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TERPENOIDS—LXIX

ABSOLUTE CONFIGURATION OF (−) α-CURCUMENE*

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Abstract—The absolute configuration of (+) 3-*p*-tolylbutanoic acid[1] (V) previously derived by the molecular rotation method has been confirmed by the conversion of (−) 3-phenylbutanoic acid[2,3] (VIII) to the (−) dicarboxylic acid (XII) enantiomeric with the oxidation product of the acid (V). The absolute configuration of (+) 4-*p*-tolylpentanoic acid (XIX) is established on the basis of its synthesis from V. The absolute configuration of (−) α-curcumene (XXI and XXII), has been derived by considering the sign of rotation of the 4-*p*-tolylpentanoic acid obtained on degradation and confirmed by a synthesis of the enantiomeric (+) α-curcumene from (+) 3-*p*-tolylbutanoic acid (V). The absolute configuration of (+) γ-curcumene[4] (XXIV) has been established by considering the sign of rotation of the 4-*p*-tolylpentanoic acid derived from it. The absolute configuration suggested by previous workers for (+) 4-*p*-tolyl-1-pentanol[5] (XXVI) on the basis of calculations using the conformational asymmetry model has been confirmed.

α-CURCUMENE[6] (I), the monocyclic sesquiterpenoid hydrocarbon was first detected as a constituent of the essential oil from the rhizomes of *Curcuma aromatica* Salisb by Simonsen *et al.* They prepared (−) α-curcumene (mixture of I and II) free from the accompanying β-curcumene by regenerating it from its liquid monohydrochloride and assigned the structure indicated by degradative studies. Subsequently they synthesized (±) α-curcumene (I and II). A large number of essential oils examined recently have been shown to contain α-curcumene.[7–11] Both (+) and (−) enantiomers have been found to occur in nature. In addition, a number of compounds such as *ar*-turmerone (III) structurally related to α-curcumene, have been isolated from essential oils. Its ready availability in optically active modifications from natural sources and in racemic form from a very elegant synthesis[4a] suitable for large scale preparation makes it an ideal starting material for the synthesis of more complex

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terpenoids. Dihydro-*ar*-curcumene[4,7,12,14] (IV), the hydrogenation product of α-curcumene, has been isolated during the dehydrogenation of some sesquiterpenes. The above factors and the ready availability of degradation products of (+) *ar*-turmerone (III) prompted us to study the absolute configuration of α-curcumene.

Recently, we established the absolute configuration of (+) *ar*-turmerone[1] (III) on the basis of molecular rotation data of its degradation products (V, VI and VII). The above assignments have been confirmed by the following transformations. (−) 3-Phenylbutanoic acid (VIII) of known absolute configuration[3] was converted to the corresponding (−) ethyl ester (IX) which yielded the keto ester (X) on Friedel-Crafts reaction. Saponification furnished the (−) keto acid (XI) which on oxidation with sodium hypobromite gave the (−) dicarboxylic acid (XII). The absolute configuration indicated for the (−) acid (XII) is based on its preparation from the (−) acid (VIII) through reactions which are not expected to change the configuration of the asymmetric centre. The (−) acid (XII) thus prepared is enantiomeric with the (+) acid[15] (XIII) obtained from the oxidation of (+) 3-*p*-tolylbutanoic acid (V), a degradation product of (+) *ar*-turmerone (III). The enantiomeric relation between the two dicarboxylic acids was proved by their identical IR spectra and m.p. and confirmed by the identical IR spectra of the corresponding dimethyl esters. Hence the (+) dicarboxylic acid (XIII) and the (+) acid (V) from which it has been prepared are correctly represented by the structures shown.

The (±) dicarboxylic acid (XV) was synthesized from (±) 3-phenylbutanoic acid using the same reactions that were employed in synthesizing the (−) enantiomer (XII). The NMR spectrum of its dimethyl ester (XVI) is in agreement with its structure It exhibited a doublet (J — 7 c/s) at 8·70τ (3H, CH_3 on benzylic carbon), a multiplet composed essentially of a doublet at 7·43 and 7·53τ with the latter peak showing signs of further splitting (2H, —$C\underline{H}_2$—$COOCH_3$), multiplet which is essentially a quartet (broad) centred at 6·69τ (J = 7·5 c/s) with the signal at the lower most field partially merged (with a —OCH_3 signal at 6·32τ), (1H, hydrogen attached to benzylic carbon), singlet at 6·32τ (3H; —$COOCH_3$ of side chain), singlet at 6·15τ (3H, —$COOCH_3$ attached to aromatic ring). In the aromatic proton region, there are four prominent signals at 2·02, 2·17, 2·68 and 2·82τ and few signals of lower intensity (4H, aromatic). These signals are symmetrical about the mid point (2·42τ) and the pattern is comparable with those of *p*-disubstituted benzenes such as *p*-chlorobenzaldehyde, *p*-iodoanisole and *p*-chloroacetophenone recorded in the literature.[16] The investigations of Corio and Dailey[17] enable us to assign the group of signals centred around 2·10τ to the protons *ortho* to the —COOMe and their symmetrical counterpart centred around 2·75τ to the protons *meta* to the —COOMe.

(+) 3-*p*-Tolylbutanol[1] (VI) prepared from the (+) acid (V) was converted to the (+) bromide (XVII) by reaction with phosphorous tribromide. The (+) nitrile

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(XVIII), prepared by the action of alcoholic potassium cyanide on the (+) bromide (XVII), yielded (+) 4-*p*-tolylpentanoic acid (XIX) on alkaline hydrolysis. Since the absolute configuration of the (+) acid (V) has been rigorously established the above transformations lead to the unambiguous assignment of absolute configuration of (+) 4-*p*-tolylpentanoic acid (XIX). Hence (−) 4-*p*-tolylpentanoic acid isolated by Simonsen *et al.* from the ozonolysis of (−) α-curcumene is to be represented by XX and (−) α-curcumene itself is a mixture of XXI and XXII.† (+) γ-Curcumene* is to be represented by XXIV since it yields (+) 4-*p*-tolylpentanoic acid (XIX) on ozonolysis.[4]

