# CCCXXXI.—*The Constituents of Some Indian Essential Oils. Part XXV.* l-α- *and* l-β-*Curcumenes.*

By B. SANJIVA RAO and JOHN LIONEL SIMONSEN.

RAO, SHINTRE, and SIMONSEN (*J. Ind. Inst. Sci.*, 1926, **9A**, 140) separated from the essential oil occurring in the rhizomes of *Curcuma aromatica*, Salisb., a sesquiterpene to which they gave the name *l*-curcumene. The hydrocarbon, characterised by the preparation of a number of crystalline derivatives, appeared to be homogeneous and to be monocyclic with three ethylenic linkages. Since it was obtainable comparatively readily in quantity, we decided to attempt to determine its constitution, a problem which it seemed all the more desirable to elucidate, since only a few monocyclic sesquiterpenes have been studied, bisabolene and zingiberene being the more important.

Early in the investigation, evidence was obtained that *l*-curcumene, in spite of its apparent homogeneity, was a mixture of at least two hydrocarbons, the crystalline nitrosate and trihydrochloride previously described being derived from two different sesquiterpenes. It was observed that the yields of these two derivatives varied very considerably with different specimens of the oil, and further, when the sesquiterpene fraction was warmed with dilute sulphuric acid or treated with sodium in amyl-alcoholic solution, the recovered hydrocarbon gave the nitrosate in undiminished yield but the crystalline trihydrochloride could no longer be obtained. Fractional distillation of the oil, from which the trihydrochloride had been separated, showed the presence of a sesquiterpene monohydrochloride, the parent hydrocarbon of which (see p. 2501) gave the crystalline nitrosate in a yield exceeding that obtained with the original terpene, whilst treatment with hydrogen chloride did not give any trihydrochloride. The presence of at least two hydrocarbons in the sesquiterpene "*l*-curcumene" having thus been proved, it became necessary to devise methods for the preparation of each of them in a pure state prior to undertaking experiments on their constitution. In this we have been successful, and as it is no longer possible for us to collaborate, we have decided to place on record the results so far obtained.

We have designated the hydrocarbon yielding the crystalline nitrosate and the liquid monohydrochloride 1-*α-curcumene.* This substance can be obtained fairly pure by treatment of the monohydrochloride with sodium acetate in acetic acid solution, but it is obtained in a much higher state of purity by a somewhat indirect method. Treatment of the nitrosate with alcoholic potassium hydroxide solution yields 1-*oximino-α-curcumene*, $C_{15}H_{22}\colon NOH$, a colourless oil which can be distilled in small quantities without decomposition. It was characterised by the preparation of a crystalline *benzoyl* derivative, m. p. 84—85°, and a *monohydrochloride*, m. p. 135—136°. The latter substance is not a salt, but is formed by the addition of hydrogen chloride to one of the ethylenic linkages, since it is not decomposed by alkali. So far as we are aware, this is the first oximino-derivative obtained directly from a sesquiterpene. Semmler and Bode (*Ber.*, 1907, **40**, 1129) and Semmler and Hoffmann (*ibid.*, p. 3527) have described the oximes of *d*-santalal, an aldehyde obtained by the oxidation of a primary alcohol present in sandal-wood oil, and of cedrone, a ketone formed by the oxidation of cedrene. We have not succeeded in converting the above-mentioned oxime into the parent ketone (or aldehyde), but further experiments in this direction are contemplated, for little appears to be known of the properties of the sesquiterpene ketones.

When *l*-oximino-α-curcumene is reduced with sodium in ethyl-alcoholic solution it is converted into 1-*dihydro-α-curcumenylamine*, $C_{15}H_{25}\cdot NH_2$, one of the ethylenic linkages having been reduced as well as the oximino-group. The base, which was most readily purified through its sparingly soluble *hydrogen oxalate*, was a viscid oil possessing a strong ammoniacal smell. The reduction of one of the ethylenic linkages on passing from the oximino-derivative to the base was not anticipated and was somewhat unfortunate, since it had been hoped to introduce a fourth ethylenic linkage by submitting the base to a Hofmann degradation process. It was then expected that, by molecular rearrangement, a substituted derivative of benzene would have resulted which might have proved suitable for oxidation experiments. This reaction would open up a new method of attacking the problem of the constitution of the sesquiterpenes. It is proposed to study the properties of the sesquiterpene amines, only two other members of the series having been previously described (Semmler and Hoffmann, *loc. cit.*; Semmler and Mayer, *Ber.*, 1911, **44**, 3678).

