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QUERCETAGETIN 3,6-DIMETHYL ETHER

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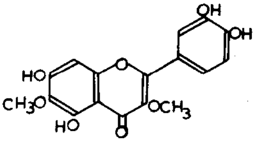
Quercetagetin methyl ethers constitute the commonest of the more highly substituted flavones found in nature[1]. Recently reported quercetagetin derivatives include spinacetin[2], jacein[3] and centaureidin[4]. With but one exception all the known naturally occurring quercetagetin ethers are methoxylated at the 6-position. We now report the occurrence of the hitherto unknown quercetagetin 3,6-dimethyl ether (I) in cocklebur (*Xanthium pensylvanicum*)



I

This flavone was first detected by paper chromatography using the solvent systems BeAW* (R_f .32) 30% HOAc (R_f .46) and BAW** (R_f .82). It appears as a dark spot under UV turning dull yellow with ammonia vapour. The compound was first extracted from leaves with ethanol, taken up into water

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* BeAW Benzene-acetic acid-water (127:72:3)

**BAW *n*-Butanol-acetic acid-water (12:3:5) and then extracted with ether. Isolation from the ether extract was by means of preparative paper chromatography, yielding milligram quantities only of total material. Successive recrystallisation from aqueous ethanol gave microscopic yellow crystals, m.p. 207-209° after thorough drying. Positive tests were given with Mg/HCl and Zn/HCl indicating that the compound is probably a 3-O-substituted flavonol[5]. It gives a green colour with ferric chloride and is readily reduced by silver nitrate. Treatment of an ethanolic solution with sodium amalgam (Barganelli test[5]) gave a brown deposit, the negative test indicating that a vicinal trihydroxy grouping is probably absent.

The structure of this new flavone was established from its NMR and UV spectra. The NMR spectrum (in deuterated dimethyl sulphoxide) showed two methoxyl groups at 3.80 (chemical shift, δ, in ppm, TMS=0). A singlet at 6.48 showed the presence of the 8-proton in ring A[6,7]. The remainders of the aromatic region showed a doublet at 6.78, 6.88 (J = 6 cps) (5'-proton) and partly resolved peaks at 7.33, 7.41 (6'- and 2'-protons) indicating a 3',4'-disubstituted pattern in ring B[6,7]. The pattern of peaks in the aromatic region is closely similar to that in the spectrum of patuletin[8], determined as a reference in this work. A singlet downfield at 12.80 was recognised as that of the hydrogen bonded 5-OH group whilst broad peaks at about 9.57 were assigned to three other OH groups. NMR evidence thus indicated the compound can be formulated as a tetrahydroxy-dimethoxy-flavone.

The UV spectrum (in 95% EtOH) is typically that of a hydroxyflavone with maxima at 259 (with shoulder at 268) and

357 mμ. Bathochromic shifts in ethanolic aluminium chloride (λmax. 270, 367) and in ethanol saturated with sodium acetate (λmax. 273, 384) indicated the presence of free 5-OH, and 7- and 4'-OH groups respectively[9]. The presence of an ortho-dihydroxy grouping was revealed by bathochromic shifts in the presence of sodium acetate-boric acid[9] (λmax. 265, 383). The spectrum in ethanolic sodium hydroxide (λmax. 271, 411) with the large shift of the long-wavelength band, indicated the presence of the 4'-OH but absence of a free 3,4'-dihydroxy system[9].

The above data establishes that three of the hydroxyl groups are located at positions 5, 7 and 4'. All available evidence indicates that the 3-hydroxyl is methylated. This leaves position 3' and 6 for the location of the remaining -OH and $-OCH_3$ groups. The bathochromic shift of the long-wavelength band in presence of sodium acetate-boric acid indicates that the o-dihydroxy grouping is in ring B. The last -OH is thus assigned to the 3'- position, with the $-OCH_3$ at position 6. This is consistent with the negative test for vicinal trihydroxy groups.

On the basis of colour reactions, NMR and UV spectral evidence the structure 5,7,3',4'-tetrahydroxy-3,6-dimethoxyflavone (I) is thus assigned to the new flavone. The synthesis of this compound is in progress.

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REFERENCES

1. F.M. Dean, Naturally Occurring Oxygen Ring Compounds, p.320, Butterworths, London, (1963).
2. A. Zane and S.H. Wender, J. Org. Chem., **26**, 4718 (1961).
3. L. Farkas, L. Horhammer, H. Wagner, H. Rosler and R. Gurniak, Chem. Ber. **97**, 610 (1964).
4. L. Farkas, L. Horhammer, H. Wagner, H. Rosler and R. Gurniak, Chem. Ber. **97**, 1666 (1964).
5. K. Venkataraman, in The Chemistry of Flavonoid Compounds, ed. T.A. Geissman, p.70, Pergamon, Oxford (1962).
6. T.J. Batterham and R.J. Highet, Aust. J. Chem., **17**, 428 (1964).
7. T.J. Mabry, J. Kagan and H. Rosler, Phytochem., **4**, 177 (1965).
8. L.R. Row and T.R. Seshadri, Proc. Indian Acad. Sci., **22**, 215 (1945).
9. L. Jurd, in The Chemistry of Flavonoid Compounds, ed. T.A. Geissman, p.107, Pergamon, Oxford (1962).