LAH reduction of (+) ethyl 4-*p*-tolylpentanoate (XXV) prepared from the (+) acid (XIX) furnished (+) 4-*p*-tolyl-l-pentanol[5] (XXVI). This alcohol, which is toxic to fish and exhibits interesting biological properties has been isolated from the product of pulping Douglas fir via the kraft process. It is an artefact formed presumably from γ-curcumene (XXIV). The synthesis of the (+) alcohol (XXVI) described above establishes its absolute configuration which was previously suggested on the basis of calculations using the conformational asymmetry model.[5]

The (+) alcohol (XXVI) was reacted with phosphorous tribromide to yield the (+) bromide (XXVII). The Grignard reagent prepared from the (+) bromide (XXVII) was treated with acetone to furnish the (+) tertiary alcohol (XXVIII) which was converted to the hydrochloric (XXIX) on reaction with dry hydrogen chloride in ether. The hydrochloride (XXIX) was dehydrohalogenated by heating to reflux with sodium acetate and acetic acid following the conditions employed by Simonsen *et al.* for the dehydrochlorination of the enantiomer. We obtained (+) α-curcumene as a mixture of isomers XXX and XXXI having an IR spectrum identical with the IR spectrum of α-curcumene isolated from ginger oil.[7] The NMR spectrum of our synthetic (+) α-curcumene shows a broad band at 4·95τ (vinyl proton of XXX) and a fairly sharp band (width at half height approximately 4 c/s) at 5·42τ due to the vinyl protons of the isopropenyl isomer (XXXI). The investigations of Simonsen *et al.* on the ozonolysis products of (−) α-curcumene, regenerated from its hydrochloride, showed that it is a mixture of approximately equal quantities of the isopropylidene (I) and isopropenyl (II) isomers whereas the naturally occurring α-curcumene exists almost entirely as the isopropylidene isomer (I). The synthesis of (+) α-curcumene, enantiomeric with the (−) α-curcumene of Simonsen *et al.* gives further support to the absolute configuration of (−) α-curcumene (XXI and XXII) established by us.

Starting from (±) 4-*p*-tolylpentanoic acid we have also synthesized (±) α-curcumene (I and II) following the route employed for the synthesis of (+) α-curcumene. The relationship between the compounds of the (±) series and (+) series was established by their identical IR spectra and vapour phase chromatography (VPC) behaviour. (±) α-Curcumene (I and II) gave (±) dihydro-ar-curcumene (IV) on hydrogenation. Its NMR spectrum (described in the Experimental) is in agreement with its structure. (+) Dihydro-*ar*-curcumene (XXXIII) was prepared by the Wolff-Kishner reduction of (+) dihydro-*ar*-turmerone (XXXII),[6a] the product of controlled hydrogenation of

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† The isolation of the (−) acid (XX) directly gives the absolute configuration of the isopropylidene isomer (XXI). Since both the isopropenyl and isopropylidene isomers are formed from the dehydrohalogenation of the same hydrochloride (XXIII) the two isomers are configurationally related.

* The position of the double bonds in the ring is not proved rigorously.[4a,b]

(+) *ar*-turmerone (III). Its IR spectrum and VPC behaviour were identical with those of (±) dihydro-*ar*-curcumene.

Investigations to obtain (+) α-curcumene (XXX) as the only hydrocarbon from the Wolff-Kishner reduction of (+) *ar*-turmerone (III) did not give encouraging results. The Wolff-Kishner reduction under comparatively mild conditions[18] and short period (15 hr) of reflux gave mostly a nitrogen-containing compound indicating incomplete decomposition of the hydrazone. Increasing the period of reflux to (48 hr) furnished in very poor yield a hydrocarbon fraction, which was found to be a mixture on VPC examination. Ozonolysis of this hydrocarbon mixture furnished the acids (V and XIX), identified by the VPC of their ethyl esters. Hence our product is a mixture of (+) α-curcumene (XXX) and the hydrocarbon (XXXIV) formed by the migration of the double bond. Wolff-Kishner reduction of (+) *ar*-turmerone (III) under more vigorous conditions[19] gave dihydro-*ar*-curcumene (XXXIII). Exploratory work†[20] on the route, *ar*-turmerone $\xrightarrow{\text{LAH}}$ allylic alcohol $\xrightarrow{\text{SOCl}_2}$ allylic chloride $\xrightarrow{\text{LAH}}$ α-curcumene (XXX) showed that the product from the above sequence is a hydrocarbon which is a mixture of dihydro-*ar*-curcumene (XXXIII), α-curcumene (XXX) and its isomer (XXXIV).

It is interesting to note that all the compounds (V, VI, XVII, XVIII, XIX, XXV, XXVI, XXVII, XXVIII, XXXII, XXXIII) prepared during this investigation, which can be regarded as being derived (rom (+) 3-*p*-tolylbutane (VII) by introducing substituents at the carbon atom *β*- to the asymmetric centre, have the S-configuration[21] and are dextrorotatory.*

EXPERIMENTAL

M.ps and b.ps are uncorrected. Elemental analysis are due to Mr. Pansare and colleagues of the Microanalytical section of our laboratory. UV spectra are taken in alcoholic solution with Beckman DK-2 instrument and IR spectra on Perkin–Elmer infracord by Gopinath and Deshpande. NMR spectra were determined in CCl_4 solution using tetramethylsilane as internal standard with Varian A 60 (60 megacycles) spectrometer by Mr. I. Mulla. Optical rotations were determined at room temp. (25–30°). VPC samples were analysed on the Griffin VPC apparatus MK II^A using polyester column and H_2 as carrier gas. We thank Dr. B. B. Ghatge for the VPC data.

(−) 3-*Phenylbutanoic acid*[2,3] (VIII)

A mixture of (±) 3-phenylbutanoic acid (14·8 g), l-menthol (15 g), benzene (80 ml) and conc. H_2SO_4 (3 ml) was heated under reflux for 20 hr, the water formed during the reaction being suitably trapped and removed. The reaction mixture was cooled and the benzene layer washed with water, 5% Na_2CO_3 aq and finally with water, dried and the solvent distilled. The residual material on distillation *in vacuo* furnished the menthyl ester of (±) 3-phenylbutanoic acid, b.p. 140–150°/0·75 mm, ($\alpha_D = -48°$ (*c*, 5; benzene). Recrystallization from EtOH furnished the ester $(\alpha)_D = -66°$, (*c*, 5; benzene) enriched with respect to the menthyl ester of (−) 3-phenyl-butanoic acid. Lit.[3] records $(\alpha)_D^{22} = -80{\cdot}3°$ for l-menthyl ester of the (−) acid (VIII). The above menthyl ester $(\alpha)_D =$

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† We are at present carrying out a systematic investigation of these reactions involving modifications of experimental conditions and reagents employed.

