Tetrahedron, 1964, Vol. 20, pp. 2921 to 2925. Pergamon Press Ltd. Printed in Northern Ireland

TERPENOIDS—LX

ABSOLUTE CONFIGURATION OF *ar*-TURMERONE[*]

V. K. HONWAD[†] and A. S. RAO
National Chemical Laboratory, Poona, India

(*Received* 27 *July* 1964)

Abstract—The absolute configuration of (+) *ar*-turmerone is shown to be II on the basis of the optical rotatory dispersion curve of the (+) hydrocarbon (VII) derived from it. The molecular rotations of the acid (III) and the alcohol (V) are in agreement with this conclusion.

THE rhizomes of *Curcuma longa* Linn. are widely used particularly for condiments and dyeing wool, silk and unmordanted cotton.[1] The rhizomes yield an essential oil whose constituents have been extensively studied.[2] The essential oil contains a high percentage of ketones, mainly turmerone and the closely related *ar*-turmerone. The structure (I) for *ar*-turmerone was proposed by Rupe *et al.*, on the basis of extensive degradation studies.[3] *Ar*-turmerone, as well as a number of its degradation products have been synthesized.[4] The data available in the literature and the investigations described in this communication lead to the assignment of absolute configuration of (+) *ar*-turmerone (II).

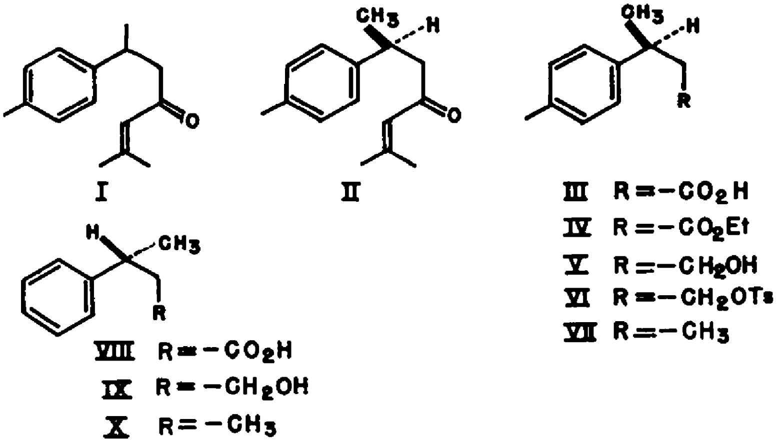

FIG. 1. *ar*–Turmerone and related compounds.

---

[*] Communication No. 704 from the National Chemical Laboratory, Poona–8, India.

[†] Recipient of a Junior fellowship of the Council of Scientific and Industrial Research.

[1] *The Wealth of India, Raw Materials* Vol. II; p. 402. Council of Scientific and Industrial Research, India (1950).

[2a] H. Rupe, G. Clar, A. Pfau and Pl. Plattner, *Helv. Chim. Acta* **17**, 372 (1934);

[b] N. C. Kelkar and B. S. Rao, *J. Indian Inst. Sci.* **17A**, 7 (1934).

[3a] H. Rupe and A. Gassmann, *Helv. Chim. Acta* **19**, 569 (1936);

[b] H. Rupe and F. Wieder-Kehr, *Ibid.* **7**, 654 (1924).

[4] R. P. Gandhi, O. P. Vig and S. M. Mukherji, *Tetrahedron* **7**, 236 (1959) and Refs cited therein.

Rupe *et al.*[3b] obtained the (+) acid (III; M_D + 110°, benzene solution) from the degradation of (+) *ar*-turmerone. The closely related acid (VIII; M_D − 96°, benzene solution) has the absolute configuration shown in the formula since it has been converted to the hydrocarbon (X) of known absolute configuration.[5] The molecular rotations of the (+) $C_{11}H_{14}O_2$ acid derived from (+) *ar*-turmerone and the (−) acid (VIII) are of the same order of magnitude, but opposite in sign and hence the former acid has the absolute configuration shown in III.