Methylation of *l*-dihydro-α-curcumenylamine with methyl iodide in the presence of alkali yields 1-*dihydro-α-curcumenyltrimethylammonium iodide*, $C_{15}H_{25}\cdot NMe_3I$, which crystallises well and gives the corresponding hydroxide on treatment with silver oxide. This substance, which was also obtained crystalline, could not be purified, since it was extremely hygroscopic, but when distilled under diminished pressure, it decomposed smoothly with formation of a mixture of a hydrocarbon and a base. The base was an oil, distilling without decomposition, and analysis showed it to be l-*dimethyldihydro-α-curcumenylamine*, $C_{15}H_{25}\cdot NMe_2$. It did not yield any crystalline derivatives.

The hydrocarbon was the main product of the degradation and was found to be very pure *l*-α-curcumene. The yield of nitrosate from the terpene prepared in this manner was very much higher than from that regenerated from the monohydrochloride (see p. 2501). On treatment with hydrogen chloride in acetic acid solution, it gives a quantitative yield of a monohydrochloride. *l*-α-Curcumene is very stable. It is not reduced by sodium when dissolved in either ethyl or amyl alcohol, nor is it attacked by dilute sulphuric acid. In alkaline solution it is only slowly oxidised by potassium permanganate, whilst titration with bromine in chloroform solution shows the presence of only one ethylenic linkage. The physical properties of the hydrocarbon indicate, however, that it is monocyclic and it must therefore contain three ethylenic linkages. Two of these are remarkably inert, and this is not without analogy (compare Ruzicka and co-workers, *Helv. Chim. Acta*, 1922, **5**, 331; 1923, **6**, 677; 1924, **7**, 1875; *Rec. trav. chim.*, 1928, **47**, 363). When *l*-α-curcumene is reduced catalytically with hydrogen in the presence of platinum oxide (Adams and Shriner, *J. Amer. Chem. Soc.*, 1923, **45**, 2171), addition of six hydrogen atoms takes place with formation of the saturated hydrocarbon, *hexahydro-α-curcumene*, $C_{15}H_{30}$, which is optically inactive.

Whilst this reaction appears to confirm the presence of three ethylenic linkages, it cannot be regarded as conclusive, since it has been shown (Iyer and Simonsen, J., 1926, 2049) that a *cyclo*propane ring can be reduced catalytically. It was therefore decided to examine the action of benzoylhydroperoxide on the terpene, since it has been shown by Nametkin (*J. pr. Chem.*, 1926, **112**, 169; 1927, **115**, 56) and Meerwein (*ibid.*, 1926, **113**, 56) that this reagent is especially suitable for the estimation of ethylenic linkages. The experiments (see p. 2505) establish definitely the presence of three such linkages in *l*-α-curcumene.

It has not been found possible to dehydrogenate the sesquiterpene with either sulphur or selenium with formation of a naphthalene derivative, as Ruzicka, Meyer, and Mingazzini (*Helv. Chim. Acta*, 1922, **5**, 345) succeeded in doing in the case of the monocyclic sesquiterpene, zingiberene. This would appear to indicate that *l*-α-curcumene does not contain a " potential " naphthalene nucleus.

*l*-β-Curcumene has been regenerated in a pure state from its trihydrochloride by treatment with anhydrous sodium acetate in acetic acid solution. It is a monocyclic terpene containing three ethylenic linkages, the presence of which can be proved readily by titration with bromine as well as by the formation of the trihydrochloride. On catalytic reduction l-*hexahydro*-β-*curcumene* is formed, the reduction proceeding much more readily than in the case of the isomeride, and the product was optically active. We are not in a position to say whether the two fully reduced hydrocarbons are structurally identical. Oxidation with benzoylhydroperoxide also proceeded smoothly and confirmed the presence of three ethylenic linkages.

