Flavone *C*-Glycosides from *Viola yedoensis* MAKINO

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A new flavone *C*-glycoside, apigenin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-L-arabinopyranoside, has been isolated from *Viola yedoensis* together with the known compounds, apigenin 6,8-di-*C*-α-L-arabinopyranoside, apigenin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-glucopyranoside (isoschaftoside), apigenin 6-*C*-β-D-glucopyranosyl-8-*C*-α-L-arabinopyranoside (schaftoside), apigenin 6-*C*-β-D-glucopyranosyl-8-*C*-β-L-arabinopyranoside (neoschaftoside), apigenin 6,8-di-*C*-β-D-glucopyranoside (vicenin-2), apigenin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-xylopyranoside, apigenin 6-*C*-β-D-xylopyranosyl-8-*C*-α-L-arabinopyranoside, luteolin 6-*C*-β-D-glucopyranoside (isoorientin) and luteolin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-glucopyranoside (isocarlinoside). The structures were determined by spectroscopic methods and new or revised ^{1}H- and ^{13}C-NMR spectral assignments are proposed for some compounds.

Key words *Viola yedoensis*; Violaceae; flavone *C*-glycoside; apigenin; luteolin; NMR

Viola yedoensis MAKINO (Violaceae) is a small perennial herb with violet flowers distributed in China, Japan and Korea.[1,2] The dried whole plant (including the roots) is known as 'Herba Violae' and is an important constituent of the Chinese traditional medicine 'Zi Hua Di Ding,' a drug for which many local uses have been documented.[3,4] The phytochemistry of this medicinal herb has not been investigated in detail, although some common phenolic acids, a fatty acid, a flavonol *O*-glycoside and the acylamide, tetracosanoyl-*p*-hydroxyphenethylamine (violayedoenamide) have been reported.[5] In addition, a sulphonated carbohydrate polymer of 10—15 kDa showing *in vitro* inhibition of HIV-1 has been partially characterised from extracts of the herb.[6] The present paper describes the occurrence of flavone *C*-glycosides in *V. yedoensis*, including a new compound, apigenin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-L-arabinopyranoside (**1**), and nine known apigenin (5,7,4′-trihydroxyflavone) and luteolin (5,7,3′,4′-tetrahydroxyflavone) *C*-glycosides (**2**—**10**).

A methanolic fraction obtained from sequential solvent extraction of the dried whole plant of *V. yedoensis* was purified by column chromatography and semi-preparative HPLC to give **1**—**10** as yellow solids. The UV spectra of **1**—**8** (λ_{max} 271—273, 334—338 nm) were characteristic of *C*-glycosides of apigenin.[7] Comparison of the ^{1}H-NMR spectra of **1**—**8** recorded in DMSO-d_6 indicated that the compounds were apigenin 6,8-di-*C*-glycosides as each spectrum comprised a downfield-shifted singlet assigned to the exchangeable 5-OH proton, two coupled 2H doublets assigned to H-2′,6′ and H-3′,5′ of the B-ring, a 1H singlet assigned to H-3, and two anomeric proton resonances. No additional aromatic resonances were present as expected. The ^{13}C-NMR assignments obtained by heteronuclear single quantum coherence spectroscopy (HSQC) for the anomeric carbons of **1**—**8** were in the range δ 70—75 and confirmed that the glycosides were *C*-linked.[8] Some of the resonances in the ^{1}H-NMR spectra of **1**—**8** were exchange-broadened at 37 °C, a feature commonly observed for flavone *C*-glycosides.[9,10] According to a recent report,[11] the origin of this phenomenon can be ascribed to the existence of two rotamers about the C-6 to C-1″ (the anomeric carbon of the 6-*C*-linked sugar) bond in flavone 6-*C*-glycosides having additional substituents in the A-ring (at C-7 or C-8). For this reason, NMR data for compounds **4**, **7**, and **8** were acquired at the higher temperature of 60 °C to improve spectral resolution. Complete assignments for the ^{1}H and ^{13}C resonances of the sugar residues were obtained using a combination of double-quantum filtered correlation spectroscopy (DQF-COSY), HSQC and heteronuclear multiple bond correlation spectroscopy (HMBC) data. The site of attachment between each sugar and the aglycone was determined from long-range correlations observed in HMBC experiments. On this basis the structures of **2**—**8** were confirmed to be those of the known compounds, apigenin 6,8-di-*C*-α-L-arabinopyranoside (**2**), apigenin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-glucopyranoside (isoschaftoside) (**3**), apigenin 6-*C*-β-D-glucopyranosyl-8-*C*-α-L-arabinopyranoside (schaftoside) (**4**), apigenin 6-*C*-β-D-glucopyranosyl-8-*C*-β-L-arabinopyranoside (neoschaftoside) (**5**), apigenin 6,8-di-*C*-β-D-glucopyranoside (vicenin-2) (**6**), apigenin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-xylopyranoside (**7**) and apigenin 6-*C*-β-D-xylopyranosyl-8-*C*-α-L-arabinopyranoside (**8**). The absolute configurations of D for β-Glc and β-Xyl, and L for α-Ara and β-Ara were assumed as those naturally occuring in flavone *C*-glycosides.

