

Beyeren-19-ol from *Helipterum craspedioides*

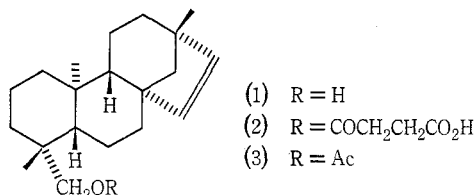
Nigel R. Dennison and Robert N. Mirrington

Department of Organic Chemistry,
University of Western Australia, Nedlands, W.A. 6009.

Abstract

The resinous coating on *Helipterum craspedioides* consists mainly of the succinate ester (2) of (+)-beyeren-19-ol (1) (monogynol, erythroxyol A).

Approximately 60 species of *Helipterum* (Compositae) are endemic to Australia and nearly 50 of these are found in Western Australia, but chemical investigation of the genus has been confined to only two species. An unstable polyacetylenic pigment has been isolated from the roots of both *H. roseum* and *H. manglesii*,¹ and peonidin 3-bioside has been detected in the bracts of the latter.²



H. craspedioides W. V. Fitzg. is an annual herb with bright yellow flowers of the 'everlasting' type, which grows to 30 cm on gravel soils in the Ereman botanic province of Western Australia. The above-ground parts of the plant were found to be coated with a sticky resin which was easily removed by washing with ether. The major component of the resin was the acid (2), whose structure followed from its hydrolysis to succinic acid and the well known (+)-beyeren-19-ol (1), otherwise referred to as monogynol³ or erythroxyol A⁴ previously isolated from *Erythroxyton monogynum*.

An earlier example of a diterpenoid alcohol occurring as its succinate ester was the major constituent of the Western Australian shrub *Goodenia strophiolata*.⁵

¹ Sorensen, J. S., Holme, D., Borlaug, E. T., and Sorensen, N. A., *Acta Chem. Scand.*, 1954, **8**, 1769.

² Gascoigne, R. M., Ritchie, E., and White, D. E., *J. Proc. Roy. Soc. N.S.W.*, 1948, **82**, 44.

³ Kapadi, A. H., and Dev, S., *Tetrahedron Lett.*, 1964, 1171, 2751.

⁴ McCrindle, R., Martin, A., and Murray, R. D. H., *J. Chem. Soc. C*, 1968, 2349.

⁵ Middleton, E. J., and Jefferies, P. R., *Aust. J. Chem.*, 1968, **21**, 2349.

Experimental

Most of the general experimental details have been described previously.⁶ Optical rotations were determined on a Perkin-Elmer 141 polarimeter in chloroform solution at 25°. A copper column, 10 ft by 0.125 in., packed with 5% DEGS on Chromosorb W (80/100 mesh) was used for g.l.c. analysis.

Dried plants (920 g) collected 110 miles north of Meekatharra, W.A., during September 1971 were rinsed several times with ether and the extract was washed with 5% NaHCO₃, then 8% NaOH solution. Acidification of the NaHCO₃ wash and isolation of the acids with ether gave a brown viscous residue (70 g) which resisted crystallization even after chromatography on silica gel. A portion of this extract (3.8 g) was dissolved with warming in 3M NaOH (70 ml) and ethanol (20 ml). After 0.25 h at room temperature a white precipitate formed and, after standing overnight, the mixture was diluted with water (100 ml) and the white solid (2.2 g) (see below) was isolated by ether extraction. The aqueous layer was acidified and the organic acids, after being isolated by ether extraction, were methylated with ethereal diazomethane. The residue oil consisted almost exclusively of dimethyl succinate, identified by g.l.c. comparison with an authentic sample and by its n.m.r. spectrum containing singlets at δ 2.52 and 3.64 in the ratio 2 : 3.

The white solid above crystallized from light petroleum as colourless needles of (+)-beyerene-19-ol (1.05 g, 2.1% of plant), m.p. 118.5–120°. An analytical sample was prepared by preparative t.l.c. followed by vacuum sublimation (100°/0.05 mm): m.p. and mixed m.p. 120–121°, $[\alpha]_D +49^\circ$ (c, 2.5) (lit.⁴ m.p. 119–120°, $[\alpha]_D +39^\circ$ (c, 1.28)) (Found: C, 83.2; H, 11.2. Calc. for C₂₀H₃₂O: C, 83.3; H, 11.2%). ν_{\max} 3625, 1440, 1016, 743 cm⁻¹; n.m.r. spectrum: three singlets, each 3H, δ 0.73, 0.93, 1.00 (3 × CMe); ABq, 2H, 3.38, 3.68 (CH₂OH), J 11 Hz; ABq, 2H, 5.42, 5.65 (CH=CH), J 6 Hz. Mass spectrum: m/e 288 (92%), 257 (61), 148 (46), 135 (85), 105 (100).

The acetate (3), obtained by treatment of (1) with acetic anhydride-pyridine, crystallized from methanol as rods, m.p. 71–72° (lit.⁴ 72–73.5°).

Acknowledgments

We are grateful to Mr R. D. Royce and Mr P. Wilson of the State Herbarium for identification of plant material, and to Professor Sukh Dev for a generous sample of monogynol.

Manuscript received 23 December 1974

⁶ Feutrill, G. I., and Mirrington, R. N., *Aust. J. Chem.*, 1972, **25**, 1719.