(+) *ar*-Turmerone has been prepared by oxidizing turmerone, a constituent of turmeric oil with lead tetracetate. Lead tetracetate gives much better results than chromic acid which was used by Rupe[3a] to bring about the same conversion. Ozonolysis of *ar*-turmerone and decomposition of the resulting ozonide under oxidative conditions furnished the (+) acid (III) which was purified through its crystalline S-benzylisothiuronium salt. The acid (III) was converted to the ethyl ester (IV). The NMR spectrum of the ester (IV) is in agreement with its structure.* The assignment of the signals for the various protons is shown in Fig. 2.

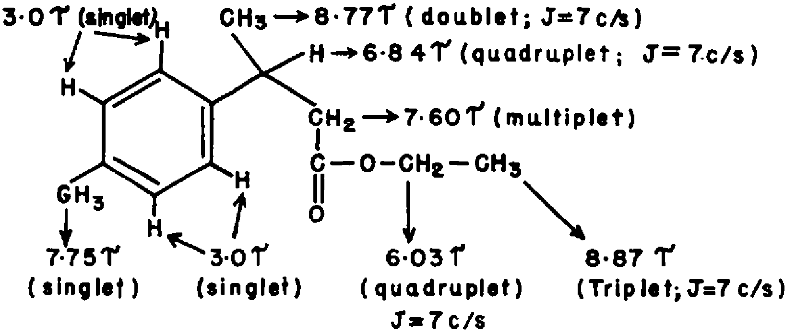

FIG. 2. NMR Signals of ethyl 3-*p*-tolybutanoate.

Lithium aluminium hydride reduction of the (+) ester (IV) furnished the (+) alcohol (V). The molecular rotation method suggests the absolute configuration (V) for the (+) alcohol derived from (+) *ar*-turmerone since the closely related alcohol (IX)[5] has negative rotation. The alcohol (V) was converted to the corresponding tosylate (VI) and then reduced with lithium aluminium hydride to furnish the (+) hydrocarbon (VII). The NMR spectrum of the hydrocarbon (VII) is in agreement with its structure.* The assignment of the signals for various protons is shown in Fig. 3. The benzylic proton at C_2 gives signals in the region 7·2 to 7·5τ and some of the signals overlap with the signal due to protons of the methyl group attached to the benzene ring. The optical rotatory dispersion curve of the (+) hydrocarbon (VII) derived from (+) *ar*-turmerone was virtually the mirror image of the optical rotatory dispersion curve of (−) 2-phenylbutane which is known to have the absolute configuration shown in X.[5,6] This leads to the absolute configuration shown in VII for the former hydrocarbon.

---

* The number of protons giving rise to the various signals have been determined by measuring the areas of the peaks and this is also in agreement with the structure of the compound.

[5] D. J. Cram, *J. Amer. Chem. Soc.* **74**, 2137 (1952).

[6] R. K. Hill and L. A. Gardella, *J. Org. Chem.* **29**, 766 (1964).

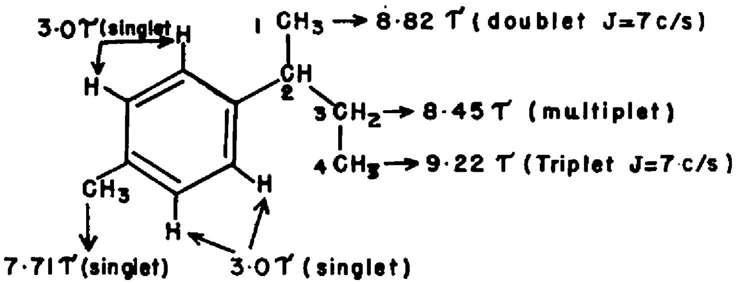

FIG. 3. NMR Signals of 2*p*-Tolylbutane.

