89. *Resolution of* dl-Δ^2-cyclo*Geranic Acid.*

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dl-Δ^2-*cyclo*Geranic acid has been resolved into its optically active enantiomorphs for comparison with an acid, $C_{10}H_{16}O_2$, m. p. 83°, obtained by the action of alkali on *l*-Δ^3-carene-5 : 6-epoxide. The acids were not identical.

By the action of cold ethyl-alcoholic potassium hydroxide on *l*-Δ^3-carene-5 : 6-epoxide an acid, $C_{10}H_{16}O_2$, m. p. 83°, was obtained and it was suggested (J., 1939, 1501) that this acid might be one of the optically active modifications of Δ^2-*cyclo*geranic acid. This acid has now been resolved by the half-molecule method by means of cinchonine and cinchonidine. The d- and the l-*acid* have m. p. 104°, $[\alpha]_{5461} \pm 395{\cdot}7°$, and neither of them can therefore be identical with the acid prepared from the epoxide. It is hoped that it may prove possible later to determine the structure of this acid.

Experimental.

Geranic acid was most conveniently prepared from citral by Bernhauer and Forster's method (*J. pr. Chem.*, 1936, **147**, 199). The acid, b. p. 160—161°/20 mm., $d_{25°}^{25°}$ 0·9594, $n_D^{25°}$ 1·4839, probably consisted essentially of the *trans*-acid and it readily gave a crystalline *p*-phenylphenacyl ester, m. p. 78—79°. The acid was prepared also by the dehydration of ethyl hydroxygeranate with either potassium hydrogen sulphate or acetic anhydride, followed by hydrolysis with alkali. These acids had somewhat different physical constants, $d_{25°}^{25°}$ 0·9662—0·9644, $n_D^{25°}$ 1·4783—1·4725; $d_{25°}^{25°}$ 0·9710, $n_D^{25°}$ 1·4988. Whilst the former gave the crystalline *p*-phenylphenacyl ester, m. p. 78—79°, in small yield, the latter gave only traces and it seems probable that geranic acid prepared from the hydroxy-ester consists largely of the *cis*-form, a view in accord with the somewhat higher density.

dl-Δ^2-*cyclo*Geranic acid (12·7 g.), prepared by the cyclisation of geranic acid with formic acid (Bernhauer and Forster, *loc. cit.*), in methyl alcohol (60 c.c.) was mixed with 0·894N-sodium hydroxide (43·2 c.c.) and cinchonine (11·16 g.), and the hot filtered solution kept for 24 hours. A cinchonine salt (10 g.) crystallised in needles, m. p. 201—204°, sintering at 180°, $[\alpha]_{5461}$ — 9·8° in chloroform (*c*, 4·244). Two crystallisations from methyl alcohol gave the pure *salt*

* The rotatory powers of the *p*-phenylphenacyl esters were kindly determined for us by Dr. L. N. Owen. They must be regarded as only very approximate, since they were made in a ½ dm. micro-tube with *ca.* 20 mg. of the ester in 0·5 c.c. of solvent.

of constant rotatory power in rosettes of soft needles, m. p. 204—206°, sintering 183°, $[\alpha]_{5461}$ − 15·4° in chloroform (*c*, 4·015) (Found : C, 75·8; H, 8·4; N, 6·3. $C_{10}H_{16}O_2$,$C_{19}H_{22}ON_2$ requires C, 75·3; H, 8·2; N, 6·1%). The l-*acid*, regenerated from the salt, crystallised from ligroin (b. p. 60—80°) in massive prisms, m. p. 104°, $[\alpha]_{5461}$ − 395·7° in ethyl alcohol (*c*, 4·865) (Found : C, 71·3; H, 9·4. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%).

The acid (7·9 g.) regenerated from the soluble cinchonine salt had $[\alpha]_{5461}$ + 200° in ethyl alcohol (*c*, 4·15). This acid (7·4 g.), in hot methyl alcohol (20 c.c.), was mixed with 0·894 N-sodium hydroxide (11·6 c.c.) and cinchonidine (9·8 g.); on keeping, the cinchonidine salt (13·5 g.) crystallised in needles, m. p. 150°. After three recrystallisations from acetone–methyl alcohol the pure *salt*, which was very sparingly soluble in acetone, separated in hair-like needles, m. p. 157—158°, $[\alpha]_{5461}$ + 81·1° in chloroform (*c*, 3·28) (Found : C, 75·7; H, 8·4. $C_{10}H_{16}O_2$,$C_{19}H_{22}ON_2$ requires C, 75·3; H, 8·2%). The d-*acid*, regenerated from the salt, crystallised from ligroin (b. p. 60—80°) in prisms, m. p. 104°, $[\alpha]_{5461}$ + 395·7° in ethyl alcohol (*c*, 4·84) (Found : C, 71·4; H, 9·6%).

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