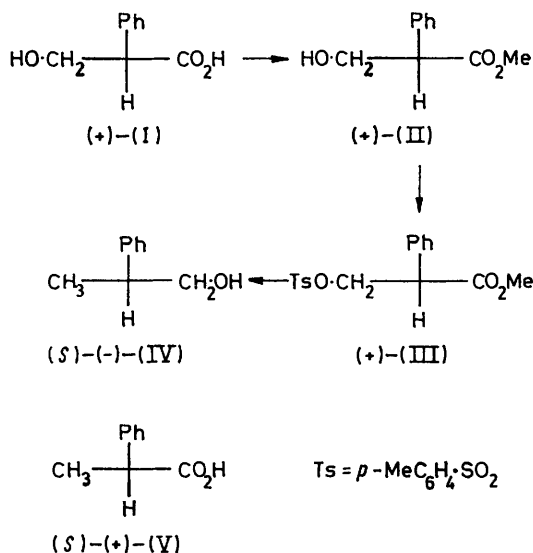


The Absolute Configuration of Tropic Acid

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(+)-Methyl tropate has been converted into (+)- β -methoxycarbonylphenethyl toluene-*p*-sulphonate and the latter reduced to (*S*)-(-)-2-phenylpropanol, thus confirming that (+)-tropic acid has the *R*-configuration.

THE configurational relationship between (-)-tropic acid and (-)-3-chloro-2-phenylpropanoic acid was determined by MacKenzie and Strathern¹ by hydrolysis of



SCHEME Formulae represent Fischer-type projections

the (-)-chloro-acid to (-)-tropic acid. By hydrogenolysis of the (-)-chloro-acid to (*R*)-(-)-2-phenyl-

propanoic acid, Fodor and Csepregy² have shown that (-)-tropic acid has the *S*-configuration. In the course of other work we have obtained the same result by a different route (see Scheme).

(+)-Tropic acid (I) was esterified to give the (+)-methyl ester (II), which was converted into (+)- β -methoxyphenethyl toluene-*p*-sulphonate (III). Reduction of compound (III) with lithium aluminium hydride gave (-)-2-phenylpropanol (IV). (+)-2-Phenylpropanol was obtained by Roger and Neilson³ by reduction of (*R*)-(-)-2-phenylpropanoic acid (V) with lithium aluminium hydride. Hence (+)-tropic acid has the *R*-configuration.

EXPERIMENTAL

I.r. spectra were measured with a Unicam SP 200 spectrophotometer and n.m.r. spectra with a Varian A60 instrument. Mass spectra were obtained by the Physico-Chemical Measurement Unit, Harwell. Etheral extracts were dried over anhydrous magnesium sulphate and solvents were removed at room temperature with a rotary film evaporator.

(+)-Methyl Tropate (II).—(+)-Methyl tropate was obtained in 80% yield by refluxing (+)-tropic acid⁴ (I) { $[\alpha]_D^{20} + 74.4^\circ$ (*c* 2.057 in EtOH); lit.,⁴ $[\alpha]_D^{20} + 72.7^\circ$ (*c* 2.7 in EtOH)} with methanol and Permutit Zeocarb 225 for 8 h. The product had b.p. 148° at 9 mmHg, $\alpha_D^{20} + 103.3^\circ$ (no solvent), $[\alpha]_D^{20} + 76.7^\circ$ (*c* 2.072 in Et₂O), $+ 69.6^\circ$ (*c* 2.154

³ R. Roger and D. G. Neilson, *J. Chem. Soc.*, 1960, 627.

¹ A. MacKenzie and R. C. Strathern, *J. Chem. Soc.*, 1925, 127, 86.

² G. Fodor and G. C. Csepregy, *J. Chem. Soc.*, 1961, 3222.

⁴ A. MacKenzie and J. K. Wood, *J. Chem. Soc.*, 1919, 115, 828.

in Me₂CO {lit.,⁵ $[\alpha]_D^{20} + 69.9^\circ$ (*c* 4.947 in Me₂CO)}; ν_{\max} . 695, 735, 1042, 1165, 1735, 2980, and 3840 cm⁻¹.

(+)-*β*-Methoxyphenethyl Toluene-*p*-sulphonate (III).—(+)-Methyl tropate (4 g) in pyridine was cooled to -8° and pure toluene-*p*-sulphonyl chloride⁶ was added slowly. After 2 days at -8° the mixture was poured on ice and hydrochloric acid. The toluene-*p*-sulphonate was extracted with ether and recovered in the usual way to give plates (4.9 g, 66%), m.p. 61–62° [from light petroleum (b.p. 60–80°)] (Found: C, 60.8; H, 5.5; S, 9.7%; *M*⁺, 334. C₁₇H₁₈O₅S requires C, 61.1; H, 5.4; S, 9.6%; *M*, 334), *m/e* 275.0740 (2%) [(C₆H₅·CH·CH₂·O·SO₂·C₆H₄·CH₃)⁺ requires 275.0742], 162.0679 (100%) [(C₆H₅·C·CH₂·CO₂·CH₃)⁺ requires 162.0681], 155 (30%) [(CH₃·C₆H₄·SO₂)⁺], and 149 (40%) [(C₆H₅·CH·CO₂·CH₃)⁺]; ν_{\max} . (Nujol and hexachlorobutadiene) 698, 840, 990, 1000, 1175, 1370, and 1735 cm⁻¹; δ (CDCl₃) 2.43 (3H, s), 3.64 (3H, s), 3.8–4.7 (3H, m), and 7.2–7.8 (9H, aromatic).

(±)-*β*-Methoxycarbonylphenethyl Toluene-*p*-sulphonate (III).—This compound, prepared similarly from (±)-

methyl tropate, gave plates, m.p. 88° [from light petroleum (b.p. 60–80°)]; i.r. spectrum as for the active ester.

Methyl Atropate.—Attempts to prepare the toluene-*p*-sulphonate of methyl tropate at or above room temperature gave only methyl atropate (2-phenylacrylate), which was identified by its i.r. and n.m.r. spectra: ν_{\max} . 689, 775, 1093, 1202, and 1715 cm⁻¹; δ (CDCl₃) 3.75 (3H, s), 5.8 (1H, d), 6.3 (1H, d, *J* 1.7 Hz), and 7.0–7.5 (5H, aromatic).

(-)-2-Phenylpropanol (IV).—(+)-*β*-Methoxycarbonylphenethyl toluene-*p*-sulphonate (III) (5 g) was stirred under reflux with an excess of lithium aluminium hydride in ether for 4 h. The product, isolated in the usual way, had b.p. 110–112° at 13 mmHg (80% yield), $\alpha_D^{20} - 17.0^\circ$ (no solvent), $[\alpha]_D^{20} - 6.8^\circ$ (*c* 2.059 in Me₂CO) [lit.,³ $\alpha_D^{20} + 16.7^\circ$ (no solvent)]; ν_{\max} . 698, 760, 1016, 1038, and 3390 cm⁻¹.

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⁵ A. MacKenzie and E. R. Winton, *J. Chem. Soc.*, 1940, 840.

⁶ S. W. Pelletier, *Chem. and Ind.*, 1953, 1034.