glycoside of *Geraea canescens* was purified by PC and obtained as a crystalline solid, R_f 60 (BAW), 64 (PhOH) and 44 (15% HOAc), λ_{max} 263, 272, 366; +NaOEt, 420; +NaOAc, 283; + H_3BO_3, 386; and + $AlCl_3$ 366, 414 nm. On acid or β-glucosidase hydrolysis, it gave galactose (with some glucose) and gossypetin 8-methyl ether (see Table 1). The aglycone was further confirmed by MS: M 332 ($C_{16}H_{12}O_8$ requires 332) (48%), M-15 (100%), M-29 (3%), M-43 (13%) and B ring fragment at 137 (12%).

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RARE METHYLATED FLAVONOLS FROM *ANGELONIA GRANDIFLORA*

A. G. RAMACHANDRAN NAIR*, P. RAMESH*, S. SANKARA SUBRAMANIAN* and B. S. JOSHI†

*Department of Chemistry, Jawaharlal Institute of Postgraduate Medical Education and Research, Pondicherry-605 006, India; †Ciba-Geigy Research Centre, Bombay-400 063, India

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Key Word Index—*Angelonia grandiflora*; Scrophulariaceae; methylated flavonols; 3,4′-,3,7- and 7,4′-dimethylquercetin; 3,4′- and 7,4′-dimethylkaempferol.

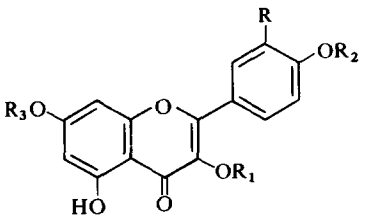
We previously identified scutellarein 7,4′-dimethyl ether and 5-hydroxy-6,7,4′-trimethoxyflavone (salvigenin) from leaf tissue of *Angelonia grandiflora* [1]. In continuation of our investigation, we now report the isolation and identification of five rare methylated flavonols: 3,4′-, 3,7- and 7,4′-dimethylquercetin and 3,4′ and 7,4′-dimethylkaempferol. All five compounds are known from other sources: quercetin 3,4′-dimethyl ether from *Baccharis sarothroides* [2], 3,7-dimethylquercetin from *Aeonium manriquiorum* [3] and *Larrea cuneifolia* [4], 7,4′-dimethylquercetin from *Phytolacca dioica* [5], 3,4′-dimethylkaempferol from propolis [6] and *Betula ermanii* [7] and 7,4′-dimethylkaempferol from *Cheilanthes farinosa* [8]. Their present isolation together with our previous finding [1] of 7,4′-dimethylscutellarein and salvigenin reveals an unusual co-occurrence of rare methylated flavonols and flavones in *A. grandiflora*.

EXPERIMENTAL

Plant material. A voucher specimen of *Angelonia grandiflora* C. Mor. has been deposited at JIPMER.

Flavonoid identification. A hot C_6H_6 extract of dried leaf material was subjected to column chromatography over silicic acid using petrol (60–80°), petrol–C_6H_6, C_6H_6–$CHCl_3$ and $CHCl_3$–MeOH as eluents. Petrol and petrol–C_6H_6 yielded carotenoids and triterpenes; other fractions gave flavone and flavonol derivatives including the five rare methylated flavonols, A–E.

Flavonol A (**1**). Major ($CHCl_3$–C_6H_6, 3.1), mp 238–39°, UV—purple UV/NH_3—dull yellow; λ_{max} (nm) . 220 *sh*, 253, 268 *sh*, 353 (MeOH); 273, 321, 367 (NaOAc); 210 *sh*, 235 *sh*, 265, 301, 363, 395 *sh* ($AlCl_3$); 210 *sh*, 237 *sh*, 264, 301, 360, 396 *sh* ($AlCl_3$/HCl) and 235 *sh* 273, 325 *sh*, 410 (NaOMe); PMR signals (CD_3SOCD_3, δ values, ppm) at 12.60 (broad *s*, 1H, disappeared on D_2O exchange, 5-O<u>H</u>) 7.73 (*d*, 2 Hz, 1H, 2′-<u>H</u>) 7.67 (*dd*, 2 Hz and 9 Hz, 1H, 6′-H) 7.05 (*d*, 9 Hz, 1H, 5′-<u>H</u>) 6.52 (unresolved *d*, 1H, 8-H) 6.28 (unresolved *d*, 1H, 6-H) 3.96 (*s*, 3H, 3-OC<u>H</u>$_3$) and 3.88 (*s*, 3H, 4′-OMe). Its MS exhibited the following ions: (*m/e*) 330 (M^+, 100%), 329 (M^+-H, 40), 315 (M^+-Me, 50), 299 (M^+-OMe, 18), 297 (315-H_2O, 18), 287 (M^+-MeCO, 90), 272 (287-Me, 18), 244 (M^+-2MeCO, 35), 153 (RDA fragment A_1 + H, 50)*, 151 (fragment C,24) and 147 (RDA fragment B_1 − OMe, 30). It had R_f (× 100, Whatman No. 1, ascending, 30°) 16 (15% HOAc), 47 (30% HOAc), 67 (50% HOAc), 94 (BAW), 93 (phenol), 84 (Forestal) and 90 (*t*BAW). On methylation, it gave quercetin pentamethyl ether and on demethylation quercetin. It was



