

SECONDFLORAN, A NOVEL ISOFLAVANONE FROM SOPHORA SECONDFLORA DC.

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Isolation of a new isoflavan from *S. secundiflora* was reported earlier¹, but not even a trace of this compound could be obtained from the plant material collected a year later from the same region. Workup of the extract afforded instead a new isoflavanone, unique in that it has a hydroxyl at C-3.

Secundifloran 1, m.p. 205°, M⁺ 386, C₂₁H₂₂O₇, λ_{max} (EtOH) 290, 312 nm (sh), ν_{max} (mull) 3400, 3320, 1680, 1620 cm⁻¹, forms a tetraacetate, m.p. 145°, τ (CDCl₃) 7.68, 7.70, 7.78, 7.84 (all s; 4xMe), 6.24 (3Hs; -OMe) but only a trimethyl ether (Me₂SO₄/K₂CO₃ or CH₂N₂) and hence of the four hydroxyls one must be alcoholic. The nmr spectrum of the methyl ether 2, m.p. 154° establishes the presence of a 1,1-dimethylallyl side chain and shows that, as in unanisoflavan¹, ring B is tetrasubstituted and ring A is resorcinol derived; 2.04 (d, J 9 Hz; 5-H), 3.34 (dd, J 9, 2 Hz; 6-H), 3.56 (d, J 2 Hz; 8-H), 2.72 (s; 2'-H). The mass spectrum of secundifloran displays only two prominent fragments C₂₁H₂₀O₆ (15%) corresponding to M⁺ - H₂O and C₇H₅O₃ (100%) arising through fission of the pyrone ring with hydrogen transfer. The RDA fragments are again missing as also is any fragment containing the intact prenyl side chain.

The 3-hydroxy-3-phenylchromanone system of the compound is defined by the doublets at 5.20 and 5.70 (J 12 Hz; ArO-CH₂) in the nmr spectrum of 2. Though their position is in better agreement with a 3-hydroxyflavanone structure absence of significant shift on acetylation — both doublets merge with the AB multiplet of the side chain olefinic protons at 5.0τ in the acetate spectrum — and transformation to isoflavanone exclude this possibility. Of interest here

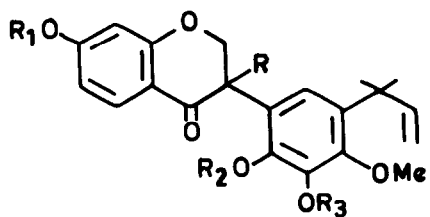
also is the comparison with eucomol² in which the doublets of these protons almost coincide at higher field (5.84 and 5.98 τ).

The methyl ether 2, degraded by Zn/ $\bar{O}H^3$ to a product with the characteristic ir spectrum of a deoxybenzoin, was largely unaffected by Zn/AcOH. The monoacetate 4, which should react more readily with this reagent⁴, was formed under severer conditions (Ac₂O/Py, 100° 20 hr) than needed for acetylation of the phenol (Ac₂O/Py, 25° 5 hr) the difference being probably due to intervention of the six membered cyclic transition state 6 in acetylation of the latter. On refluxing 4 with Zn/AcOH the isoflavanone 5 was obtained in almost quantitative yield, m.p. 115°, M⁺ 412, C₂₄H₂₈O₆, τ (CDCl₃) 5.90 (q, \underline{J} 5 Hz; X), 5.42 (dd, \underline{J} 5, 12 Hz; AB). Of particular interest is the position of the aromatic singlet, 3.22 (2'-H), the same as in unanisoflavan, as against 2.72 in both 2 and 3. The C-3 hydroxyl is thus responsible for the deshielding of the 2'-H as well as absence of any shift on acetylation.

