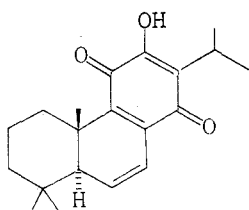


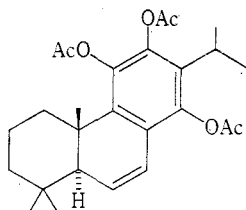
# DEHYDROROYLEANONE IN *PLECTRANTHUS* SPECIES\*

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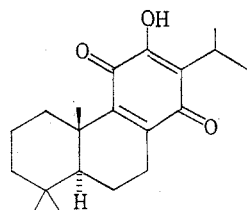
A steam-distillation of leaves and stems of a suspected mixture of species‡ of *Plectranthus* (Labiatae) from Springbrook yielded a little essential oil and some orange crystals,  $C_{20}H_{26}O_3$ , m.p.  $166.5-167^\circ$ , in 0.025% yield. The chemical and physical properties of this substance agree closely with those of the diterpene quinone dehydroroyleanone (I), first described as a constituent of the roots of *Inula royleana* by Edwards, Feniak, and Los.<sup>1</sup> No depression of the mixed melting point was observed. The leucoacetate (II) shows ultraviolet absorption very similar to that of



(I)



(II)



(III)

1,2-dihydronaphthalene<sup>2</sup> and thus supports the structure (I) proposed by Edwards, Feniak, and Los. Royleanone<sup>1</sup> (III) is also present as a relatively minor constituent of *Plectranthus*, the p.m.r. spectrum of the above crystals, m.p.  $166.5-167^\circ$ , indicating c. 10% of royleanone as contaminant. Edwards *et al.* noted that these two substances are inseparable by fractional crystallization. The high field position of the angular methyl protons in (I) (8.97 or 9.03  $\tau$ , cf.  $\alpha$ -pinene<sup>3</sup>) as compared with those of (III) (8.74  $\tau$ ) and the low field position of the olefinic protons (3.13 and 3.52  $\tau$ , cf. indene<sup>4</sup>) are worthy of note.

A previous steam-distillation of *Plectranthus parviflora* var. *major* (identified by the late Mr C. T. White) from Binna Burra yielded some dehydroroyleanone, whereas specimens from Numinbah Valley appeared to contain no diterpene quinones. Plant material from Springbrook, with more prominent purplish coloration of the leaves and stems, yielded twice as much quinone as less highly coloured specimens.

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‡ Our thanks for this information are due to Dr S. T. Blake, who is studying the taxonomy of the genus.

<sup>1</sup> Edwards, O. E., Feniak, G., and Los, M., *Canad. J. Chem.*, 1962, **40**, 1540.

<sup>2</sup> Friedel, R. A., and Orchin, M., "Ultraviolet Spectra of Aromatic Compounds." (John Wiley: New York 1951.)

<sup>3</sup> Jackman, L. M., "Nuclear Magnetic Resonance Spectroscopy." p. 129. (Pergamon: London 1959.)

<sup>4</sup> Bhacca, N. S., Johnson, C. F., and Shoolery, J. N., "N.M.R. Spectra Catalog." (Varian Associates: Palo Alto, Cal., 1962.)

### Experimental

(i) *Isolation of 9-Dehydroroyleanone*.—Exhaustive steam-distillation of 5 lb of *Plectranthus* leaf and stem yielded, by isolation of the crystals from the distillate and by aqueous sodium hydroxide extraction of the oil, a total of 590 mg of orange crystals (0.025%). Three recrystallizations from ethanol gave orange crystals, m.p. 166.5–167°,  $[\alpha]_D -620 \pm 30^\circ$  (*c*, 0.26 in  $\text{CHCl}_3$ ) (Found: C, 76.3; H, 8.4. Calc. for  $\text{C}_{20}\text{H}_{26}\text{O}_3$ : C, 76.4; H, 8.3%). The light absorption spectrum showed  $\lambda_{\text{max}}$  213, 245sh, 329, and 455 m $\mu$  ( $\epsilon_{\text{max}}$  16300, 7750, 7450, and 750 respectively) in ethanol. A mixture of these crystals with authentic 9-dehydroroyleanone showed m.p. 166.5–167° also.

9-Dehydroroyleanone (21.8 mg) was hydrogenated in acetic acid using 10% palladized charcoal catalyst and consumed hydrogen equivalent to 2.01 double bonds. The product was spontaneously oxidized by air to royleanone. Two recrystallizations from acetic acid yielded yellow prisms, m.p. 179–180.5°,  $[\alpha]_D +140 \pm 8^\circ$  (*c*, 1.05 in  $\text{CHCl}_3$ ) (Found: C, 75.9; H, 8.9. Calc. for  $\text{C}_{20}\text{H}_{28}\text{O}_3$ : C, 75.9; H, 8.9%). A solution of the crystals in chloroform showed  $\lambda_{\text{max}}$  278, 283sh, and 408 m $\mu$  ( $\epsilon_{\text{max}}$  15700, 15400, and 430 respectively).

(ii) *Reductive Acetylation of 9-Dehydroroyleanone*.—To a cooled solution of 9-dehydroroyleanone (80 mg) in acetic anhydride (6 ml), zinc dust (0.3 g) and sodium acetate (0.3 g) were added. After 1 hr the very pale yellow solution was filtered onto ice and the crude precipitate twice recrystallized from c. 60% aqueous methanol to give colourless microcrystals, m.p. 129–131° (Found: C, 70.6; H, 7.8. Calc. for  $\text{C}_{26}\text{H}_{34}\text{O}_6$ : C, 70.6; H, 7.7%). The ultraviolet spectrum showed  $\lambda_{\text{max}}$  219 and 267 m $\mu$  ( $\epsilon_{\text{max}}$  26100 and 10400 respectively) in ethanol.