Previous work. Alkaloids of *Antirrhinum majus* L.[2,3]

Present work. Dried, aerial parts extracted with 95% ethanol. Ethanol free extract fractionated by the standard procedure for alkaloidal bases.

Tertiary fraction. Chromatography on alumina columns ($CHCl_3$–EtOH mixtures) followed by preparative TLC purification (alumina 1 mm–$CHCl_3$ and $CHCl_3$–EtOH, 3:1) yielded seven alkaloids. Four were obtained in insufficient quantity for further investigation at this stage.

Base A. White needles, m.p. 78°. Shown by UV, IR and MS to be identical with 4-methyl-2,6-naphthyridine previously isolated from *A. majus*.[2,3]

Base B. Yellow solid, m.p. above 250° (decomp). $C_{15}H_9N_3O$ (by mass spectrometry). UV λ_{max} 207(s), 224, 228, 254(s), 280(s), 352 nm; IR 800, 850, 1040, 1140, 1180, 1230, 1320, 1430, 1460, 1600, 1630, 1690 cm^{-1}; MS *m/e* (rel. intensity) M^+247 (100), 220(6), 192(8), 164(11), 135(9), 122(8), 164(11), 135(9), 122(8), 110(8), 94(14).

Base C. White solid. MW 208 (mass spectrometry). UV λ_{max} 212, 245, 282(s) nm; MS *m/e* (rel. intensity) M^+208(10), 193(11), 176(43), 162(11), 149(10), 121(100), 107(33), 87(32), 69(41), 47(68).

Water-soluble fraction. Single component isolated by reineckate precipitation.[4] By paper chromatography (Whatman No. 1, *n*-butanol saturated dilute HCl, hR_f 22) and comparison of IR spectra shown to be identical with choline chloride.

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IDENTIFICATION OF SCUTELLAREIN 4′-METHYL ETHER IN *LINARIA AERUGINEA*

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Abstract—Scutellarein 4′-methyl ether has been isolated for the first time from plants, from leaves of *L. aeruginea*. It is accompanied by acacetin and occurs in association with glucose and rhamnose.

DURING an earlier chemotaxonomic survey of flavonoids in the genus *Linaria*, a partly characterized methyl ether of scutellarein was found in two of the 12 species studies, in

L. aeruginea and *L. nevadensis*.[1,2] It was shown to be a useful taxonomic marker, since it distinguished *L. aeruginea* from the morphologically similar *L. tristis* (nine populations of both species studied). This pigment has now been isolated in quantity from *L. aeruginea* and identified unambiguously (see Experimental) as the 4′-methyl ether of scutellarein.

This structure, 5,6,7-trihydroxy-4′-methoxyflavone, was earlier proposed for dinatin, a leaf pigment from *Digitalis lanata* (Schrophulariaceae)[3] but more recent work showed that dinatin is the isomeric 6-methyl ether of scutellarein.[4,5] The present isolation of the 4′-methyl ether from *Linaria* thus represents the first report of this compound in nature. The discovery of this scutellarein derivative in *Linaria* is not surprising, since such compounds have been found in several genera of the Scrophulariaceae and the related 6,4′-dimethyl ether (pectolinarigenin) has recently been reported in *L. vulgaris*.[6]

EXPERIMENTAL

The solid flavonoid material obtained by concentrating an alcoholic extract of *L. aeruginea* leaf was hydrolysed in 2 N HCl–dioxan (1:1) for 2 hr and the two aglycones formed were separated by paper chromatography in 50% HOAc and BAW. The aglycone of higher R_f was identified as acacetin (apigenin 4′-methyl ether) by direct comparison with authentic material. The aglycone of lower R_f was obtained as a pale green amorphous powder, which was unstable in solution and also was partly degraded during chromatography in some solvents. R_fs were as follows (scutellarein values in parentheses): Forestal, 0·73 (0·60); 50% HOAc 0·52 (0·40); BAW 0·66 (0·66); and PhOH 0·88 (0·69). On demethylation, it gave scutellarein and it was formulated as a monomethyl ether from the mass spectrum (mol. wt. 300·0632; $C_{16}H_{12}O_6$ requires 300·0634). The absence of 6-methoxylation was indicated by the lack of a M-CH_2 ion in the mass spectrum. That it was the 4′-methyl ether was indicated by the UV spectral properties, which also showed that the 5- and 7-hydroxyls were free: λ_{max}^{MeOH} 287, 335; λ_{max}^{NaOMe} 364 (with decrease in intensity); $\lambda_{max}^{AlCl_3}$ 303, 377; and λ_{max}^{NaOAc} 277, 295(sh), 358 nm. This identification was confirmed by direct spectral and chromatographic comparison with synthetic material obtained by partial demethylation of pectolinarigenin.

Two glycosides separated on chromatography in BAW of the crude solid from the leaf extract. One was provisionally identified as the 7-rhamnosylglucoside of scutellarein 4′-methyl ether on the basis of hydrolytic and other data: colour in UV dark; λ_{max}^{MeOH} 291, 332; λ_{max}^{alk} 293, 350sh; $\lambda_{max}^{AlCl_3}$ 302, 356 nm; R_f 0·30 in BAW, 0·06 in H_2O and 0·31 in 15% HOAc. The second glycoside (R_f 0·43 in BAW, 0·14 in H_2O) was an inseparable mixture of the above compound with acacetin 7-rhamnosylglucoside.

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