* Empirical methods are available for calculating the molecular rotation of these compounds which have only one flexible chain.[22]

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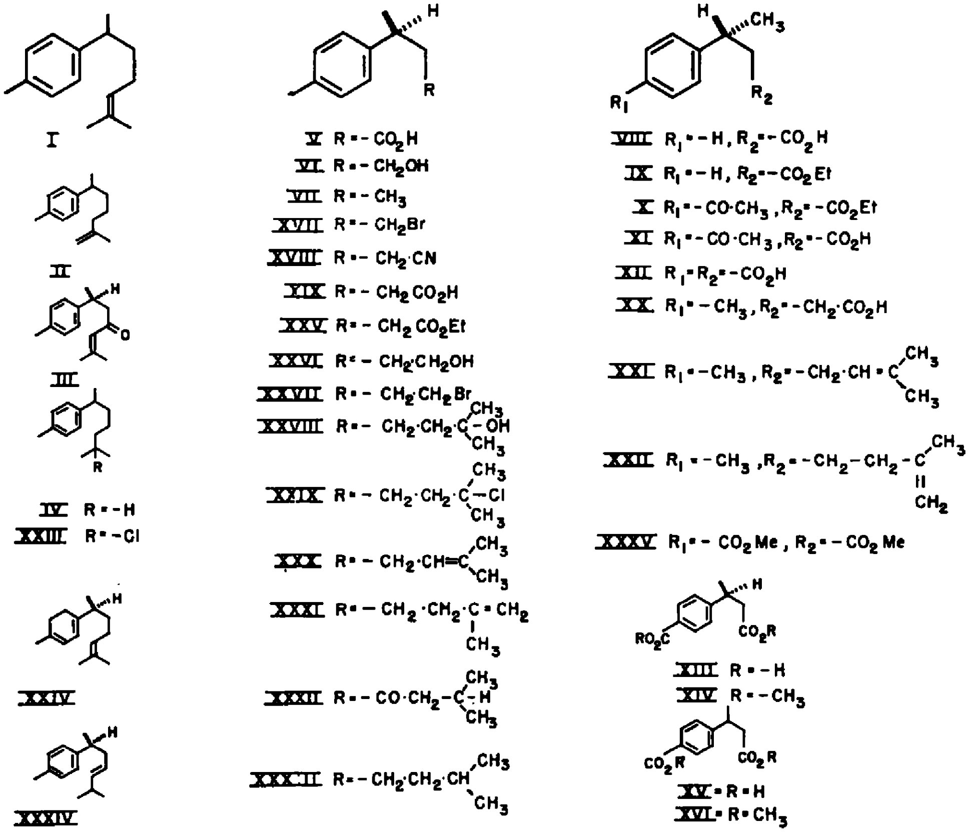

FIG. 1 α-Curcumene and related compounds

−66° (2·17 g) was saponified with KOH (4 g), dissolved in alcohol (40 ml) on a steam bath for 4 hr. It was then cooled, diluted with water (100 ml) and extracted with ether to remove neutral material. The aqueous alkaline layer was acidified with cold dil. HCl (1 : 1) and extracted with ether (25 × 2 ml). This ether extract was washed with water, dried and the solvent distilled. The residue on distillation *in vacuo* furnished (−) 3-phenylbutanoic acid (VIII), b.p. 130–135° (bath)/1 mm, n_D^{25} 1·5100; $(\alpha)_D = -37$ (*c*, 7·4; benzene) yield, 1·19 g. Lit.[8] records $(\alpha)_D = -57$ (*c*, 9; benzene) for (−) acid VIII. Rotation value shows that our sample of (−) 3-phenylbutanoic acid is a mixture of 84% of (−) enantiomer and 16% of (+) enantiomer.

(−) *Ethyl* 3-*phenylbutanoate* (IX)[24] The (−) acid VIII, $(\alpha)_D = -37°$ (1·19 g), EtOH (25 ml) and conc. H_2SO_4 (0·5 ml) was refluxed on a steam bath for 7 hr. On working up IX (1·2 g), b.p. 120–125° (bath)/2 mm, n_D^{25} 1·4851 was obtained $(\alpha)_D = -25°$ (*c*, 2·4; $CHCl_3$) calculated value[25] for the ester

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[23] H. Rupe and A. Steinbach, *Ber. Dtsch. Chem. Ges.* **44**, 584 (1911).

[24] The corresponding (±) compounds were also prepared using the same method. The IR spectra and vapour phase chromatography retention times—where these figures are given—of optically active modifications were identical with the IR spectra and vapours phase chromatography behaviour of the corresponding (±) modifications.

[25] On the basis of optical purity of our starting acid (VIII). This optical purity obviously would be unchanged when distillation and sublimation are employed in subsequent operations. Since the optical purity of the final compound, the (−) dimethyl ester (XXXV) is almost identical with that of the starting material, it is clear that even during recrystallization of solid intermediates, there has been no significant change in optical purity. A careful check of the yields of recrystallized solids shows that we are in all cases dealing with the major enantiomer.

