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C-GLYCOSYLFLAVONES OF *MUCUNA SEMPERVIRENS*

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Key Word Index—*Mucuna sempervirens*, Leguminosae, 8-*C*-α-L-arabinosylluteolin, 6,8-di-*C*-α-L-arabinosylapigenin, isoorientin

Abstract—8-*C*-α-L-Arabinosylluteolin, 6,8-di-*C*-α-L-arabinosylapigenin and isoorientin were isolated from leaves of *Mucuna sempervirens* and identified by UV-, ^{1}H and ^{13}C NMR and FDMS.

INTRODUCTION

The flowers pigments of *Mucuna sempervirens* Hemsl have been characterized as the 3-monoglucosides of delphinidin, petunidin and cyanidin [1]. In the present study, the leaf tissue of this plant was found to contain the *C*-glycosylflavones, 8-*C*-α-L-arabinosylluteolin (**1**), 6,8-di-*C*-α-arabinosylapigenin (**2**) and isoorientin (**3**). 8-*C*-α-L-arabinosylluteolin has not previously been reported. The structural elucidation of these *C*-glycosylflavones is now described

RESULTS AND DISCUSSION

The UV spectra of three compounds (**1–3**) isolated from *Mucuna* leaves showed absorption typical for flavone glycosides, and were non-hydrolysable with hydrochloric acid and non-extractable with diethyl ether, so that they are probably *C*-glycosidic structures. Compounds **1** and **2** have UV absorption spectra consistent with their being luteolin and apigenin derivatives, respectively, in which all the hydroxyl functions are unsubstituted Chemical shifts of sugar carbons for the 8-*C*-arabinoside in the ^{13}C NMR spectra of **1** were 74.6 *d*, 74.6 *d*, 70.8 *t*, 69 0 *d*, and 68 4 *d* [cf 2], and also the FDMS gave a M_r of 418 corresponding to 8-*C*-α-L-arabinosylluteolin, a compound which has not previously been reported. The R_f values of **2** were similar to those reported for 6,8-di-*C*-α-L-arabinosylapigenin [3] and ^{1}H and ^{13}C NMR and FADMS of **2** confirmed this structure.

Compound **3** was readily identified from its ^{1}H and ^{13}C NMR spectra and chromatographic behaviour as 6-*C*-β-D-glucosylluteolin (isoorientin) by direct comparison with an authentic sample. FDMS studies confirmed the identification and on acid treatment, **3** produced orientin as an isomer due to a Wessely–Moser rearrangement [cf 2].

EXPERIMENTAL

Plant material and extraction. Fresh leaves (1 kg) of *Mucuna sempervirens* Hemsl were collected in June and extracted with Me_2CO (12 l) The extract was evapd *in vacuo* to remove Me_2CO and the aqueous fraction obtained successively washed with petrol and Et_2O The Et_2O extract contained no flavonoid

Separation and identification The aqueous fraction was concd to small vol giving **3** in a semicrystalline state, which was recryst from 70% EtOH (yield 120 mg) The remainder of the aqueous fraction was applied to a Sephadex LH-20 column, equilibrated with 70% EtOH, and eluted with the same soln to give **1** and **2**, which were purified by TLC cellulose (avicel) in *n*-BuOH–HOAc–H_2O (4 1 5) (BAW) and 15% HOAc Compound **1** separated was crystallized from H_2O and **2**, from EtOH (yields 94 and 177 mg, respectively)

