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4'-METHYLSCUTELLAREIN AND PECTOLINARIGENIN FROM *CLERODENDRON INERME*

T. N. C. VENDANTHAM*
S. SANKARA SUBRAMANIAN* and J. B. HARBORNE†

*Department of Chemistry, Jawaharlal Institute of Postgraduate, Medical Education and Research, Pondicherry-605006, India;

†Phytochemical Unit, Department of Botany, The University of Reading, RG6 2AS, England

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Flavonoid patterns in the majority of families of the Englerian order Tubiflorae are characterised by the presence of luteolin, apigenin and of the two corresponding 6-hydroxyflavones and their methyl ethers. While 6-hydroxyluteolin and scutellarein (6-hydroxyapigenin) and their derivatives have been found with some frequency in such families as the Plantaginaceae, Globulariaceae, Labiatae and Scrophulariaceae, they have rarely been found in Verbenaceae [1]. However, there are reports of 6-hydroxyluteolin and its 6- and 3'-monomethyl ethers in *Lippia nodiflora* [2, 3] and recently the 6-glucoside of 6-hydroxyluteolin 7,3'-dimethyl ether has been found in leaves of *Citharexylum subserratum* [4]. Also, previous examination of *Clerodendron inerme* leaves yielded the 7-glucuronides of apigenin and scutellarein [5].

In a continuing survey of these families for flavonoids, we now report the presence of two 6-hydroxyflavones which are new to the family, the 4'-methyl ether and 6,4'-dimethyl ether of scutellarein: both substances occur in the free state in the leaves of *Clerodendron inerme*. This is the first time that scutellarein 4'-methyl ether has been found occurring free, but it has been reported in glycosidic form twice previously, in *Linaria aeruginea* (Scrophulariaceae) [6] and in *Stachys annua* (Labiatae) [7]. It appears to be a taxonomic marker for *Clerodendron inerme*, since it does not occur in any other species of the genus so far investigated. It is interesting that the same compound is restricted in its occurrence in *Linaria* to only one of 12 species studied (cf. ref. [8]). The 6,4'-dimethyl ether (pectolinarigenin) first isolated from *Linaria* (Scrophulariaceae) has since been found with some frequence in Tubiflorae families and in the Compositae and its occurrence here in Verbenaceae is expectable.

EXPERIMENTAL

Plant material. Fresh leaves of *Clerodendron inerme* (L.) Gaertn. were collected locally in India and voucher specimens 8/76 deposited at JIPMER herbarium.

Extraction and identification. Fresh leaves were extracted with hot 80% EtOH, and the concentrate fractionated into C_6H_6, Et_2O and EtOAc soluble portions. The light yellow flavone from C_6H_6 extract on crystallisation (EtOAc) yielded pale yellow needles, mp 268–70°. It was purple under UV and UV/NH_3, gave a green colour with Na_2CO_3, and had λ_{max} (nm) 286, 334 (MeOH); 269, 292, 366 (NaOMe); 276, 298, 364 (NaOAc); 303, 380 ($AlCl_3$) and R_f values (PC): 0.06 (15% HOAc); 0.28 (30% HOAc); 0.52 (50% HOAc); 0.72 (BAW); 0.76 (Forestal); 0.88 (PhOH); 0.80 (*t*-BAW) and 0.73 ($CHCl_3$–HOAc–H_2O). Its triacetate melted at 228–29°. On methylation, it gave scutellarein tetramethyl ether, mp 160–62° and on demethylation scutellarein (mmp and co-PC). Its MS showed a 100% peak at *m/e* 300, agreeing with the MW $C_{16}H_{12}O_6$. The absence of a 6-methoxyl was indicated by the lack of M-CH_2 ion; other characteristic peaks were at *m/e* 168 ($C_7H_4O_5$, 25.5%, due to A-ring fragment), 136 (2.9%) and 135 ($C_8H_7O_2^+$, 0.5%, due to B-ring). From these data, the flavone was identified as 4'-methylscutellarein and the identity was confirmed by direct comparison with the compound obtained by partial demethylation scutellarein (mmp and co-PC). Its MS showed a 4'-methylscutellarein from *Linaria aeruginea*. C_6H_6 mother liquor on column chromatography over Si gel yielded pectolinarigenin (mp, PC and co-PC) and some more 4'-methylscutellarein.

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