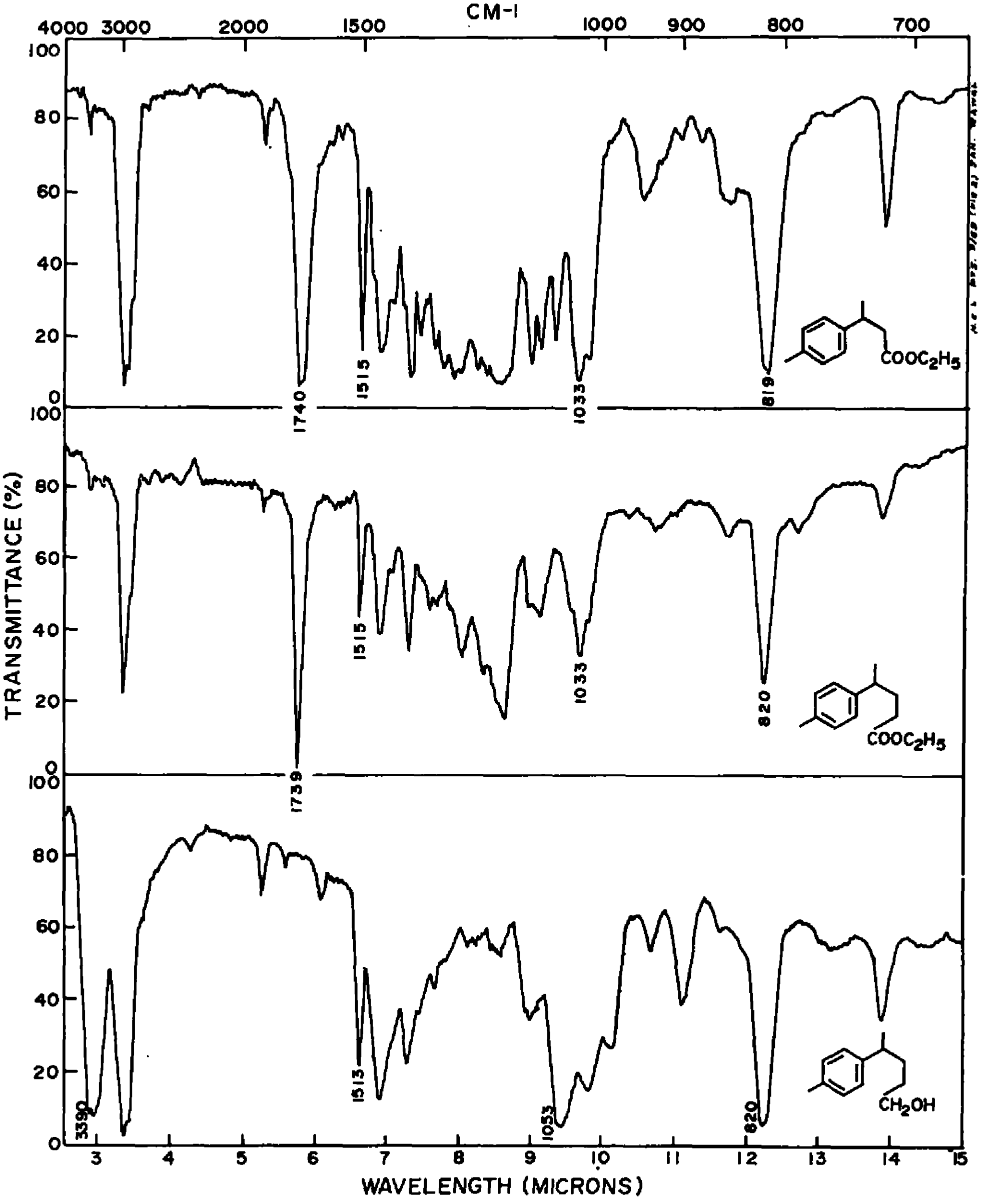


Fig. 2

(IX) of 100% optical purity $(\alpha)_D = -36°$. IR spectrum (liquid film), the ester (IX) showed a prominent band at 1739 cm^{-1} due to the ester grouping. Other bands at: 1961, 1887, 1608, 1493, 1449, 1370, 1333, 1266, 1170, 1093, 1031, 947, 909, 854, 763 and 699 cm^{-1}.

(−) 3-(p-*acetylphenyl*) *butanoic acid* (XI)[14]

To a mixture of IX $(\alpha)_D$ −25° (1·12 g), dry CS_2 (15 ml) and freshly distilled acetyl chloride (2 g) kept at 0° (ice bath), $AlCl_3$ (anhydrous 5 g) was added slowly with stirring under anhydrous conditions. After the addition of $AlCl_3$ was complete, the reaction mixture was stirred for 3 hr, at room temp and poured on ice. Extraction with ether, washing with water, drying and subsequent removal of the solvent furnished a residue which on distillation *in vacuo* gave the ethyl ester (X) yield, 1·26 g. The ethyl ester (X; 1·26 g) was saponified by heating to reflux with a solution of KOH (2 g) in EtOH (20 ml) for 4 hr. The crude acidic material (XI) isolated from this reaction was converted to the s-benzylisothiouronium salt, which after recrystallization from EtOH had m.p. 145°, yield 1·85 g. (Found: N, 7·58. $C_{19}H_{24}O_3N_2S$ requires: N, 7·77%.) The above s-benzylisothiouronium salt, HCl (1N, 25 ml) and ether (25 ml) was stirred at room temp for 1 hr. Extraction with ether, washing the ether extract with water, drying and removal of solvent furnished the regenerated acid (XI) which on recrystallization from pet. ether–ether and subsequent sublimation under red press had m.p. 75°, yield 1·0 g; $(\alpha)_D = -41°$ (*c*, 5·7; $CHCl_3$). Calculated[25] $(\alpha)_D$ for XI of 100% optical purity $(\alpha)_D = -58°$. (Found: C, 71·0; H, 6·77. $C_{12}H_{14}O_3$ requires: C, 69·98; H, 6·84%.)

IR spectrum ($CHCl_3$, 5%). There were two prominent bands at 1724 cm^{-1} (C=O of acid) and 1681 cm^{-1} (C=O group in conjugation with aromatic ring), other bands were observed at: 3012, 2618, 2336, 1608, 1575, 1408, 1351, 1266, 1205, 1124, 1015, 956 and 830 cm^{-1}.

UV spectrum. Max at 254 mμ log ε 4·23). The (±) acid corresponding to the acid (XI) had m.p. 84–85° and s-benzyliosthiuronium salt had m.p. 154–155°.

(−) 3 p-(*carboxyphenyl*)*butanoic acid* (XII)[24]

To a solution of NaOH (5 g) in water (20 ml) kept cooled at 5–10° and protected from light, Br_2 (1 ml) was added slowly. After addition of Br_2, XI (850 mg) dissolved in NaOH was added and the reaction mixture stirred for 6 hr at 10–15°. The alkaline solution was extracted with ether to remove $CHBr_3$, acidified with dil. HCl (1:1) and the liberated XII was extracted with ether (25 × 3 ml). The ether layer was washed with water, dil. $Na_2S_2O_3$ aq and finally with water, dried and the solvent removed. Sublimation of the residue and subsequent recrystallization from EtOH gave XII (775 mg) m.p. 219–220° $(\alpha)_D = -20°$ (*c*, 2·4; EtOH). (Found: C, 63·48; H, 5·96. $C_{11}H_{12}O_4$ requires: C, 63·45; H, 5·81%.) Calc. value[26] for XII of 100% optical purity: $(\alpha)_D = -31°$.