8-*C*-α-L-*Arabinosylluteolin* (**1**) Yellow needles mp 213–214°; UV light black, $+NH_3$ yellow, UV λ_{max}^{MeOH} nm 257, 269, 293sh, 350, $+AlCl_3$ 276, 303sh, 330sh, 422, $+AlCl_3$/HCl 265sh, 277, 298, 360, 388, +NaOAc 274, 325, 396, +NaOAc–H_3BO_3 266, 377, 430sh. PC R_f 0 35 (BAW), 0 15 (15% HOAc), 0 46 (*n*-BuOH–EtOH–H_2O, 4 1 2 2) (BEW), 0 05 (H_2O), 0.02 (3% HOAc) Diazotized *p*-nitroaniline brown. FDMS Found *m/z* 419 Calcd for $C_{20}H_{18}O_{10}$ M, 418, ^{1}H NMR δ (DMSO-d_6) 2 5–5 5 (11H, *m*, aliphatic and OH), 6.265 (1H, *s*, H-6), 6.674 (1H, *s*, H-3), 6.890 (1H, *d*, J = 8.3 Hz, H-5′), 7 35–7.50 (2H, *m*, H-2′ and H-6′), 9 101 (1H, *s*, OH), 9 919 (1H, *s*, OH), 10 5 (1H, *br s*, OH), and 13.270 (1H, *s*, OH-5) ^{13}C NMR δ (DMSO-d_6), 68 367 (*d*, –OCH), 69.013 (*d*, –OCH), 70 774 (*t*, C-5(a)), 74 590 (*d*, 2 × –OCH), 98 455 (C-6), 102 067 (*d*, C-3), 103 767 (*s*, C-10), 104 298 (*s*, C-8), 113 513 (*d*, C-2′), 116 040 (*d*, C-5′), 119.755 (*d*, C-6′), 121 324 (small *d*, C-1′), 145 334 (*s*, C-3′), 149 594 (*s*, C-4′), 156 104 (*s*, C-5), 160 397 (*s*, C-9), 162.539 (*s*, C-7), 164 004 (*s*, C-2) and 181.908 (*s*, C-4). (a) = α-L-arabinose

6,8-di-C-α-L-*Arabinosylapigenin* (**2**) Yellow needles mp 217–218°, UV light black, $+NH_3$ yellow; UV λ_{max}^{MeOH} nm 273, 333, +NaOMe 284, 334, 402, $+AlCl_3$ 280, 306, 352, 385 sh, $+AlCl_3$–HCl 280, 305, 349, 380 sh, +NaOAc 283, 310 sh, 336, 398, +NaOAc–H_3BO_3 285, 320, 350 sh, 411 PC R_f 0 34 (BAW), 0.43 (15% HOAc), 0 50 (BEW), 0 28 (H_2O), 0 18 (3% HOAc) Diazotized *p*-nitroaniline brown FABMS Found· 534. Calcd for $C_{25}H_{26}O_{13}$ M, 534 ^{1}H NMR (DMSO-d_6) 3–5 (10H, *m*, aliphatic plus *n*OH), 6.858 (1H, *s*, H-3), 6 902 (2H, *d*, H-3′ and H-5′), *ca* 9 (2H, *d*, H-2′ and H-6′), 9.196 (1H, *s*, OH), 10.334 (1H, *s*, OH), and 13.792 (1 H, *s*, OH-5) ^{13}C NMR δ (DMSO-d_6), 68 5, 68.9, 70.1, 70 9, 74 0, 74 5 (aliphatic carbons), 102 1 (*d*, C-3), 103 4 (*s*, C-10), 104 6 (*s*, C-8), 108 1 (*s*, C-6), 115 922 (*d*, C-3′ and C-5′), 120 972 (*s*, C-1′), 129 3 (*d*, C-2′ and C-6′), 154 8 (*s*, C-5), 158.5 (*s*,

C-7), 161 036 (s, C-4′ and C-9), 164 032 (s, C-2), and 182 200 (s, C-4)

Isoorientin (**3**) was identified by PC, UV, ^{1}H NMR, ^{13}C NMR and FDMS spectral studies and also by co-TLC, mp and mmp with an authentic sample

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FLAVONOIDS AND A COUMARIN FROM *GUTIERREZIA SPHAEROCEPHALA*

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Key Word Index—*Gutierrezia sphaerocephala*; Compositae; Astereae; flavones; flavonols; flavanones; 5,3′,4′,5′-tetrahydroxy-6,7-dimethoxyflavone, 5,7,4′-trihydroxy 6,3′-dimethoxyflavanone

