Synthesis of (±)-Deoxybruceol

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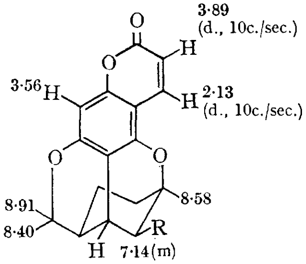
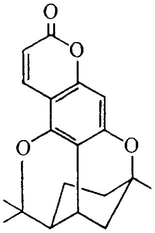
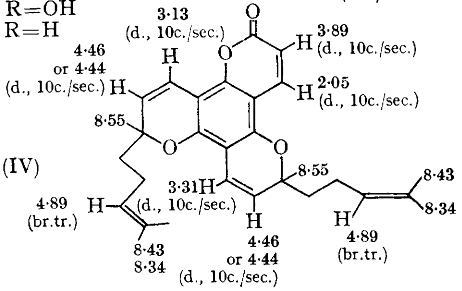
BRUCEOL (I)[1] and deoxybruceol (II)[2] occur in the leaves and branches of *Eriostemon brucei* F. Muell (Rutaceae). The structure of the former rests on *X*-ray analysis of the monobromo-derivative, but no attempts to synthesise the system have been recorded. We now report a two-step synthesis of (±)-deoxybruceol.



(I) R=OH
(II) R=H



(III)



(IV)

5,7-Dihydroxycoumarin was prepared (90%) by condensing phloroglucinol with ethyl propiolate.[3] On heating the coumarin (110°) with equimolar quantities of citral and pyridine, a mixture of products was obtained from which (±)-deoxybruceol (II) m.p. 152°, $\lambda_{\max}$ (EtOH) 217 (27,700), 235 shoulder (12,100), 253 (5180), 261 (5070), 331 (17,600) mμ; $\nu_{\max}$ ($CHCl_3$) 1725, 1615, 1570 cm.$^{-1}$, was isolated chromatographically (10%). Its u.v., n.m.r., and i.r. spectra in solution were identical with those of natural (−)-deoxybruceol kindly supplied by Professor R. R. Jeffries: mass spectra were also identical. By these spectral criteria, and by thin-layer chromatography in a number of systems, no evidence for the presence of the (±)-isomer (III) was found in the synthetic sample. Also formed in the reaction product is the bischromene (IV) (5%), $\lambda_{\max}$ (EtOH) 223 (16,200), 251 (20,500), 289 (19,300), 297 (19,200), 341 (11,200) mμ, $\nu_{\max}$ (film) 1738, 1640, 1615, 1595 cm.$^{-1}$, and a mixture of the two related monochromenes. This reaction (*cf.* the formation of "citrylidene malonic acid")[4] has synthetic promise for certain other bridged *p*-menthanes and chromenes.

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[2] Personal communication, Professor P. R. Jeffries.
[3] K. D. Kaufman and R. C. Kelly, *J. Heterocyclic Chem.*, 1965, **2**, 91.
[4] C. E. Berkoff and L. Crombie, *J. Chem. Soc.*, 1960, 3734.