Isolation of 3-Methoxyfisetin from *Acacia mearnsii*

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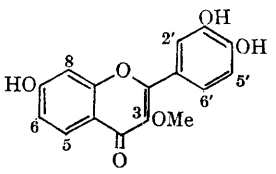
RE-EXAMINATION of the water-insoluble fraction of black wattle (*Acacia mearnsii*) heartwood extract has led to the isolation of a new naturally occurring derivative of fisetin, 3-methoxyfisetin (I). On two-dimensional paper chromatograms [butan-2-ol saturated with water and 2% (v/v) acetic acid] the compound partly underlies fisetin but it is readily detected by its bright blue fluorescence under u.v. light.

The compound, $C_{16}H_{12}O_6$, m.p. 268—270°, crystallised from ethanol–water as needles and was obtained pure by repeated preparative paper chromatography. With the Mg–HCl reagent, the compound gave a typical cherry-red colour[1] while with ammoniacal silver nitrate a black, after transient yellow (due to ammonia), colour was obtained. The i.r. spectrum showed carbonyl absorption at 1607 cm.$^{-1}$. The main peak in the u.v. spectrum at 350 mμ was unaffected by the addition of aluminium chloride but underwent a bathochromic shift of 13 mμ with boric acid–sodium acetate.[2] Fusion with potassium hydroxide yielded protocatechuic acid and β-resorcylic acid and this, together with the evidence above, suggested a flavonol with free phenolic groups at the 3′-,4′-, and 7-positions and methoxy-substitution at C-3.

Acetylation with acetic anhydride–pyridine yielded the 3′,4′,7-triacetoxy-3-methoxy-derivative as white prisms (m.p. 145—147°) from methanol. In the n.m.r. spectrum of this derivative, the 3-methoxy-single is centred at τ 6·07. In agreement with earlier findings the proton at C-5 is strongly deshielded (τ 1·75) by the carbonyl group at C-4.[4] Mass spectrometry gave M^+ 426 for this derivative.

Methylation of the free phenolic form with diazomethane gave the tetramethyl ether (M^+ 342, by mass spectrometry) as elongated prisms, m.p. 152°. A mixed m.p. with authentic tetra-*O*-methylfisetin showed no depression and comparison of the mass and n.m.r. spectra of these two compounds showed complete identity.



(I)

Apart from the flavonol glycoside mearnsitrin,[5] isolated from wattle leaves with a methoxy-group probably in the C-4′ position, no other methoxylated derivatives have been obtained from wattle. The present isolation of 3-methoxyfisetin is of interest particularly in the light of speculation regarding the biosynthesis of C_{16} flavonoids either through condensation with formaldehyde[6] or through photochemical oxidative cyclisation.[7]

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