Unlike the α-hydrocarbon, *l*-β-curcumene is very unstable and is readily isomerised. After treatment of the hydrocarbon with 10% sulphuric acid or with sodium in amyl-alcoholic solution, the crystalline trihydrochloride can no longer be isolated, although no reduction takes place in the latter reaction. It seems probable from the properties of the recovered hydrocarbon that the action of dilute sulphuric acid results in the formation of a dicyclic terpene, and this will be further investigated. Dehydrogenation with either sulphur or selenium did not lead to any recognisable products.

Reference has been made above to the fact that *l*-dihydro-α-curcumenylamine belongs to a type of base which has been little studied, and it therefore appeared of interest to have its physiological properties examined. Dr. T. A. Henry kindly arranged for the base to be tested by Dr. J. Trevan at the Wellcome Physiological Research Laboratories, and we are very much indebted to him for the following report :

> " (1) On the pithed cat (brain destroyed) : 0·4 mg. as hydrochloride, no effect ; 4·0 mg., a very slight rise in blood pressure ; 40 mg. caused a fall in blood pressure from heart failure.
>
> " (2) On isolated rabbit's uterus in Ringer's solution, a concentration of 1/5000 of the hydrochloride killed the muscle.
>
> " (3) In an etherised cat with intact brain, 4 mg. produced a slight fall in blood pressure.
>
> " The base has therefore no characteristic physiological action beyond a general toxic action."

In its toxic properties this base thus resembles the unsaturated amine obtained by the reduction of santonin oxime (Fränkel, " Die Artzneimittel-Synthese," p. 737) and the unsaturated dicyclic amine, camphenamine (*op. cit.*, p. 743).

## Experimental.

The sesquiterpene used in these experiments was separated as described in the previous communication (*loc. cit.*, p. 143). It was carefully purified by distillation over sodium and had b. p. 127—129°/6 mm. The constants of the oil obtained in different preparations varied somewhat ($d_{30^\circ}^{30^\circ}$ 0·8760—0·8764; $n_D^{30^\circ}$ 1·4929—1·4940; $[\alpha]_D^{30^\circ}$ − 19·4° to − 25·9°; $[R_L]_D$ 67·67—67·74). This somewhat large variation was due to the different proportions of *l*-α- and *l*-β-curcumenes present in the oil, as indicated by a similar variation in the respective yields of nitrosate and trihydrochloride obtained. Since *l*-β-curcumene is readily isomerised, it appeared possible that distillation over sodium might be injurious, but this was found not to be the case. A specimen of the original sesquiterpene was purified by repeated distillation without the use of sodium, and the constants were very similar (b. p. 129—130°/7 mm.; $d_{30^\circ}^{30^\circ}$ 0·8790; $n_D^{30^\circ}$ 1·4944; $[\alpha]_D^{30^\circ}$ −20·8°). The relative yields of nitrosate and trihydrochloride were not affected by distillation over sodium. An attempt was made to separate *l*-α- and *l*-β-curcumene by fractional distillation through a four-pear Young still-head; ten fractions, b. p. 129—131°/7 mm., were taken, but the difference in physical properties was small [(1) $d_{30^\circ}^{30^\circ}$ 0·882; $n_D^{30^\circ}$ 1·4932; $[\alpha]_D^{30^\circ}$ −22·0°; (5) $d_{30^\circ}^{30^\circ}$ 0·881; $n_D^{30^\circ}$ 1·4940; $[\alpha]_D^{30^\circ}$ −24·8°; (10) $d_{30^\circ}^{30^\circ}$ 0·8740; $n_D^{30^\circ}$ 1·4940; $[\alpha]_D^{30^\circ}$ −24·1°]. No difference was observed in the yields of nitrosate and of trihydrochloride from the ten different fractions of the hydrocarbon.