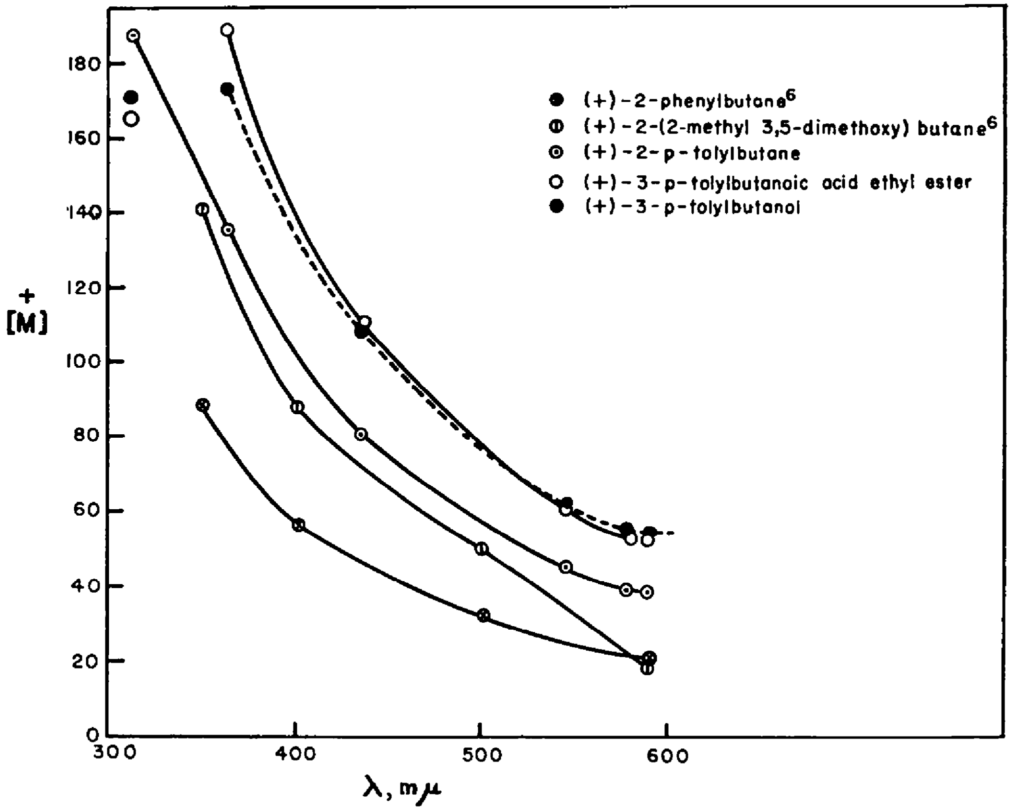

FIG. 4. O.R.D. curves (chloroform).

The absolute configuration indicated for the acid (III) and its transformation products, the alcohol (V) and the hydrocarbon (VII) by the molecular rotation method are mutually consistent. Hence (+) *ar*-turmerone has the absolute configuration shown in II. The ORD curves of the (+) ester (IV) and (+) alcohol (V) have also been determined and they are virtually superimposable on the ORD curve of the (+) hydrocarbon (VII).

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 silicontetramethyl as internal standard with Varian A 60 spectrometer by Mr. I. Mulla. Optical rotations were determined at room temp (25–30°).

ar-*Turmerone.* Commercial turmeric oil having n_D^{29} 1·5060 purchased from Techno Chemical Industries, Calicut, India, was fractionated and the fractions b.p. 80–110°/1 mm, n_D^{28} 1·5000–1·5115, α_D −7 to −27 (neat) were oxidized to give *ar*-turmerone. Low temp chromic acid oxidation[8a] of the above fractions gave *ar*-tumerone in poor yield. After a few trial runs with lead tetracetate the following conditions were found to be satisfactory. The tumeric oil fraction b.p. 80–110°/1 mm (10 g) was dissolved in glacial acetic acid (25 ml) and to this was added lead tetracetate (5 g) in glacial acetic acid (10 ml). The mixture was stirred at room temp for 15 min in the absence of light and then poured in ice-water (200 ml). It was extracted twice with ether (100 × 2 ml) and the ether extract washed with water, Na_2CO_3 aq and again with water and dried (Na_2SO_4). Removal of solvent and distillation of residue furnished *ar*-turmerone, b.p. 120–130°/2 mm (8·58 g), α_D −68° (neat). The IR spectrum showed bands at: 1689 and 1618 cm^{-1} due to the conjugated ketone system. UV spectrum showed maximum at 239 mμ, ε 11,750. This sample was found satisfactory for our studies described below.