The anomeric protons in the ^{1}H-NMR spectrum of **1** were observed at δ 5.40 (br s) and 4.47 (d, J=9.4 Hz). HSQC data gave the corresponding ^{13}C-NMR spectral assignments at δ 70.4 and 74.1, respectively. Long-range correlations in the HMBC spectrum from δ 5.40 to ^{13}C resonances at δ 104.5 (C-8) and 154.4 (C-9) and from δ 4.47 to ^{13}C resonances at δ 110.0 (C-6) and 159.3 (C-5) indicated that these sugars were attached at C-8 and C-6, respectively (Fig. 1). The assignments of C-5 and C-6 were also confirmed by long-range correlations from δ 13.56 (s, 5-OH) to these carbons (Fig. 1). Analysis of the DQF-COSY and HSQC spectra of **1** indicated that both sugars were pentoses. This was supported by the additional $^3J(^1\mathrm{H},^{13}\mathrm{C})$ long-range correlations observed between δ 5.40 and the ^{13}C resonance at δ 67.1 (5‴-CH$_2$) and between δ 4.47 and the ^{13}C resonance at δ 69.6 (5″-CH$_2$). The 6-*C* pentose of **1** was confirmed to be α-L-arabinopyranose on the basis of the characteristic chemical shift value

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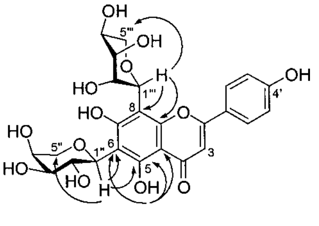

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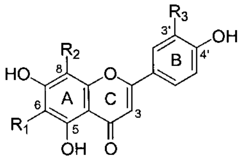

	R_1	R_2	R_3
2	α-Ara	α-Ara	H
3	α-Ara	β-Glc	H
4	β-Glc	α-Ara	H
5	β-Glc	β-Ara	H
6	β-Glc	β-Glc	H
7	α-Ara	β-Xyl	H
8	β-Xyl	α-Ara	H
9	β-Glc	H	OH
10	α-Ara	β-Glc	OH

Fig. 1. Flavone *C*-Glycosides of *Viola yedoensis*.

Key HMBC correlations are indicated for compound **1**.

Table 1. ^{1}H- and ^{13}C-NMR Resonance Assignments for Compound **1** in DMSO-d_6 at 37 °C

		δ^1H	δ^{13}C
Apigenin	2		161.5
	3	6.60 s	101.9
	4		180.8
	5		159.3
	6		110.0
	7[a)]		—
	8		104.5
	9		154.4
	10		100.0
	1′		121.8
	2′,6′	7.93 d (8.8)	127.9
	3′,5′	6.89 d (8.8)	115.7
	4′		160.5
	5-OH	13.56 s	
6-*C*-α-Ara	1″	4.47 d (9.4)	74.1
	2″	4.33 m	68.2
	3″	3.32 m	75.1
	4″	3.68 m	69.2
	5″	3.68 m	69.6
		3.43 m	
8-*C*-β-Ara	1‴	5.40 br s	70.4
	2‴	3.68 m	72.9
	3‴	3.83 m	70.3
	4‴	4.01 m	63.5
	5‴	3.62 (2H) m	67.1

[a)] Not detected in either 1D ^{13}C or HMBC experiments. The ^{13}C resonances of other A-ring carbons (notably C-6, C-8 and C-10) show significant broadening.

and $^3J_{\text{H-1,H-2}}$ coupling constant of the anomeric proton[10)] and the similarity of the sugar ^{13}C-NMR spectral assignments with those of the 6-*C*-α-L-arabinopyranosyl units of **2**, **3** and **7**. The 8-*C* pentose of **1** was confirmed to be β-L-arabinopyranose on the basis of the characteristic chemical shift value of the anomeric proton (an anomeric proton resonance appearing as a broad singlet at approximately 5.50 ppm in ^{1}H-NMR spectra recorded in DMSO-d_6 is characteristic of an 8-*C*-β-L-arabinopyranosylflavone)[10)] and the similarity of the sugar ^{1}H- and ^{13}C-NMR spectral assignments to those of the 8-*C*-β-L-arabinopyranosyl unit of **5** (neoschaftoside). The set of ^{13}C-NMR chemical shift values obtained for the 8-*C*-β-Ara moiety of **5** was found to be identical to that published previously for neoschaftoside.[12)] However, the tentative assignments of C-2‴, C-3‴ and C-4‴ of this sugar proposed in the original report were based solely on chemical shift comparisons with model compounds and no ^{1}H-NMR spectral assignments were made for H-2‴ to 5‴-CH_2. The original ^{13}C-NMR spectral assignments were found to require revision following our more extensive analysis using two-dimensional NMR data (DQF-COSY, HSQC and HMBC). The ^{1}H-NMR spectral assignments of the 8-*C*-β-Ara moiety of **5** were determined from the DQF-COSY spectrum, in which the resonances of these sugar protons were sufficiently well-dispersed for the complete spin–spin coupling pattern to be traced sequentially from H-1‴ to 5‴-CH_2. The corresponding ^{13}C resonance assignments were obtained from the HSQC spectrum and are listed in the Experimental section together with the new ^{1}H-NMR spectral assignments. These data confirmed that the most upfield-shifted ^{13}C resonance of the 8-*C*-β-Ara moiety of neoschaftoside is that of C-4‴ and not C-2‴, as previously proposed.[12)] The structure of **1** was therefore confirmed to be apigenin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-L-arabinopyranoside, a new flavone di-*C*-glycoside. The molecular formula of $C_{25}H_{26}O_{13}$ determined for **1** by high-resolution MS was consistent with this conclusion. An unusual feature of compound **1** is the inclusion of both α- and β-anomers of arabinopyranose as *C*-linked sugars. The positional isomer of **1**, apigenin 6-*C*-β-L-arabinopyranoside-8-*C*-α-L-arabinopyranoside, was reported recently as a constituent of the aerial parts of *Schnabelia tetradonta* (Y. Z. Sun) C. Y. Wu & C. Chen (Lamiaceae).[13)]