### l-α-*Curcumene.*

*Nitrosate.*—To a well-cooled mixture of *l*-curcumene (10 c.c.), amyl nitrite (8 c.c.), and acetic acid (20 c.c.), nitric acid (*d* 1·42; 8 c.c.) was gradually added, efficient stirring being essential during the addition; the mixture was kept for some hours, then alcohol was added, and the voluminous precipitate collected and well washed with alcohol. As previously found (*loc. cit.*, p. 143), the nitrosate after crystallisation from methyl alcohol had m. p. 100—101°, but a sample which was recrystallised after 3 weeks' keeping had m. p. 110° (compare Earl and Kenner, J., 1927, 1275). The nitrosate is readily soluble in most of the ordinary organic solvents with the exception of methyl and ethyl alcohols and light petroleum. In chloroform solution ($c$ = 5·634) $[\alpha]_D^{30^\circ}$ −20·4°. A chloroform solution of the nitrosate did not decolorise bromine and was not acted upon by hydrogen chloride in ethereal solution. The yield of the nitrosate varied considerably (2·3—4·5 g. from 10 g.), depending upon the sample of *l*-curcumene used in its preparation.

l-α-*Curcumenenitrolbenzylamine.*—A mixture of the nitrosate (5 g.), benzylamine (3·6 g.), and alcohol (20 c.c.) was heated on the water-bath for 1 hour. On cooling and addition of water, an oil separated which slowly crystallised. It separated from dilute alcohol in leaflets, m. p. 102—104°. In methyl alcohol ($c = 2{\cdot}46$) $[\alpha]_D^{30°}$ $-19{\cdot}5°$ (Found : N, 8·5. $C_{22}H_{32}ON_2$ requires N, 8·2%).

l-α-*Curcumene Monohydrochloride.*—A well-cooled solution of *l*-curcumene (10 g.) in acetic acid (30 c.c.) was saturated with hydrogen chloride, and after standing over-night the mixture was poured on ice. The partly crystalline oil was dissolved in ether, the ether dried and evaporated, and the residue cooled in a freezing mixture. The solid, *l*-β-curcumene trihydrochloride, was removed by filtration through an ice-cooled funnel, and when the liquid hydrochlorides were fractionated under diminished pressure, l-α-*curcumene monohydrochloride* was readily obtained pure, b. p. 150—155°/8 mm. (Found : Cl, 14·7. $C_{15}H_{25}Cl$ requires Cl, 14·8%). The hydrochloride is a colourless oil which has no tendency to crystallise. As was the case with the nitrosate, the relative yields of trihydrochloride and monohydrochloride showed very considerable variation.

In an experiment made with the object of regenerating the parent hydrocarbon, a mixture of the monohydrochloride (40 g.), acetic acid (100 c.c.), and anhydrous sodium acetate (50 g.) was heated in a bath at 140° for 2½ hours. The hydrocarbon separated by distillation in steam and fractionation over sodium had b. p. 118—120°/5 mm.; $d_{30°}^{30°}$ 0·8690, $n_D^{30°}$ 1·4926, $[\alpha]_D^{30°}$ $-22{\cdot}1°$; when it was titrated with bromine in chloroform solution, 1 mol. of bromine was absorbed, and treatment with hydrogen chloride did not yield any crystalline trihydrochloride, indicating the absence of *l*-β-curcumene. The hydrocarbon did not, however, consist of pure *l*-α-curcumene, since the yield of nitrosate was low (2 g. from 10 g.).

l-*Oximino*-α-*curcumene.*—When *l*-α-curcumene nitrosate in acetic acid was treated with zinc dust, a vigorous reaction ensued which was difficult to control, and a mixture of hydrocarbons and alcohols was formed. The following method was adopted as the most convenient for the preparation of the oximino-derivative.