1 R = OH, R_3 = H, R_1 = R_2 = Me
2 R = OH, R_2 = H, R_1 = R_3 = Me
3 R = OH, R_1 = H, R_2 = R_3 = Me
4 R = R_3 = H, R_1 = R_2 = Me
5 R = R_1 = H, R_2 = R_3 = Me

*For explanations of A_1, B_1, etc, see [9].

identified as 3,4′-dimethylquercetin and the identity confirmed by mmp and co-TLC with an authentic sample from *Baccharis sarothroides* [2].

Flavonol B (**2**). Major ($CHCl_3$–MeOH, 9:1) mp 250–51°, UV—purple; UV/NH_3—yellow; λ_{max} . 253, 268 *sh*, 290 *sh*, 354 (EtOH); 255, 269 *sh*, 325 *sh*, 360 (NaOAc); 256, 355, 405 *sh* ($AlCl_3$) and 270, 329, 411 (NaOEt). Its MS exhibited peaks at 330 (M^+, 100%), 329 (M^+-H, 50), 315 (M^+-Me, 45), 301 (M^+-CHO, 15), 299 (M^+-OMe, 15), 287 (M^+-COMe, 80), 244 (M^+-2COMe, 22), 151 (RDA fragment A_1-Me, 25), 135 (A_1-OMe, 22) and 123 (151-CO, 18). PMR spectrum (90 MHz, $CDCl_3$) of its triacetyl derivative (mp 197–98°, λ_{max} :242, 323 (EtOH) had signals at 7.75 (*d*, 2 Hz, 1H, 2′-H) 7.68 (*dd*, 2 Hz and 9 Hz, 1H, 6′-H) 7.32 (*d*, 2 Hz, 1H, 8-H) 7.17 (*d*, 9 Hz, 1H, 5′-H) 6.84 (*d*, 2 Hz, 1H, 6-H) 3.96 (*s*, 3H, 7-OCH_3) 3.88 (*s*, 3H, 3-OCH_3) 2.48 (*s*, 3H, 5-$OCOCH_3$) and 2.36 (*s*, 6H, 3′ and 4′-$OCOCH_3$). The MS of the acetate showed the parent ion at *m/e* 456 with fragment ions at 414 (M^+-CH_2CO), 372 (M^+-$2CH_2CO$, 100%), 357 (372-Me), 330 (M^+-$3CH_2CO$), 329 (357-CO), 315 (330-Me) and 287 (315-CO) confirming the dimethoxytriacetatoxyflavone structure. On PC, this flavonol had the same R_f as A, but could be differentiated by TLC. It was identified as 3,7-dimethylquercetin.

Flavonol C (**3**). ($CHCl_3$–C_6H_6, 3:2), mp 198–200°, UV and UV/NH_3—yellow. λ_{max} . 254, 289, 363 (MeOH); 254 *sh*, 289, 368, 410 *sh* (NaOAc); 223, 265 *sh*, 311, 375 *sh*, 420 ($AlCl_3$) and 247, 289, 359, 447 (NaOMe). MS peaks at 330 (M^+, 100%) 329, 316 (M^+-14,70). R_f : 4, 20, 51, 91, 91, 79 and 86 in the above solvents. Demethylation gave quercetin and the compound was identified as 7,4′-dimethylquercetin by direct comparison with the compound synthesised [9] from penta-acetylquercetin and 2 equivalents of Me_2SO_4 and dry K_2CO_3 in Me_2CO for 10 hr.

Flavonol D (**4**). ($CHCl_3$–C_6H_6, 1:3), mp 188–90°, UV—purple; UV/NH_3—yellow; λ_{max} . 267, 295, 342 (MeOH); 274, 300, 358 (NaOAc); 232, 271 *sh*, 303, 348 ($AlCl_3$) and 248 *sh*, 262, 298, 370 (NaOMe). MS had a peak at 314 (M^+, 100%). R_f . 17, 50, 72, 94, 96, 92 and 95 in the above solvents. Its acetate had the M^+ at 398 and on demethylation gave kaempferol. It was identified as 3,4′-dimethylkaempferol.

Flavonol E (**5**). ($CHCl_3$–C_6H_6, 1:3), mp 180–81°, UV and UV/NH_3—yellow; λ_{max} . 225 *sh*, 270, 365 (MeOH); 256, 268, 383 (NaOAc); 268, 350, 420 ($AlCl_3$) and 266, 410 (NaOMe). MS peak at 314 (M^+, 100%), 300 (M^+-14,24). Its acetate had M^+ at 398 and a prominent ion at 384 besides other expected ions; it gave kaempferol on demethylation and had R_f 7, 18, 51, 85, 91, 79 and 87 in the above solvents; It was identified as 7,4′-dimethylkaempferol.

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