Abstract—The ethyl acetate extract of the aerial parts of *Gutierrezia sphaerocephala* afforded, in addition to one coumarin, 10 known and two new flavonoids The structures were elucidated by spectroscopic methods. The new flavonoids are 5,3′,4′,5′-tetrahydroxy-6,7-dimethoxyflavone and 5,7,4′-trihydroxy-6,3′-dimethoxyflavanone

As a part of our chemosystematic survey of the '*Gutierrezia–Xanthocephalum* complex' [1–9], we have investigated the *Gutierrezia sphaerocephala* Gray Chromatographic separation of the ethyl acetate and dichloromethane extracts of a concentrated aqueous methanol extract of aerial parts of *G sphaerocephala* afforded one coumarin, 7,8-dihydroxy-6-methoxycoumarin (**13**) [10] and 12 flavonoids. The 10 known flavonoids are 5,7-dihydroxy-6,4′-dimethoxyflavone (**1**) [11], 5,7,3′,4′-tetrahydroxy-6-methoxyflavone (**2**) [11], 5,7,4′-trihydroxy-6,3′-dimethoxyflavone (**3**) [11], 5,7-dihydroxy-6,3′,4′-trimethoxyflavone (**4**) [11], 5,7,4′-trihydroxy-6,3′,5′-trimethoxyflavone (**5**) [12], 3,5,7,3′,4′-pentahydroxyflavone (**6**) [11], 3,5,7,3′,4′-pentahydroxy-6-methoxyflavone (**7**) [11], 3,5,7,4′-tetrahydroxy-6,3′-dimethoxyflavone (**8**) [11], 3,5,7,3′,4′-pentahydroxyflavone 3-galactoside (**9**) and 5,7,3′,4′-tetrahydroxy-6-methoxyflavanone (**10**) [13] The new flavonoids are 5,3′,4′,5′-tetrahydroxy-6,7-dimethoxyflavone (**11**) and 5,7,4′-trihydroxy-6,3′-dimethoxyflavanone (**12**).

The ^{1}H NMR spectrum (90 MHz) of the TMSi ether derivative of **11** (Table 1) exhibited two one-proton singlets at δ6 27 and 6 51 characteristic of H-3 and H-8, respectively, and a two-proton singlet at δ6.96 typical of protons at 2′ and 6′ in a symmetrically substituted B-ring. Since the remaining signals in the ^{1}H NMR spectrum were in accord with two methoxyl groups, **11** has a 5,6,7,3′,4′,5′-oxygenation pattern The MS of **11** exhibited a molecular ion peak at *m/z* 346 (100%) in accord with an aglycone containing four hydroxyl and two methoxyl groups Compound **11** appeared as purple spot on paper under UV light and changed to yellow with ammonia, suggesting the presence of free 5 and 4′-hydroxyl groups Compound **11** also gave an orange colour with NA, which, together with the symmetrical substituted B-ring already established, indicated a B-ring with 3′,4′,5′-trihydroxyl groups. With the establishment of 5,3′,4′,5′-tetrahydroxyl groups and to accommodate the 5,6,7,3′,4′,5′-oxygenation pattern, the two methoxyl groups must be at the 6 and 7 positions These conclusions are supported by the UV spectra (Table 2) Thus, **11** is 5,3′,4′,5′-tetrahydroxy-6,7-dimethoxyflavone

The ^{1}H NMR signals at δ2 65 (1H, *d*) 2 77 (1H, *d*) and 5 20 (1H, *dd*) characteristic for H-3 *cis*, H-3 *trans* and H-2 and a molecular ion at *m/z* 332 (99%) in the MS spectrum indicated that **12** is a flavanone with three hydroxyl and two methoxyl groups The ^{1}H NMR spectrum of the

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