IR spectrum (in nujol). Compound XII showed a prominent band at 1695 cm^{-1} due to C=O of the acid groupings. Other prominent bands at: 2941, 2703, 2957, 1818, 1695, 1613, 1515, 1460, 1429, 1383, 1316, 1290, 1220, 1183, 1117, 1020, 938, 862, 830, 781 and 709 cm^{-1}.

UV spectrum. Max 235 mμ (log ε 4·22) shoulder at 278 and 270 mμ (log ε 2·83 and log ε 3·02).

The (±) dicarboxylic acid (XV) corresponding to XII prepared by the method used for (−) enantiomer had m.p. 223°. Lit.[15] value m.p. 226°.

(−) *Methyl* 3-(p-*methoxycarbonylphenyl*) *butanoate* (XXXV)[24]

(−) Dicarboxylic acid (XII, 662 mg) on treatment with diazomethane furnished XXXV (664 mg) on distillation *in vacuo* b.p. 150–160° (bath)/1 mm, n_D^{24} 1·5100; $(\alpha)_D = -24°$ (*c*, 7·2; $CHCl_3$). Calc. value[25] for XXXV of 100% optical purity: $(\alpha)_D = -34°$ (Found: C, 66·10; H, 6·73. $C_{13}H_{16}O_4$ requires: C, 66·08; H, 6·83%.)

IR spectrum (liquid film). There was a prominent band at 1739 cm^{-1} due to an ester group. Other bands at: 3461, 3030, 2632, 2564, 2336, 2083, 1923, 1616, 1577, 1439, 1274, 1176, 1111, 1020, 969, 860, 833, 775 and 707 cm^{-1}.

UV spectrum. Max at 236 mμ (log ε 4·26) shoulder at 271 and 279 (log ε 3·02 and log ε 2·87).

The (+) dicarboxylic acid methyl ester (XVI) and (−) methyl ester (XXXV) had identical refractive index, UV and IR spectra.

(+) 3-(p-*carboxyphenyl*) *butanoic acid* (XIII)

(+) Compound V (1·01 g) was dissolved in sat. Na_2CO_3 aq (15 ml), the mixture cooled to 0° and $KMnO_4$ aq (2·4 g) added slowly. After addition, it was stirred in the cold for 1 hr and excess $KMnO_4$ destroyed by adding EtOH (25 ml). The reaction mixture was filtered and the residue washed with hot water. The alkaline filtrate together with washings was extracted with ether to remove neutral compounds. The alkaline solution was acidified with dil. HCl and the liberated acid extracted with ether (25 × 2 ml). The ether extract was washed with water, dried and the solvent evaporated slowly. Solid obtained was recrystallized from EtOH, yield 130 mg, m.p. 221–222° $(\alpha)_D = +36°$ (*c*, 4·1; EtOH). Lit.[15] value m.p. 227–229° $(\alpha)_D = +35°$ (*c*, 5; EtOH).

IR spectrum (nujol) and UV spectrum (EtOH) are identical with those of (−) dicarboxylic acid (XII) and (±) dicarboxylic acid (XV).

(+) *Methyl* 3(p-*methoxycarbonylphenyl*) *butanoate* (XIV)

The (+) dicarboxylic acid XIII; 95 mg) on treatment with diazomethane gave XIV (88 mg) $(\alpha)_D + 37°$ (*c*, 7; $CHCl_3$). The IR spectrum of this was identical with that of (−) methyl ester (XXXV) and (±) methyl ester (XVI).

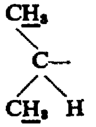
Hydrogenation of (+) ar-*turmerone* (III)

ar-Turmerone III, $\alpha_D = +60°$ (13·58 g) in EtOH (100 ml) with 5% Pd-C (1·5 g) as catalyst was subjected to hydrogenation, 1·780 l. H_2 being absorbed at 27° and 712 mm. The reaction mixture was filtered carefully and the EtOH removed. The residue on fractionation *in vacuo* furnished XXXII, b.p. 100–102°/1 mm, n_D^{27} 1·4862, $\alpha_D = 34°$ (neat); $(\alpha)_D = +31°$ (*c*, 7·2; $CHCl_3$). Lit. value[2a] $(\alpha)_D^{20} + 44·2°$ (Found: C, 81·89; H, 10·25. $C_{15}H_{22}$ requires: C, 82·51; H, 10·15%.)

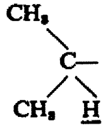
The IR spectrum showed a prominent band at 1715 cm^{-1} due to a carbonyl group; other bands at: 1890, 1515, 1460, 1408, 1370, 1307, 1290, 1235, 1170, 1143, 1111, 1042, 1012, 961, 820 and 719 cm^{-1}.

UV spectrum. Max at 272, 264 and 259 mμ (log ε 2·43; 2·52 and 2·42 respectively and shoulder at 252 mμ (log ε 2·24).

NMR spectrum. Doublet at 9·20τ (J = 7 c/s) (6H



doublet at 8·81τ (J = 7 c/s) (3H CH_3 attached to benzylic carbon) singlet at 7·74τ (3H, CH_3 attached to benzene ring), two groups of multiplets at ca. 7·50τ and 7·90τ (2H + 2H − $C\underline{H}_2$—CO—$C\underline{H}_2$—Is), multiplet at 6·75τ (1H hydrogen attached to benzylic carbon) a singlet at 2·98τ (4H, aromatic protons) and a broad signal in the region 8·20–8·60τ (1H;



VPC. Retention times for *ar*-turmerone $\alpha_D = +60°$, and dihydroarturmerone $\alpha_D = +34°$ are 7 min 51 sec and 4 min 11 sec respectively. Under identical condition retention time for longifolene was 53 sec (conditions: flow of H_2 0·71 ml/sec temp 200°).

