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IDENTIFICATION OF 3',4',5',5,7-PENTAHYDROXYFLAVONE AND ITS 3'-MONOGLUCOSIDE

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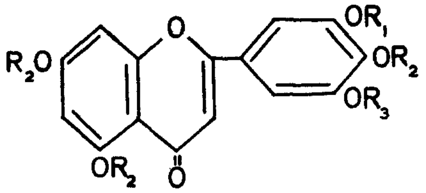
Malcher and Lamer(1) recently isolated a new flavone glucoside from the leaves of *Lathyrus pratensis* L. and *Thuja occidentalis* L. The glucoside was isolated in a pure state by chromatography over cellulose and perlon powders. This glucoside (I) crystallised from aqueous acetone as needles, $C_{21}H_{20}O_{12}.H_2O$, m.p. 284-285° and showed Rf 0.26 in n-butanol, acetic acid, water (4:1:5); Rf 0.17 in 30% acetic acid; Rf 0.40 in ethyl acetate, formic acid, water (10:2:3); and Rf 0.46 in acetic acid, concentrated hydrochloric acid, water (15:3:82) on descending paper chromatography. The U.V. spectrum in ethanol showed λ_{max} 354 mμ (log ε 4.26), λ_{max} 270 mμ (log ε 4.17), λ_{max} 245 mμ (log ε 4.18). Quantitative hydrolysis with 20% sulphuric acid indicated it to be a monoglucoside.

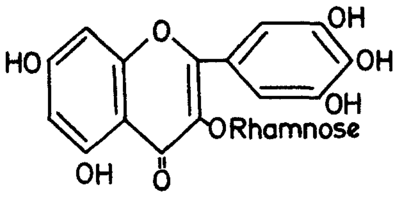
The aglucone $C_{15}H_{10}O_7.\frac{1}{2}H_2O$, crystallised from methanol as deep yellow needles, m.p. above 360° and had Rf 0.60 in n-butanol, acetic acid, water (4:1:5); Rf 0.22 in 60% acetic acid; Rf 0.58 in ethyl acetate, formic acid, water (10:2:3); and Rf 0.44 in acetic acid, concentrated hydrochloric acid, water (30:3:10). Glucose was the only sugar detected by paper chromatography of the filtrate from hydrolysis of the glycoside after neutralisation with barium carbonate, The osazone, m.p. 204-205°, was formed. The U.V. spectrum of the aglucone in ethanol showed λ_{max} 362 mμ (log ε 4.32), λ_{max} 271 mμ (log ε 4.16), inflexion at 261 mμ. In the presence of boric acid and sodium acetate the long wavelength absorption maximum showed a shift to 380 mμ indicating the presence of a catechol group(2). The aglucone was decomposed by sodium ethoxide



I : R_1 = glucose, R_2 = R_3 = H

II : R_1 = R_2 = R_3 = H

III : R_1 = R_3 = Me, R_2 = H



IV

The aglucone gave a penta-acetate, m.p. 248-250° and a penta-O-methyl ether, m.p. 192-193°. These derivatives correspond in m.p. to those of 3',4',5',5,7-pentahydroxyflavone (tricetin)(3) (II) and the colour reactions of the aglucone, red colouration on reduction with magnesium and hydrochloric acid, no yellow colouration with zirconyl chloride and citric acid(4), indicate it to be a flavone. The aglucone is therefore (II) previously known as the demethylation product of its 3',5'-dimethyl ether, tricin (III).

The glucoside was stable to sodium ethoxide and showed a bathochromic shift of the long wavelength absorption maximum to 376 mμ in the presence of boric acid and sodium acetate. This strongly suggested structure (I) for the glucoside which has the pyrogallol system protected from alkali attack and retains a catechol group for the boric acid reaction(2). As further proof of the structures assigned, proton magnetic resonance spectra of the aglucone and glucoside were measured in wet deuteriodimethyl sulphoxide for interpretation using the extensive series of spectra recorded by Batterham and Highet(2). The spectrum of myricitrin (IV) isolated from *T. occidentalis* was also obtained.

P.M.R. Spectra (τ -scale) in CD_3SOCD_3

Substance	5-OH	other phenolic groups	2',6'-H	3-H	6-H	8-H	Sugar
IV	-2.7	-	3.1,s(2H)	-	3.58,d*	3.78,d*	4.80,s(1H); 9.10,d(3H)
II	-2.95	-	2.98,s(2H)	3.39,s	3.50,d*	3.78,d*	-
I	-2.95	-0.95(1H),0.50(1H), 0.92(1H)	2.58,s(1H) 2.75,s(1H)	3.19,s	3.41,d*	3.73d*	5.10,d J=3cps (1H)

s = singlet, d = doublet *J ≙ 1.5 cps.

Other resonances expected were obscured by broad bands due to CHD_2SOCD_3 and H_2O. Proton assignments are based on the tables given by Batterham and Highet. The two equivalent protons in the aglucone which give the line at τ 3.1 must be the 2' and 6' protons. In the glucoside these become non-equivalent so the glucoside must be 3',4',5',5,7-pentahydroxyflavone 3'-glucoside (I). The spectrum of the aglucone provides additional evidence for its structure (II).

References

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