the water-bath with acetic anhydride (5 c.c.) and sodium acetate (1 g.) for 2 hours (Found : N, 6·1. $C_{15}H_{21}N$ requires N, 6·5%). For conversion into the acid the nitrile (2 g.) was digested with an excess of ethyl-alcoholic potassium hydroxide solution for 48 hours; evolution of ammonia had then ceased. β-Curcumenylic acid, isolated in the usual manner, was a viscid oil. The *methyl* ester, prepared by the action of diazomethane, was a mobile oil, b. p. *ca.* 180—182°/16 mm. (Found : C, 77·5; H, 9·3. $C_{16}H_{24}O_2$ requires C, 77·4; H, 9·7%). The *anilide*, prepared by Ritchie's method (J., 1936, 398), crystallised from methyl alcohol or ligroin (b. p. 60—80°) in felted needles, m. p. 87° (Found : C, 81·8; H, 8·4. $C_{21}H_{27}ON$ requires C, 81·6; H, 8·7%).

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