

## CYCLOCOLORNONE IN *BORONIA LEDIFOLIA* GAY\*

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Steam distillation of the leaves and terminal branchlets of *Boronia ledifolia* Gay (family Rutaceae) collected at Bowen's Creek, near Mt. Irvine, N.S.W., yielded a volatile oil in 0.42% yield. A gas chromatographic analysis of the oil showed it to consist predominantly of a single compound (70%) which, on separation by vacuum fractionation followed by column chromatography, was found to be a high-boiling ketone which yielded a 2,4-dinitrophenylhydrazone, m.p. 217–218°. The n.m.r. spectrum of this compound indicated the presence of a cyclopropane ring (signals in the 0–1  $\tau$  region) and the infrared spectrum showed the presence of a carbonyl group (1698  $\text{cm}^{-1}$ ) and of olefinic unsaturation (1629  $\text{cm}^{-1}$ ). Consequently the compound was thought to be cyclocolornone.<sup>1</sup> It was epimerized by passing it through an alumina column<sup>2</sup> or by refluxing it with alcoholic potassium hydroxide<sup>3</sup> to form epicyclocolornone, which was identified by a mixed melting point determination and a comparison of the infrared spectrum with that of an authentic specimen kindly donated by Professor R. E. Corbett of the University of Otago, New Zealand.

This is the second recorded occurrence of cyclocolornone: Corbett and Speden<sup>1</sup> found the leaf oil of the New Zealand shrub *Pseudowintera colorata* to contain 7.5% of this ketone.

Penfold and Morrison<sup>4</sup> examined the leaf oil from a population of *B. ledifolia* at Grafton, N.S.W., and reported this oil to consist chiefly of methyl n-heptyl ketone and methyl n-nonyl ketone, together with  $\alpha$ -pinene, methyl anthranilate, and sesquiterpenes. Examination by us of *B. ledifolia* leaf oils from populations in other localities in New South Wales has also failed to detect the presence of cyclocolornone. This is not surprising in view of the considerable morphological variation which occurs in the *B. ledifolia* group and the current uncertainty of the taxonomic status of some populations.

### Experimental

All melting points are uncorrected. Light petroleum had b.p. 40–60°. Gas chromatography was carried out in a Perkin-Elmer 226 gas chromatograph, using a 150-ft Golay column with Silicone oil DC 200 as stationary phase. Infrared spectra were recorded on a Perkin-Elmer 221 spectrophotometer.

### Isolation of Cyclocolornone

Steam distillation of leaves and terminal branchlets of *Boronia ledifolia* (14.52 kg) yielded 0.42% of oil (60 ml) which had the following constants:  $d_{15}^{20}$  0.9630;  $\alpha_D^{20}$   $-218.8^\circ$ ;  $n_D^{20}$  1.5129.

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<sup>1</sup> Corbett, R. E., and Speden, R. N., *J. chem. Soc.*, 1958, 3710.

<sup>2</sup> Buchi, G., and Loewenthal, H. J. E., *Proc. chem. Soc.*, 1962, 200.

<sup>3</sup> Corbett, R. E., and Young, H., *Aust. J. Chem.*, 1963, **16**, 250.

<sup>4</sup> Penfold, A. R., and Morrison, F. R., *J. Proc. R. Soc. N.S.W.*, 1948, **82**, 71.

A vacuum fractionation of the oil gave a residue, b.p.  $105^{\circ}/4$  mm, which was further purified by adsorbing it onto a silica gel column, and eluting it with n-hexane and then diethyl ether. The ethereal eluate yielded a fraction which contained 95% of a single compound as shown by gas chromatography. The fraction yielded a red 2,4-dinitrophenylhydrazone, m.p.  $217-218^{\circ}$  (lit.<sup>1</sup>  $217-218^{\circ}$ ). The fraction had  $[\alpha]_{\text{D}}^{22} -355^{\circ}$  (c, 8.75 in ethanol);  $\nu_{\text{max}}$  1698 and  $1629\text{ cm}^{-1}$ .

*Epimerization of Cyclocolorenone*

(1) The cyclocolorenone fraction (5 g) was refluxed with alcoholic potassium hydroxide (150 ml, 0.5N) for 2 hr. The reaction product was acidified and extracted with ether to yield a crystalline compound (3 g) which on recrystallization from light petroleum gave epicyclocolorenone, m.p.  $68^{\circ}$  (2,4-dinitrophenylhydrazone  $192^{\circ}$ ), identical by mixed melting point and comparison of the infrared spectrum with that of an authentic specimen.

(2) The cyclocolorenone fraction (1 ml) was dissolved in light petroleum, adsorbed onto an alumina column (activity I), and eluted with light petroleum/chloroform mixture (60/30). The eluate yielded a product (0.5 ml), which on recrystallization gave epicyclocolorenone, m.p.  $68^{\circ}$ .

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