(+) *Dihydro*-ar-*curcumene* (XXXIII)

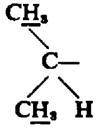
A mixture of XXXII, ($\alpha_D = +34°$; 2·64 g), hydrazine hydrate 80% (5 ml) and freshly distilled diethylene glycol (15 ml) was warmed on steam bath for 10 min and kept at room temp for ½ hr with occasional shaking. KOH (4 g) was added and the reaction mixture was refluxed for 2 hr (115–120°) in an atm of N_2. The temp was raised slowly and finally the reaction mixture was heated under reflux for 2 hr more at 200 to 210°. After cooling it was diluted with water (50 ml) and extracted with ether (25 × 2 ml). The ether extract was washed with water, dried and the ether removed. The residue was chromatographed on alumina (gr.I; 50 g; neutral). The fraction eluted with pet. ether (b.p. 60–80°; 200 ml) on evaporation of the solvent followed by distillation of residue over Na furnished XXXIII (1·67 g), b.p. 100–105° (bath)/1 mm, n_D^{25} 1·4792; $(\alpha)_D = +24°$ (*c*, 4·7; $CHCl_3$); $\alpha_D = +21°$ (neat), (Found: C, 88·1; H, 12·1. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%.)

Optical rotatory dispersion. At 589, 578, 546, 436, 364 and 313 mμ, the dihydro-*ar*-curcumene showed the following specific rotations: +24, +24, +27, +48, +79 and +80 respectively (*c*, 4·71; $CHCl_3$).

IR spectrum (liquid film 0·05 mm thickness). These were bands at: 2732, 2632, 2353, 1887, 1786, 1739, 1639, 1511, 1449, 1362, 1300, 1205, 1164, 1109, 1039, 1018, 975, 934, 822, 757, 740 and 719 cm^{-1}.

UV spectrum. Max at 272, 264 and 259 mμ (log ε 2·53, 2·65 and 2·54 respectively) and shoulder at 252 and 246 (log ε 2·39 and 2·30). Lit. values[7] λ_{max} 211, 222, 248, 254, 260, 265, 267 and 263 with (log ε 4·04, 3·8, 2·15, 2·25, 2·43, 2·54, 2·51 and 2·57 respectively).

NMR spectrum. It showed the following signals: doublet at 9·20τ (J = 5·5 c/s) (6H,



singlet at 7·73τ (3H, CH_3 attached to aromatic ring) multiplet centred at 7·41τ (1H hydrogen attached to benzylic carbon), singlet at 3·05τ (4H, aromatic protons) and a multiplet in the region 8·30–9·00τ (10H, all the protons not accounted for before) in which one can clearly see the doublet centred at 8·82τ (J = 7 c/s) due to the CH_3 attached to benzylic carbon.

VPC. It gave a single peak retention time—1 min 32 sec; under identical conditions the retention time for longifolene was 1 min 13 sec (flow rate of H_2 1 ml/sec; temp 174°).

(+) Dihydro *ar*-curcumene (XXXIII) and (±) dihydro-*ar*-curcumene (IV) prepared by us had identical IR spectra, which also agree with the literature spectrum.[7]

(+) -*Dihydro*-ar-*curcumene* (IV)

(+) *ar*-Curcumene (XXX and XXXI; 365 mg) was hydrogenated in EtOH (5 ml) with 5% Pd–C (50 mg) at 23° and 712 mm press; H_2 absorbed (46·4 ml) corresponded to one double bond. The reaction mixture was carefully filtered and after removal of the solvent was distilled over Na, n_D^{24} 1·4839.

(+) 3-p-*Tolylbromobutane* (XVII)

To (+) 3-*p*-tolylbutanol[1] (VI; 4·52 g) freshly distilled PBr_3 (2·50 ml) was added slowly in the cold and the mixture kept overnight at room temp under anhydrous conditions. The mixture was then heated on a water bath for 1 hr with occasional shaking, cooled and then poured into ice-cold water, and extracted with ether (25 × 2 ml). Ether extract was washed with water, dried and the ether removed. The residue on vacuum distillation furnsihed XVII 110–120° (bath)/1 mm, yield 4·69 g, n_D^{27} 1·5281; $(\alpha)_D + 109°$ (*c*, 2·27; $CHCl_3$) (Found: C, 58·61; H, 6·66. $C_{11}H_{15}Br$ requires: C, 58·17; H, 6·60%.)

IR spectrum (liquid film). There were bands at: 1898, 1645, 1511, 1449, 1370, 1348, 1252, 1220, 1111, 1042, 1020, 990, 943, 877, 820, 790, 765 and 720 cm^{-1}.

UV spectrum. Max at 272, 264 and 258 mμ (log ε 2·55, 2·70 and 2·56 respectively) and shoulder at 251 mμ (log ε 2·36).

VPC. It gave a single peak with retention time 4 min 30 sec; under identical conditions, retention time for longifolene 1 min 30 sec (conditions: flow of H_2 0·5 ml/sec temp 224°).

(+) 3-p-*Tolyl*-1-*cyanobutane* (XVIII)

To a solution of KCN (2·5 g) in water (5 ml), XVII (4·5 g) together with EtOH (50 ml), was added and the mixture heated under reflux for 15 hr. After cooling and diluting with water, it was extracted with ether. The ether extract was washed with water, dried and the solvent evaporated. The residue was distilled *in vacuo* to yield XVIII 110–120° (bath)/0·75 mm, n_D^{26} 1·5048, $(\alpha)_D = +106°$ (*c*, 1·9, $CHCl_3$) (Found: C, 83·05; H, 8·83; N, 8·0. $C_{12}H_{15}N$ requires: C, 83·19; H, 8·73; N, 8·09%.)

IR spectrum (liquid film). It gave a band at 2268 cm^{-1} characteristic of a nitrile group. Other bands at: 1905, 1802, 1724, 1681, 1600, 1515, 1449, 1389, 1374, 1348, 1302, 1235, 1183, 1117, 1107, 1043, 1020, 961, 926, 820, 775 and 725 cm^{-1}.

UV spectrum. Max at 271, 263 and 258 mμ (log ε 2·51, 2·62 and 2·49 respectively) with shoulder at 251 mμ (log ε 2·29).

