Synthetic Approaches to Some Naturally Occurring Phenalenones and Related Compounds: Synthesis of 3,4,6,9-Tetrahydroxy-7-methylphenalenone

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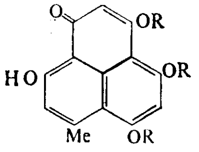
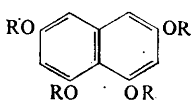
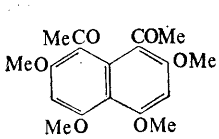
STUDIES by Thomas[1] suggest that the biosynthesis of the phenalenones, atrovenetin and herqueinone, proceeds through the acetate-derived tetrahydroxyphenalenone (Ia). More recently Shibata[2] has suggested that the same intermediate or its tautomeric equivalent is involved in the biosynthesis of the dimeric modified phenalenones (*e.g.*, duclauxin). We report a convenient route to (Ia) which is also the key intermediate in our projected biogenetic type approach to the synthesis of these compounds.



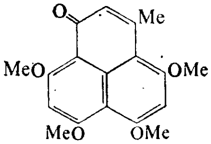
(Ia) R = H
(Ib) R = Me



(IIa) R = H
(IIb) R = Me



(III)



(IV)

The tetramethoxynaphthalene (IIb) derived from the previously described tetrahydroxy-compound[3] (IIa) afforded upon acetylation with acetic acid and trifluoroacetic anhydride, the diacetyl derivative (III), 60%, m.p. 195—197°. The simple n.m.r. spectrum ($CDCl_3$) τ, 3·48 (2H), 6·04 (6H), 6·08 (6H) and 7·45 (6H) and subsequent reactions of (III) established that acetylation had occurred in both the *peri*-positions. Treatment of (III) with base furnished the tetramethoxyphenalenone (IV), m.p. 218—220°, λ_{max} (EtOH) 239, 260, 285, 362, 415, and 435 mμ (log ϵ, 4·35, 4·25, 4·43, 4·24, 4·28, and 4·28). Selective demethylation of (IV) with magnesium iodide etherate gave a trimethoxyphenalenone, m.p. 262—264°, which appears to exist predominantly as the tautomer (Ib). Total demethylation of (IV) with hydrogen bromide in acetic acid yielded the tetrahydroxyphenalenone (Ia, or its tautomeric equivalent) m.p. 230 (decomp.), λ_{max} (EtOH) 238, 257, 277, 365, 385, and 401 mμ (log ϵ, 4·25, 4·22, 3·99, 4·18, 4·20, and 4·23); τ (CD_3SOCD_3), 3·29 (1H), 3·65 (1H), 3·88 (1H) and 7·26 (3H).

All new compounds had the requisite spectral and analytical properties.

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[1] R. Thomas, *Biochem. J.*, 1961, **78**, 807.
[2] S. Shibata, *Chem. in Britain*, 1967, **3**, 110.
[3] P. M. Baker and B. W. Bycroft, preceding Communication.