

STUDIES IN RELATION TO BIOSYNTHESIS

XLV.* PROBABLE ORIGIN OF A B-NORFLAVONE

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The substance leptorumol (1; R = Me, R' = OH), its 7-glucoside, and protofarrerol (2; R = Me, R' = OH) occur together in *Leptorumohra miqueliana* H. Ito.¹ The comparatively rare methylation pattern of the phloroglucinol ring, also found in farrerol (3; R = Me, R' = OH), indicates a probable common origin of these constituents, and a possible relation to (3; R = Me, R' = OH). The scheme below (Scheme 1), based on a phenol oxidation² of the 4-hydroxychalcone (3), rationalizes this relationship, although the key reaction, the removal of the B-ring, has not been observed despite its mechanistic acceptability. Accordingly, we have provided an efficient model based on (3; R,R' = H).

2,6-Disubstituted-4-*t*-butylphenols give, by the action of thallium trifluoroacetate in trifluoroacetic acid, the 2,6-disubstituted benzoquinones and isobutene³ through a hypothetical hydroxydienone ester which was not isolated. Support for this hypothetical intermediate is given by conversion of oestrone into the 10 β -trifluoroacetoxy-19-norandrosta-1,4-diene-3,17-dione in 75% yield.⁴

Application of the procedure also to (3; R,R' = H) did not permit isolation of the intermediate, but gave the quinol and the chromone (1; R,R' = H) in good yields. The electron-releasing properties of the ether oxygen atom would be expected to lead to particular instability in this instance. The flavanone (3; R,R' = H) with lead tetraacetate gave a complex mixture, but the dihydrochalcone (4) produced some of the dienone (5) which, in trifluoroacetic acid, gave quinol and a complex mixture probably derived from the expected vinyl ketone (6).

This type of cleavage may have biosynthetic implications in other areas.

* Part XLIV, *Tetrahedron*, 1972, in press.

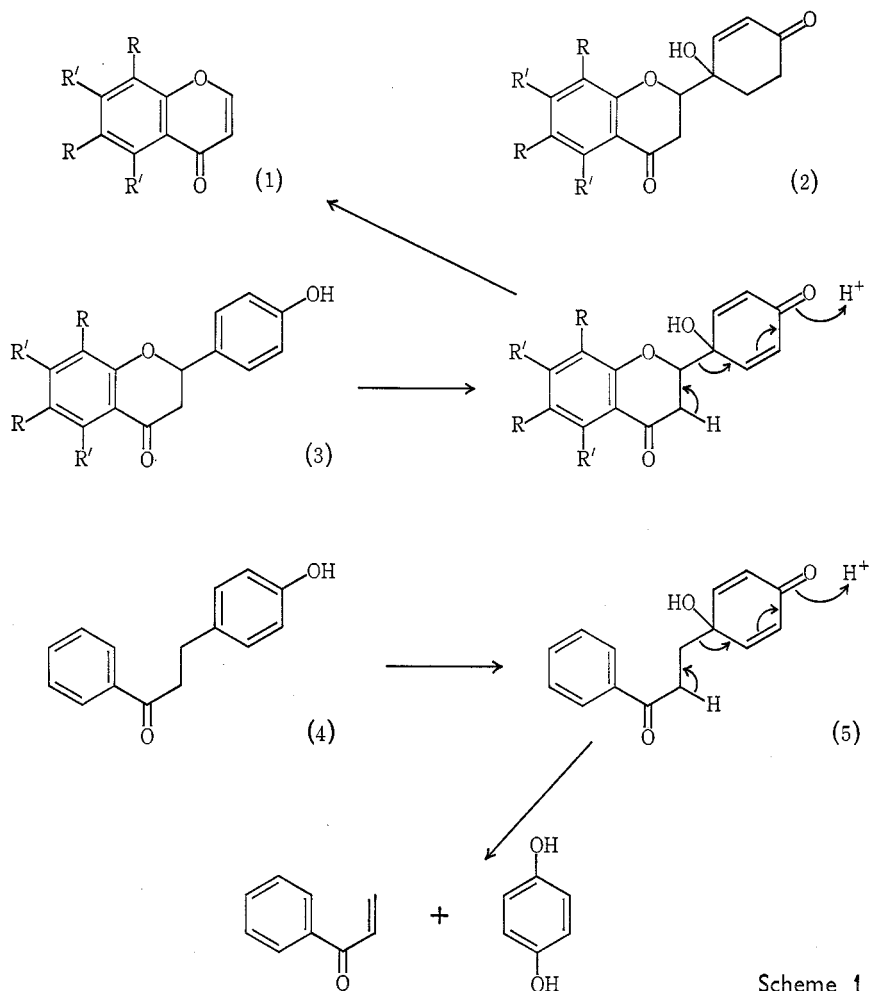
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¹ Fukushima, S., Noro, T., Saiki, Y., Ueno, A., and Akahori, Y., *J. pharm. Soc. Japan*, 1968, **88**, 1135; Noro, T., Fukushima, S., Saiki, Y., Ueno, A., and Akahori, Y., *J. pharm. Soc. Japan*, 1969, **89**, 851.