(+) 4-p-*Tolylpentanoic acid* (XIX)*[26]

The (+) cyano compound (XVIII) was heated under reflux with 10% alcoholic KOH (75 ml) for 24 hr. After cooling the reaction mixture was diluted with water, and extracted with ether to eliminate the neutral fraction. The alkaline aqueous layer was acidified with dil. HCl (1:1) and the

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* (±) 4-*p*-Tolylpentanoic acid was prepared by the method of H. Rupe.[26]

liberated acid (XIX) extracted with ether (25 × 2 ml). The ether extract was washed with water dried and the ether removed. The S′-benzylisothiouronium salt was prepared and recrystallized from EtOH, yield 5·15 g, m.p. 147°. (Found: C, 66·95; H, 7·22; N, 7·58. $C_{20}H_{26}O_2N_2S$ requires: C, 67·02; H, 7·31; N, 7·82%.) Lit.[4] value m.p. 139–139·5°. Acid XIX was regenerated from the S′-benzylisothiouronium salt and after distillation *in vacuo* had b.p. 130–140° (bath)/1 mm, yield 2·97 g, n_D^{27} 1·5082 $(\alpha_D) = +29°$ (*c*, 12·92; EtOH). Lit. value $(\alpha)_{5461} = -13·8°$ (*c*, 13·2, alcohol), $(\alpha)_D = +19·2°$.

Optical rotatory dispersion. At 589, 578, 546 and 436 mμ the acid XIX showed following specific rotations: +29, +30, +34 and +60 respectively (*c*, 12·92; EtOH).

IR spectrum. There were prominent bands at: 2941, 2632, 1695, 1504, 1439, 1408, 1370, 1275, 1212, 1163, 1099, 1015, 935, 820 and 720 cm⁻¹.

UV spectrum. Max at 258, 263 and 271 mμ (log ε 2·47, 2·57, 2·48 respectively) with shoulder at 251 mμ (log ε 2·29).

(+) *Ethyl-4-*p*-tolylpentanoate* (XXV)[24]

A mixture of the acid XIX (2·5 g) purified through s-benzylisothiouronium salt, alcohol (50 ml) and conc. H_2SO_4 (1 ml) was heated under reflux for 6 hr. It furnished the ethyl ester XXV (2·6 g), b.p. 120–130° (bath)/1 mm, n_D^{34} 1·4921; $(\alpha)_D = +32°$ (*c*, 6; $CHCl_3$).

IR spectrum. Showed a prominent band at 1739 cm⁻¹ due to C=O of ester grouping. Other bands at: 1912, 1515, 1449, 1370, 1332, 1302, 1250, 1205, 1163, 1117, 1099, 1033, 935, 855, 820, 793 and 725 cm⁻¹.

UV spectrum. Max at 258, 264 and 272 mμ (log ε 2·46, 2·56 and 2·45 respectively) with shoulder at 2·51 mμ (log ε 2·29).

VPC. It gave a single peak with retention time—6 min 52 sec and conditions were same as for XXVII.

NMR spectrum. It showed the following signals: triplet at 8·83τ (J = 7 c/s) and doublet at 8·75τ (J = 6 c/s) (6H—$CO_2{\cdot}CH_2\,\underline{CH}_3$ and —CH_3 on benzylic carbon), singlet at 7·71τ (3H, CH_3 attached to aromatic ring), multiplet centred at 7·36τ (1H, hydrogen attached to benzylic carbon), quadruplet at 5·99τ (J = 7 c/s) (2H, —$CO_2\underline{CH}_2CH_3$) a singlet at 3·0τ (4H, aromatic protons) and a multiplet in the region 7·80–8·60τ (4H, all the protons not accounted for before).

(+) 4-p-*Tolylpentanol*[5] (XXVI)[24]

The ethyl ester XXV (2·5 g) in dry ether (15 ml) on reduction with LAH (1 g) in dry ether (20 ml), furnished the alcohol XXVI (2·1 g), b.p. 130–135° (bath)/2 mm, n_D^{20} 1·5100 $(\alpha)_D = +30°$ (*c*, 3·5; EtOH). Lit. value[5] $(\alpha)_D^{25} = +38·1°$ (*c*, 64 mg/ml EtOH), n_D^{29} 1·5051.

IR spectrum. It showed a prominent OH band at 3390 cm⁻¹. Other bands at: 2326, 1890, 1786, 1639, 1513, 1449, 1370, 1302, 1163, 1111, 1053, 1020, 990, 935, 900, 820 and 720 cm⁻¹.

NMR spectrum. It showed the following signals: doublet at 8·81τ (J = 7 c/s) (3H, CH_3 attached to benzylic carbon), singlet at 7·74τ (3H, CH_3 attached to aromatic ring), multiplet at 7·42τ (1H, hydrogen attached to benzylic carbon), multiplet at 6·68τ (3H, $\underline{H}$—O—$\underline{CH}_2$), singlet 3·02τ (4H, aromatic protons) and a multiplet in the region 8·30–8·70τ (4H, all the protons not accounted for before).

VPC. The alcohol XXVI gave a single peak. Retention time 10 min 42 sec; under identical conditions retention time for longifolene was 1 min 9 sec (conditions—flow of H_2 gas 0·5 ml/sec temp 200°).

(+) 4-p-*Tolyl-*1*-bromopentane* (XXVII)[24]

Compound XXVI (3·1 g) was treated with freshly distilled PBr_3 (3 ml) under anhydrous conditions After working up and distillation *in vacuo*, it furnished the bromide XXVII (3·4 g), 110–120°(bath)/1 mm, n_D^{25} 1·5221 $(\alpha)_D = +85°$ (*c*, 5; $CHCl_3$). (Found: C, 60·12; H, 7·23. $C_{12}H_{17}Br$ requires: C 59·74; H, 7·1%.)

IR spectrum. There were prominent bands at: 1887, 1505, 1439, 1370, 1235, 1205, 1106, 1031, 1015, 813, 763 and 720 cm⁻¹.

VPC. Under the conditions described for XXVI, the bromide XXVII gave a single peak, retention time 5 min 22 sec.