3-*p-Tolylbutanoic acid* (III). *ar*-Turmerone, α_D +68° (neat) (2 g) prepared as described above was dissolved in purified ethyl acetate (100 ml) and ozonized for 8 hr (rate of ozone production = 65 mg/hr) below 10°. To the ozonized solution 30% H_2O_2 (4 ml) and dil. acetic acid (1:1; 10 ml) were added and the mixture was shaken thoroughly and left overnight. The ethyl acetate layer was washed with water (100 × 3 ml). Mixture of 4% Na_2CO_3 aq (15 ml) and the ethyl acetate layer was evaporated slowly. After slow evaporation of ethyl acetate, the Na_2CO_3 solution was heated on a steam bath for 1–1/2 hr, cooled and extracted with ether (100 ml). The ether extract was washed with Na_2CO_3 aq (5%; 10 ml) and then with water. The Na_2CO_3- extract was acidified with dil HCl aq (1:1) and the acidified solution extracted with ether and washed with water. The ether extracts after drying and solvent removal furnished the crude acid (III) as a residue (1·06 g). *ar*-Turmerone (7·6 g) was ozonized in 4 batches as described above to furnish 3·3 g of the crude acid (III). The crude acid was distilled (b.p. 130–140° (bath)/1 mm) n_D^{28} 1·5082; $(\alpha)_D$ +45° (*c*, 6·53, $CHCl_3$). Lit.[3b] records $(\alpha)_D$ +62° (benzene) for the acid (III). It was converted to the s-benzylisothiuronium salt which was recrystallized from dil. alcohol, m.p. 151–152°, yield, 3·95 g, (Found: C, 66·22; H, 7·33; N, 8·37. $C_{19}H_{24}N_2SO_2$ requires: C, 66·28; H, 7·02; N, 8·13%). A mixture of the above s-benzylisothiuronium salt (3·11 g), ether (100 ml) and 1N HCl (50 ml) was stirred at room temp for 1 hr. The ether layer was washed with water, dried and evaporated to furnish the acid (III; yield 1·88 g). After distillation the acid showed $(\alpha)_D$ +65° (*c*, 4·6, benzene).

Ethyl 3-p-*tolylbutanoate* IV

A mixture of the acid (III; 1·88 g) purified through the s-benzylisothiuronium salt, alcohol (50 ml) and conc. H_2SO_4 (1 ml) was refluxed on a steam bath for 5 hr. The reaction mixture was cooled, diluted with water and extracted with ether (75 ml × 2). The ether extract was washed with water, 5% Na_2CO_3 aq (10 ml) and again with water and dried. Evaporation of the solvent and distillation of the residue furnished the ethyl ester (IV), b.p. 130–135° (bath)/1·5 mm, yield 1·84 g, $(\alpha)_D$ +25° (*c*, 2·17, $CHCl_3$), n_D^{25} 1·4890, (Found: C, 75·58; H, 8·90. $C_{13}H_{18}O_2$ requires: C, 75·69; H, 8·80%).

IR spectrum. The ester (IV) showed a prominent band at 1740 cm^{-1} due to the ester grouping. Other bands at: 1887, 1605, 1575, 1515, 1449, 1408, 1370, 1342, 1307, 1282, 1250, 1212, 1163, 1112, 1094, 1070, 1033, 1020, 952, 925, 900, 885, 854, 819, and 719 cm^{-1}.

*Optical rotatory dispersion.** At λ_{max} 589, 578, 546, 436, 364 and 313, the ester showed the following specific rotations +25, +26, +29, +54, +92 and +80 respectively (*c*, 2·17, $CHCl_3$).

UV spectrum. Max at 257, 263 and 272 mμ (log ε 2·57, 2·63 and 2·55 respectively shoulder at 251 mμ log ε 2·47.

VPC.† The ester (IV) gave a single peak in the vapour phase chromatography using polyester column maintained at 208° and H_2 as carrier gas. Retention time was 4 min 20 sec. Under identical conditions retention time for longifolene was 1 min 50 sec.

---

* Taken in Perkin-Elmer polarimeter. We thank Dr. Sukh Dev for these measurements.

† Taken in the Griffin VPC apparatus MK IIA. We thank Dr. B. B. Ghatge for providing VPC data of our compounds.