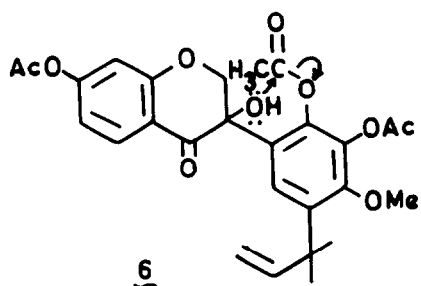
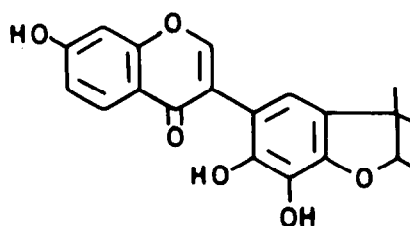
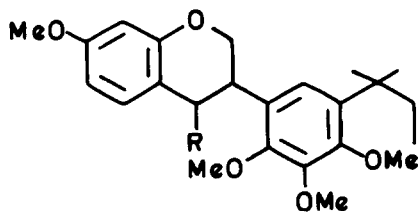
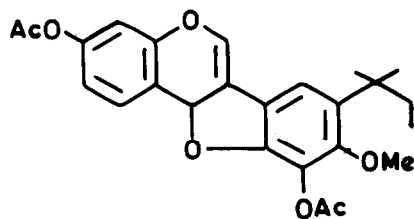
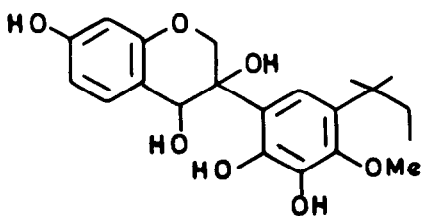
Treatment of secondifloran with methanolic HCl at 100° for 5 hr effects dehydration and cyclisation of the side chain with concomitant demethylation to give the isoflavone 7, m.p. 237°, M⁺ 354, C₂₀H₁₈O₆, τ (CDCl₃:DMSO) 2.0 (s; 2-H), 5.50 (q, \underline{J} 6.5 Hz; MeCH₂O), 8.56 (d, \underline{J} 6.5 Hz; CH₃CH), 8.86 and 8.66 (s each; CMe₂).

All evidence thus points to the substitution pattern in secondifloran being the same as in unanisoflavan. Final confirmation was obtained by hydrogenation of 2 (Pd/C, EtOH) which gave two products, one identical with dihydro-unanisoflavan dimethyl ether 8 (ir and nmr comparison) the other shown by its nmr spectrum to be the corresponding benzyl alcohol 9, 5.24 (d, \underline{J} 2.6 Hz; Ph-CH₂OH)⁵. Hydrogenation of secondifloran, attempted initially, also led to a mixture which could not be resolved because of the marginal difference in Rf values of the two components. Acetylation of the crude hydrogenation product gave unexpectedly 10, m.p. 105°, M⁺ 438, C₂₅H₂₆O₇, τ (CDCl₃) 2.48 (d, \underline{J} 9 Hz; 1-H), 2.70 (s; 6-H), 4.36 (s; 11a-H), 7.52, 7.70 (s each; 2xOAc), 8.16 (q, \underline{J} 7 Hz; CH₂CH₃), 9.34 (t, \underline{J} 7 Hz; CH₃CH₂), 8.60 (s; CMe₂) formation of which is understandable only on the basis of the diol 11 being the intermediate.

Unlike pisatin, variabilin and tuberosin⁶, secondifloran is optically



- 1 R = OH, R₁ = R₂ = R₃ = H
2 R = OH, R₁ = R₂ = R₃ = Me
3 R = OAc, R₁ = R₂ = R₃ = Ac
4 R = OAc, R₁ = R₂ = R₃ = Me
5 R = H, R₁ = R₂ = R₃ = Me

678 R = H9 R = OH1011

inactive suggesting that it arises through photochemical hydroxylation. The possibility of its being an artifact is ruled out by the resistance of isoflavanone 5 to aerial oxidation and the fact that tlc shows 1 to be present in the extract from the outset.

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References :

1. N. Minhaj, H. Khan, A. Zaman and F.M. Dean, Tetrahedron Letters, 2391 (1976).
2. P. Bohler and Ch. Tamm, Tetrahedron Letters, 3479 (1967).
3. L. Crombie and P.J. Godin, J. Chem. Soc., 2861 (1961).
4. R.S. Rosenfeld, J. Amer. Chem. Soc., 79, 5540 (1957).
5. S. Yamaguchi, S. Ito, A. Nakamura and N. Inoue, Bull. Chem. Soc. Japan, 38, 2187 (1965).
6. B.S. Joshi and V.N. Kamat, J. Chem. Soc. (C), 907 (1973).