(+) 6-p-*Tolyl-2-methylheptane-2-ol* (XXVIII)[24]

To an ice cooled solution of 4-*p*-tolyl-1-pentyl magnesium bromide (from 1·45 g of (+) 4-*p*-tolyl-1-bromopentane and 350 mg Mg) in dry ether (15 ml), dry acetone (2 g) in dry ether (10 ml) was added slowly. The Grignard product was heated under reflux for 1 hr and decomposed with sat. NH_4Cl aq (15 ml). The reaction mixture was extracted with ether and the extract washed with water, dried and evaporated. The residue on distillation *in vacuo* furnished alcohol XXVIII (0·88 g), n_D^{26} 1·5095. (Found: C, 82·62; H, 10·43. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%); $(\alpha)_D = +36°$ (*c*, 3; $CHCl_3$).

IR spectrum. There were prominent bands at: 3448, 3030, 1905, 1517, 1460, 1379, 1307, 1198, 1156, 1111, 1020, 943, 820, 760 and 721 cm^{-1}.

6-p-*Tolyl-2-methyl-2-chloroheptane* (XXIX)[24]

The alcohol XXVIII (800 mg) dissolved in dry ether (20 ml) was cooled to −5° and saturated with dry HCl gas. It was left overnight under anhydrous condition and solvent removed slowly *in vacuo*. The IR spectrum of the residue showed the absence of an hydroxyl group. This crude product was used as such in the next step without further purification.

VPC. Under the conditions described for XXVI the *p*-tolyl-2-methyl-2-chloroheptane gave a single peak. Retention time 2 min 17 sec.

(+) α-*Curcumene* (XXX and XXXI)[24]

Chloro compound XXIX (0·760 g), glacial acetic acid (20 ml) and anhydrous sodium acetate (1·5 g) was refluxed in oil bath for 2·5 hr (bath temp 140–150°), cooled, diluted with water (50 ml) and extracted with ether (25 × 2 ml). The ether extract was washed with water, 5% Na_2CO_3 aq. solution, finally with water, dried and the solvent removed. The residue was chromatographed on alumina (15 g, gr. I, neutral). The fraction eluted with pet. ether (b.p. 60–80°, 100 ml), on evaporation of solvent followed by distillation over Na furnished the mixture of hydrocarbons XXX and XXXI (210 mg), b.p. 105–110° (bath)/1 mm, n_D^{24} 1·5020; $(\alpha)_D = +40°$ (*c*, 3·3; $CHCl_3$). Lit. value[6,7] n_D^{20} 1·4976; 1·4989 $(\alpha)_D^{20} = +36·2$; $(\alpha)_{5461} = +34·3°$*. (Found: C, 89·13; H, 10·91. $C_{15}H_{22}$ requires: C, 89·04; H, 10·96%.)

Optical rotatory dispersion. At 589, 578, 546, 436, 364 and 313 mμ, the (+) α-curcumene showed the following specific rotations, +40, +41, +47, +85, +146 and +149 respectively.

IR spectrum (liquid film) 0·05 mm thick). The bands were observed at: 1905, 1786, 1653, 1515, 1449, 1379, 1307, 1212, 1121, 1111, 1042, 1020, 985, 940, 893, 847, 820, 757 and 724 cm^{-1}.

UV spectrum. Max at 272, 264 and 259 mμ (log ε 2·71, 2·81 and 2·73 respectively) with shoulder at 252 mμ (log ε 2·63). Lit. value[7] 211, 217, 222, 248, 254, 259, 265 and 273 mμ with (log ε 3·85, 3·80, 3·70, 2·3, 2·4, 2·50, 2·59 and 2·60 respectively).

VPC. Under the conditions described for XXXIII, (+) α-curcumene gave a single peak retention time—2 min 22 sec.

Wolff–Kishner reduction of (+) ar-*turmerone* (III)

Potassium t-butoxide was prepared from K (4·7 g) and dry t-butanol (75 ml). Excess t-butanol was removed under anhydrous conditions. The hydrazone of *ar*-turmerone prepared from (+) *ar*-turmerone (5 g) by refluxing with hydrazine hydrate (80%) in EtOH for 20 hr) was heated under reflux with potassium t-butoxide and dry toluene for 15 hr. The reaction mixture was cooled and diluted with water (50 ml). The toluene layer was washed with water, dried and the solvent removed *in vacuo*. The residue was distilled twice over Na. The reaction product so obtained (1·10 g) gave a positive test for nitrogen, $(\alpha)_D = +45°$ (*c*, 6·7; $CHCl_3$), n_D^{26} 1·5078.

A similar experiment with reflux period of 48 hr yielded a residue which was chromatographed on alumina (100 g; gr. II; neutral) and the fraction eluted with pet. ether (b.p. 60–80°, 200 ml), on evaporation of the solvent and followed by distillation over Na furnished 160 mg of the hydrocarbon. (Found: C, 89·06; H, 11·09. $C_{15}H_{22}$ requires: C, 89·04; H, 10·96%) $(\alpha)_D = +38·3°$ (*c*, 1·1, $CHCl_3$).

The hydrocarbon fraction showed two peaks on VPC one of which was identified as dihydro-*ar*-curcumene by comparison with an authentic sample.

The acidic fraction obtained from the ozonolysis of the above hydrocarbon was analysed on VPC,

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* The value given in the literature[6] is for (−) enantiomer.

as ethyl ester, which showed two peaks corresponding to the ethyl esters of the acids V and XIX

Wolff-Kishner reduction of (+) ar-*turmerone* (III)

A mixture of (+) *ar*-turmerone (3·2 g), diethylene glycol (25 ml) and 80% hydrazine hydrate (7 ml) was warmed on a water bath for 5 min and then kept at room temp for 30 min with occasional shaking. KOH (4 g) was added, and the mixture heated at 110–120° for 2 hr in a N_2 atm. The temp of the reaction mixture was raised slowly to and maintained at 190° for 2 hr more, then cooled, diluted with water (75 ml) and extracted with ether. The ether extract was washed with water, dried and the solvent removed. The residue was chromatographed on alumina (60 g; gr.III; neutral). The fraction eluted with pet. ether (b.p. 60–80° 150 ml) on evaporation of the solvent, followed by distillation over Na furnished the hydrocarbon (365 mg), b.p. 140–150° (bath)/10m, n_D^{24} 1·4 872, $(\alpha)_D = +30°$ (*c*, 3·1; $CHCl_3$). (Found: C, 89·06; H, 10·69%.)

The IR spectrum and VPC behaviour of the above hydrocarbon were identical with IV and XXXIII.

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