The freshly prepared nitrosate was dissolved in the minimum quantity of hot alcohol and heated on the water-bath with an equivalent amount of alcoholic potassium hydroxide for 20 minutes. An excess of water was added, the oil which separated extracted with ether, the ether dried, and evaporated. l-*Oximino*-α-*curcumene* is best purified by distillation under diminished pressure, but it is necessary to distil only small quantities at a time to avoid decomposition. It is thus obtained as a colourless, viscid oil, b. p. 182—

185°/7 mm., $d_{30^\circ}^{30^\circ}$ 0·9817; $n_D^{30^\circ}$ 1·5134; $[\alpha]_D^{30^\circ}$ − 27·2°; $[R_L]_D$ 71·37 (Found: C, 77·5; H, 9·6. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9%). On titration with bromine in chloroform solution, the presence of only one ethylenic linkage was indicated, although the molecular refraction agrees fairly closely with the value (72·07) required for three such linkages. The oxime is insoluble in aqueous potassium hydroxide and in both aqueous and alcoholic solutions of hydrochloric acid; it is, however, soluble in alcoholic potassium hydroxide. Attempts to prepare a crystalline acetyl derivative or oximino-oxime were unsuccessful.

The *benzoyl* derivative, prepared by the Schotten–Baumann reaction, was only obtained crystalline with difficulty and could not be recrystallised, m. p. 84—85° (Found: N, 4·7. $C_{22}H_{27}ON$ requires N, 4·4%). The *monohydrochloride* was formed when an ethereal solution of the oxime was saturated with hydrogen chloride. It crystallised from alcohol in plates, m. p. 135—136° (Found: Cl, 12·9. $C_{15}H_{24}ONCl$ requires Cl, 13·2%). The hydrochloride was very stable and was not acted upon by cold alkali.

l-*Dihydro-α-curcumenylamine.*—To a boiling solution of *l*-oximino-α-curcumene (10 g.) in ethyl alcohol (120 c.c.), sodium (15 g.) was 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 (1 : 1). The well-cooled solution of the hydrochloride was basified with sodium hydroxide solution and the resulting oil (5 g.) isolated by extraction with ether. The crude base was mixed with an excess of an aqueous solution of oxalic acid, and the sparingly soluble *hydrogen oxalate* which separated was collected; when crystallised from water it separated in clusters of fine needles, m. p. 143—144°, containing 1 mol. of water of crystallisation, which was lost at 100°. It was readily soluble in methyl alcohol, acetone, and benzene, but very sparingly soluble in cold water, ethyl acetate, and chloroform. A chloroform solution of the oxalate was stable to bromine (Found: C, 62·2; H, 9·3; N, 4·1; $H_2O$, 5·3. $C_{17}H_{29}O_4N,H_2O$ requires C, 62·0; H, 9·4; N, 4·3; $H_2O$, 5·5%).

l-*Dihydro-α-curcumenylamine*, obtained by the decomposition of the pure oxalate, is a colourless, viscid oil with a strong basic smell, b. p. 151—152°/17 mm.; $d_{30^\circ}^{30^\circ}$ 0·9026; $n_D^{30^\circ}$ 1·4983; $[\alpha]_D^{30^\circ}$ − 22·2°; $[R_L]_D$ 71·85. The molecular refraction agrees closely with the value (71·76) required for two ethylenic linkages (Found: C, 81·6; H, 11·9; N, 6·5. $C_{15}H_{27}N$ requires C, 81·4; H, 12·2; N, 6·3%). Crystalline derivatives of the base could not be obtained with hydrochloric, perchloric, tartaric, or picric acid; the sulphate was a solid, but was not obtained pure. The base can also be prepared by the reduction of *l*-α-curcumenylamine nitrosate with sodium and alcohol, and this is probably the most convenient method for its preparation in quantity.

The *acetyl* derivative was formed when a mixture of the base (3 g.) and acetic anhydride (1·4 g.) was allowed to remain in a desiccator over sulphuric acid for 24 hours. The crystalline solid which separated was purified from light petroleum and obtained in needles, m. p. 109—110° (Found: C, 77·9; H, 10·7; N, 5·5. $C_{17}H_{29}ON$ requires C, 77·6; H, 11·0; N, 5·3%).

