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5,6,7-TRIMETHOXYFLAVONE AND 5,6,7,4′-TETRAMETHOXYFLAVONE FROM *KICKXIA LANIGERA*

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Key Word Index—*Kickxia lanigera*; Scrophulariaceae; 5,6,7-trimethoxyflavone; 5,6,7,4′-tetramethoxyflavone.

5,6,7-Trimethoxyflavone (I) or trimethyl-baicalein was reported for the first time by Kutney and Hanssen[1] in *Zeyhera tuberculosa* and subsequently by a Japanese team[2] in *Callicarpa japonica.* Swift[3] found 5,6,7,4′-tetramethoxyflavone (II) or tetra-*O*-methyl-scutellarein in orange peel; the same compound was later found in *Marrubium peregrinum.*[4]

This note describes the isolation of the above mentioned flavones from *Kickxia lanigera* (Desf.) Hand-Mazz. These two compounds were isolated in 0·02 and 0·005% yield respectively from the whole dired plant.

EXPERIMENTAL

Roots, stems, leaves and flowers of *Kickxia lanigera* were collected in Valdemoro (Madrid), October 1970. Legit et determinavit Dr. José Borja voucher specimens (No. 78579) were deposited in the Herbarium Faculty of Pharmacy (Ciudad Universitaria, Madrid). NMR spectra were measured on a Perkin-Elmer R12, MS were taken with a MAT 711.

Extraction and purification. The plant material (2 kg) was extracted 3 × MeOH containing 1% HOAc at 50°. The extract was filtered and the solvent removed. The residue was extracted several times with aq. 1% HCl. This aqueous extract was made alkaline with NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ was evaporated and the residue chromatographed on a column of silica gel (Merck 0·05–0·2) eluting with $CHCl_3$, to give 390 mg of (I) and 68 mg of a mixture of (I) and (II). This mixture was separated by preparative TLC (Merck, silica gel 60 PF_{254}, acetone–hexane, 2:3) to give 10 mg (I) and 52 mg (II).

5,6,7-Trimethoxyflavone. m.p. 166–167° (needles, MeOH). λ_{max} (EtOH); 216 nm (log ϵ 4·58), 264 (4·40), 306 (4·35); ν (KBr), 1638, 1620, 1603, 1579 cm^{-1}. NMR ($CDCl_3$); signals: δ 7·85, 7·53, 6·85, 6·66, 4·01, 3·99, 3·94. The signals of the synthetic compound[5] are similar. MS: 312 (M^+, 24), 297 (100), 281 (5), 269 (10), 266 (5), 254 (12), 167 (8), 152 (6), 148 (11), 102 (3).

5,6,7,4′-Tetramethoxyflavone. m.p. 162–163° (prisms, MeOH). λ_{max} (EtOH) 216 (4·62), 266 (4·24), 319 (4·52); ν (KBr) 1638, 1603, 1574 cm^{-1}. NMR ($CDCl_3$), signals: δ, 7·82 and 7·00 (A_2B_2 J 9 Hz), 6·83, 6·59, 4·00, 3·92, 3·87. The signals of the synthetic compound[6] are similar. MS: 342 (M^+, 22), 327 (100), 312 (4), 297 (8), 295 (6), 284 (19), 281 (5), 269 (10), 266 (5), 254 (11), 167 (6), 152 (4).

Alkaline degradation of (I) *and* (II): The alkaline degradation of (I) and (II), was performed as previously reported.[7] (I) gave benzoic acid and 2-hydroxy-4,5,6-trimethoxyacetophenone; (II) yielded the same com-

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pound ketone and anisic acid, which were identified by a comparison (m. m.p., TLC, IR and NMR) with authentic samples.

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ABSCISIC ACID IN *HYACINTHUS ORIENTALIS* BULBS

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INTRODUCTION

The plant growth hormone abscisic acid (ABA) has been detected in many different plants.[1–3] Hyacinth bulbs (*Hyacinthus orientalis* L.) require a period of high temperature treatment (20°) for flower bud development, then a period of low temperature treatment, a few degrees above the freezing point, for dormancy release and flower growth.[4,5] Consideration of hormonal control of the dormancy state in a plant[6–8] requires the identification of abscisic acid, and this was undertaken.

RESULTS AND DISCUSSION

The presence of an acidic inhibitor in dry and fleshy scales of hyacinth bulbs was found by PC and growth inhibition of wheat coleoptiles. This showed a potent inhibitory substance at R_f corresponding to those of synthetic ABA. Further purification of the inhibitory fraction by TLC and GLC of the methylated derivative of this inhibitor on two different columns identified it as abscisic acid.

Abscisic acid was identified in dry as well as in fleshy scales of hyacinth bulb.

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