² Taylor, W. I., and Battersby, A. R., "Oxidative Coupling of Phenols." (Dekker: New York 1967.)

³ McKillop, A., Swann, B. P., and Taylor, E. C., *Tetrahedron*, 1970, **26**, 4031.

⁴ Coombs, M. M., and Jones, M. B., *Chem. Ind.*, 1972, 169.



Scheme 1

Experimental

Oxidation of 4'-Hydroxyflavanone

2,4'-Dihydroxychalcone, m.p. 156–158°, was prepared⁵ and cyclized with acid to 4'-hydroxyflavanone, m.p. 191–193°. The flavanone (240 mg, 1 mmol) and thallium trifluoroacetate⁷ (1.09 g, 2 mmol) reacted in trifluoroacetic acid (10 ml) at 20° for 3 hr, to give a deep green solution. Most of the solvent was removed by evaporation under reduced pressure and the residue, in ether, was extracted successively with aqueous sodium hydrogen carbonate, sodium hydroxide (5%), and water. The neutral ethereal solution was evaporated to give a crystalline solid and recrystallization from light petroleum (b.p. 60–80°) gave chromone (110 mg), m.p. 58–60° (lit.⁸ 59°); m/e 146; λ_{\max} 243 (10500), 298 (7500) nm; ν_{\max} 1655, 1615, 1600 cm^{-1} .

⁵ Udupa, S. R., Banerji, A., and Chadha, M. S., *Tetrahedron*, 1969, **25**, 5415.

⁶ Klinke, P., and Gibian, H., *Chem. Ber.*, 1961, **94**, 26.

⁷ McKillop, A., Fowler, J. S., Zelesko, M. J., Hunt, J. D., Taylor, E. C., and McGillivray, G., *Tetrahedron Lett.*, 1969, 2423.

⁸ Schonberg, A., and Sina, A., *J. Am. chem. Soc.*, 1950, **72**, 3396.

δ (CDCl_3) 6.37 d (1H) 6 Hz; 7.36–7.76 m (3H); 7.88 d (1H) 6 Hz; 8.24 d (1H) 8 Hz. The sodium hydroxide extract after acidification and extraction with ether gave quinol (65 mg) identical in properties with an authentic specimen.

Boiling carbon tetrachloride was used as solvent in an attempt to isolate the intermediate, but the slow reaction in this solvent gave the same products as in trifluoroacetic acid.

Oxidation of 3-(4'-Hydroxyphenyl)propiophenone

This compound, m.p. 116–118° (lit.⁹ 118–120°), was obtained by hydrogenation (Adams catalyst) of 4'-hydroxychalcone. To the propiophenone (1.6 g) in acetic acid (20 ml) was added with stirring lead tetraacetate (3.5 g) in acetic acid (20 ml). After 24 hr, the mixture was poured into water, extracted with ether, and the ether washed with sodium carbonate solution. The resulting yellow oil (1.5 g) was chromatographed in chloroform on silica gel. After an initial mixed fraction, some starting material (200 mg) was recovered, and the final fraction (150 mg) consisted of the hydroxydienone (5), m.p. 116–118° (mass spectrum: m/e 242. $\text{C}_{15}\text{H}_{14}\text{O}_2$ requires **M**, 242). λ_{max} (EtOH) (ϵ): 241 (26000), 280 (3200) nm; ν_{max} (CHCl_3) 3360, 1685, 1650, 1615 cm^{-1} . δ (CDCl_3) 2.24 t (2H) 7 Hz; 3.06 t (2H) 7 Hz; 3.20 br s (1H, OH); 6.28 d (2H) 10 Hz; 6.88 d (2H) 10 Hz; 7.5 m (3H); 7.92 dd (2H) 6, 2 Hz. Reaction of this product with trifluoroacetic acid gave a complex mixture which was shown to contain quinol.

⁹ Von Strandtmann, M., Cohen, M. P., Puchalski, C., and Shavel, J., *J. org. Chem.*, 1968, **33**, 4306.