l-*Dihydro-α-curcumenyltrimethylammonium Iodide and Hydroxide.*—The trimethylammonium iodide is obtained in a poor yield when the base in either methyl-alcoholic or acetone solution is treated with methyl iodide. For its preparation in quantity the following method was adopted: The base (1 mol.) was suspended in aqueous sodium hydroxide solution (1 : 2; 5 mols.), and to the hot solution methyl iodide (4—5 mols.) was added drop by drop, the reaction being complete in 4—5 hours. After the reaction mixture had stood for 2 days, the greater portion of the iodide had separated as a crystalline solid. A further quantity can be obtained by saturating the alkaline solution with carbon dioxide, evaporating it to dryness under diminished pressure, and extracting the inorganic salts with alcohol. The crude iodide was best purified by solution in water, saturation of the solution with carbon dioxide, and evaporation to dryness under diminished pressure. The dry residue was dissolved in alcohol and filtered from inorganic salts, and after removal of the alcohol the residue was finally recrystallised from ether, the *trimethylammonium iodide* being obtained in needles, m. p. 163—164° (Found: C, 55·5; H, 8·9; I, 2·8. $C_{18}H_{34}NI$ requires C, 55·2; H, 8·7; I, 3·2%).

For the preparation of the hydroxide, the iodide was shaken in aqueous solution with an excess of freshly prepared silver oxide for several hours. The filtered, strongly alkaline solution was concentrated under diminished pressure at the ordinary temperature, and finally dried over phosphoric oxide, a crystalline solid being obtained. The hydroxide was extremely hygroscopic and became pasty immediately on exposure to the atmosphere. It was not found possible to purify and analyse it.

l-*α-Curcumene and* l-*Dimethyldihydro-α-curcumenylamine.*—The hydroxide (10 g.) was distilled under diminished pressure (400 mm.), the distillate being collected in dilute sulphuric acid. After separation of the insoluble oil (A) by ether, the acid solution was basified with dilute sodium hydroxide solution, and the organic base extracted with ether. On removal of the solvent, an oil (2 g.) remained, b. p. 130—140°/15 mm.; $d_{30^\circ}^{30^\circ}$ 0·8824; $n_D^{30^\circ}$ 1·4913;

$[\alpha]_D^{30^\circ}$ −23·0° (Found : C, 82·0; H, 12·2; N, 5·6. $C_{17}H_{31}N$ requires C, 81·9; H, 12·4; N, 5·9%). l-*Dimethyldihydro-α-curcumenylamine* was a viscid oil with a strong basic smell; it did not yield any crystalline derivatives.

The oil (A) was distilled over sodium, b. p. 128—130°/7 mm.; $d_{30^\circ}^{30^\circ}$ 0·8633; $n_D^{30^\circ}$ 1·4944; $[\alpha]_D^{30^\circ}$ −22·9°; $[R_L]_D$ 68·23. It was identified as very pure l-*α-curcumene.* It was only very slowly attacked by potassium permanganate in alkaline solution, and when dissolved in chloroform it absorbed one mol. of bromine. Treatment with hydrogen chloride in acetic acid solution gave a quantitative yield of the monohydrochloride (Found : Cl, 14·6. Calc. : Cl, 14·8%) and no trace of a trihydrochloride. The yield of nitrosate was very much higher than that obtained from any other sample of the hydrocarbon examined (0·45 g. from 0·8 g. of the hydrocarbon). *l*-α-Curcumene was not reduced by sodium in ethyl-alcoholic solution, the physical constants of the recovered oil being unchanged, nor was it isomerised by heating at 380° in an inert atmosphere. It did not yield a naphthalene derivative when heated at 270° with sulphur or selenium. A solution in acetic acid gives, with a drop of sulphuric acid, a yellow coloration gradually changing to pink.

*Hexahydro-α-curcumene.*—A mixture of *l*-α-curcumene (10 c.c.), acetic acid (40 c.c.), and platinum oxide (0·3 g.) (Adams and Shriner, *loc. cit.*) was shaken with hydrogen at a pressure of 2 atm. Reduction was complete after 50 hours and it was necessary to revive the catalyst twice by treatment with oxygen. The *hexahydro-α-curcumene* was a viscid, colourless oil, b. p. about 128°/7 mm.; $d_{30^\circ}^{30^\circ}$ 0·8283; $n_D^{30^\circ}$ 1·4592; $[\alpha]_D^{30^\circ}$ + 0°; $[R_L]_D$ 69·36 (Calc., 69·27) (Found : C, 86·0; H, 14·0. $C_{15}H_{30}$ requires C, 85·7; H, 14·2%). It did not absorb bromine in chloroform solution.