3-p-*Tolylbutanol* (V)

A solution of the ethyl ester (IV; 1·62 g) in dry ether (15 ml) was slowly added to a suspension of $LiAlH_4$ (0·75 g) in dry ether (15 ml) kept cooled at 0°. The reaction mixture was then heated to reflux for 3 hr, cooled to 0° and the excess $LiAlH_4$ decomposed initially with alcohol and subsequently with ice–water. Acidification with dil. H_2SO_4 aq (1:1), extraction with ether (50 ml × 2), washing of the ether extract with water, drying and evaporation of solvent furnished a residue which was distilled to give the alcohol (V), b.p. 120–140° (bath)/1 mm, n_D^{25} 1·5081; $(\alpha)_D$ +33°. (Found: C, 81·02; H, 9·55. $C_{11}H_{16}O$ requires: C, 80·44; H, 9·82%).

IR spectrum. There was no band at 1740 cm^{-1} (absence of ester group). There was a prominent band at 3390 cm^{-1} due to hydroxyl group. Other prominent bands were observed at: 1887, 1786, 1639, 1613, 1575, 1449, 1370, 1342, 1300, 1274, 1242, 1211, 1182, 1105, 1087, 1042, 1020, 995, 952, 917, 854, 820, 793, and 724 cm^{-1}.

VPC. On using a polyester column under conditions described for the ester (IV), the alcohol (V) gave a single peak, retention time 5 min 55 sec.

Optical rotatory dispersion. At λ mμ 589, 578, 546, 436, 364 and 313 mμ, the alcohol (V) showed the following specific rotations +33°, +33°, +38°, +66°, +105° and +104° respectively (*c*, 1·89, $CHCl_3$).

Tosyl ester (VI)

To a solution of the alcohol (V; 0·8 g) in dry pyridine (5 ml) was added slowly at 0° a solution of *p*-toluenesulphonyl chloride (1·5 g) in dry pyridine (5 ml). The reaction mixture was allowed to stand in the cold for 15 min, subsequently at room temp (15 min) and finally at 40° (20 hr). It was then cooled and poured in ice water. Extraction with ether (50 ml × 2), washing with dil. HCl and subsequently with water, drying over Na_2SO_4 and evaporation of solvent furnished the crude tosylate (VI; yield 0·55 g). The IR spectrum showed the absence of hydroxyl group. This crude product was used as such in the next step without further purification.

2-P-*Tolylbutane* (VII)

A solution of the tosylate (VI; 0·55 g) in dry ether (10 ml) was added slowly to a suspension of $LiAlH_4$ (0·75 g) in dry ether (15 ml). The mixture was refluxed for 13 hr and then cooled and treated carefully with ice–water to decompose excess $LiAlH_4$. It was acidified with dil. H_2SO_4 aq (1:1) and extracted with ether (50 ml × 2). The ether extract was washed with water and dried. The solvent was removed from the extract at 50° (atm. press.) and the residue chromatographed on alumina (25 g, grade II; neutral). The fraction eluted with pet. ether (60–80° b.p.; 150 ml) on evaporation of solvent followed by distillation of residue over Na furnished the hydrocarbon (VII; 125 mg), b.p. 140–150° (bath)/60 mm, n_D^{25} 1·4865; $(\alpha)_D$ +25° (*c*, 1·27; $CHCl_3$). (Found: C, 89·41; H, 10·79. $C_{11}H_{16}$ requires: C, 89·12; H, 10·88%).

VPC. On using a polyester column maintained at 122° and using H_2 as carrier gas, the hydrocarbon (VII) gave a single peak, retention time being 7 min 5 secs. Under identical conditions *p*-cymene had a retention time of 4 min 45 secs.

IR spectrum taken as liquid film showed bands at: 1894, 1639 (weak), 1580, 1515, 1449, 1376, 1342, 1307, 1204, 1183, 1145, 1111, 1073, 1058, 1042, 1020, 1000, 953, 943, 917, 820, 793, 787 and 725 cm^{-1}.

Optical rotatory dispersion. At λ mμ 589, 578, 546, 436, 364 and 313 mμ the hydrocarbon (VII) showed following specific rotations: +25°, +26°, +30°, +54°, +91° and +127° respectively (*c*, 1·27, $CHCl_3$).

UV spectrum. Max at 259, 264 and 272 mμ, log ε 2·27, 2·36 and 2·26 respectively and shoulder at 252 mμ, log ε 2·12.

Acknowledgements—We thank Dr. S. C. Bhattacharyya for his interest in this investigation.