### l-β-*Curcumene.*

A mixture of the trihydrochloride (see p. 2501) (80 g.), acetic acid (300 c.c.), and anhydrous sodium acetate (110 g.) was heated at 140° for 8 hours. After addition of water, the sesquiterpene was distilled in steam, dried, and purified by repeated distillation over sodium. l-β-*Curcumene* is a thick, colourless oil, b. p. 128—130°/6 mm.; $d_{30^\circ}^{30^\circ}$ 0·8810; $n_D^{30^\circ}$ 1·4940; $[\alpha]_D^{30^\circ}$ −27·9°. The hydrocarbon did not yield a crystalline nitrosate, and on treatment with hydrogen chloride the trihydrochloride (m. p. 84—85°) was regenerated in a yield of more than 50% of the theoretical. Titration with bromine in chloroform solution gave figures agreeing closely with those required for the presence of three ethylenic linkages, whilst in the presence of alkali a solution of potassium permanganate was immediately decolorised. An acetic acid solution gives with a drop of sulphuric acid a deep brown coloration.

When the hydrocarbon was heated on the water-bath for some hours with a dilute solution of sulphuric acid (10%), it was converted into what would appear to be a dicyclic terpene, b. p. 115—117°/7 mm.; $d_{30^\circ}^{30^\circ}$ 0·8932; $n_D^{30^\circ}$ 1·4936; $[\alpha]_D^{30^\circ}$ – 11·9°; $[R_L]_D$ 66·43. This new hydrocarbon, which awaits investigation, does not yield any crystalline derivatives. *l*-β-Curcumene is not reduced by sodium in amyl-alcoholic solution, but undergoes isomerisation and no longer yields the characteristic trihydrochloride (b. p. 129—130°/7 mm.; $d_{30^\circ}^{30^\circ}$ 0·8780; $n_D^{30^\circ}$ 1·4936). Isomerisation was also observed when the terpene was heated in an inert atmosphere at 380° under pressure. No naphthalene derivatives were formed when the terpene was heated at 270° with either sulphur or selenium.

l-β-*Hexahydrocurcumene.*—*l*-β-Curcumene was catalytically hydrogenated under the same conditions as were used for *l*-α-curcumene. The hydrogenation proceeded with greater ease and was complete in 10 hours. The saturated hydrocarbon had b. p. about 128°/7 mm.; $d_{30^\circ}^{30^\circ}$ 0·8283; $n_D^{30^\circ}$ 1·4552; $[\alpha]_D^{30^\circ}$ + 6·3° (Found: C, 85·9; H, 14·2. $C_{15}H_{30}$ requires C, 85·7; H, 14·2%).

*Oxidation of* l-α- *and* l-β-*Curcumenes with Benzoylhydroperoxide.*—Weighed quantities of each of the sesquiterpenes were mixed with an excess of a standard solution of benzoylhydroperoxide (von Pechmann and Vanino, *Ber.*, 1894, **27**, 1511; Levy and Legrange, *Bull. Soc. chim.*, 1925, **37**, 1597) in chloroform solution, and maintained at 10—15° until oxidation was complete. A portion of the solution was removed from time to time for titration against sodium thiosulphate in the presence of potassium iodide. Oxidation was found to be complete after about 478 hours, during which period a solution of benzoylhydroperoxide in chloroform kept under similar conditions showed no appreciable alteration in strength. The results confirmed the presence of three ethylenic linkages in each hydrocarbon (*l*-α-Curcumene : peroxide used corresponded to 133·2 c.c. of $Na_2S_2O_3$ solution; calc., 137·3 c.c. *l*-β-Curcumene : peroxide used corresponded to 140·4 c.c. of $Na_2S_2O_3$ solution; calc., 133·6 c.c.).

INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

[*Received, July 20th,* 1928.]