Compounds **9** and **10** had UV and ^{1}H-NMR spectra typical of those of *C*-glycosides of luteolin (5,7,3′,4′-tetrahydroxyflavone).[7)] Their structures were confirmed to be those of the known compounds, luteolin 6-*C*-β-D-glucopyranoside (isoorientin) and luteolin 6-*C*-α-L-arabinopyranosyl-8-*C*-β-D-glucopyranoside (isocarlinoside), respectively, based on the analysis of two-dimensional NMR data (DQF-COSY, HSQC and HMBC). The ^{1}H-NMR spectrum of **10** showed evidence of exchange-broadening at 37 °C and the data were therefore acquired at higher temperature (60 °C).

Flavone *C*-glycosides have not been reported previously in *V. yedoensis*, although they are known from a small number of other species of *Viola*. The aerial parts of *V. arvensis* Murray were found to contain the new apigenin di-*C*-glycoside, violarvensin (apigenin 6-*C*-β-D-glucopyranosyl-8-*C*-β-D-deoxygulopyranoside) together with violanthin (apigenin 6-*C*-β-D-glucopyranosyl-8-*C*-α-L-rhamnopyranoside).[14)] Violanthin, isoorientin, orientin, saponaretin, vicenin-2 and vitexin have also been reported as constituents of *V. tricolor* L.[15,16)] Of the known compounds **2**—**10**, most are relatively common, with the exception of **7**, **8** and **10** which have been found in only a few species of plants.[17)] NMR data for these rarer compounds and for compound **2** have not been published previously, and are included in the Experimental section for reference. NMR spectral assignments for the remaining compounds are listed where previous data[18—20] are incomplete or require revision.

Experimental

UV spectra were recorded online by HPLC coupled to diode-array detection (Waters 996 photodiode array detector). ^{1}H- and ^{13}C-NMR spectra were recorded in DMSO-d_6 on Bruker 400 MHz or Varian 500 MHz instruments. Standard pulse sequences and parameters were used for the experiments. Chemical shift references were obtained from the solvent resonances of DMSO-d_6 at δ_H 2.50 and δ_C 39.5, relative to TMS. High resolution electrospray ionization (ESI)-MS (positive mode) were obtained on a Bruker Apex II instrument with an internal calibrant. Positive ion atmospheric pressure chemical ionization (APCI)-MS were obtained using a quadrupole ion-trap instrument (Finnigan LCQ) as described previously.[21] Analytical and semi-preparative HPLC were carried out using a Waters LC600 pump and a 996 photodiode array detector. A Merck LiChrospher 100RP-18 (250×4.0 mm i.d.; 5 μm particle size) column was used for analytical HPLC with a flow rate of 1 ml/min. An identical LiChrospher column but with 10 mm i.d. was used for semi-preparative HPLC with a flow rate of 4.5 ml/min. The column temperature was maintained at 30 °C in both cases.

Plant Material *Viola yedoensis* Makino was collected in May 2000 from the Botanical Garden of the Institute of Medicinal Plant Development (IMPLAD), Beijing, China. A voucher specimen has been deposited at the Herbarium, Royal Botanic Gardens, Kew (No. TCMK134).

Extraction and Isolation The ground whole plant of *V. yedoensis* (200 g) was extracted sequentially with 10 times (v/w) petroleum ether, EtOAc, MeOH and 50% aqueous MeOH (MeOH–H_2O, 1 : 1) at room temperature. Each extraction was carried out twice. The MeOH fraction (49.5 g) was dissolved in 1 l H_2O, partitioned twice with EtOAc (700 ml, 300 ml) then twice with *n*-BuOH (700 ml, 300 ml). The aqueous fraction was taken to dryness (44.5 g), redissolved in H_2O and adsorbed onto an Amberlite XAD-2 column of 40 cm×12 cm (i.d.). Elution with H_2O followed by 2 l each of 10, 30, 50, 70 and 90% aqueous MeOH afforded 6 fractions (A.1—A.6), of which A.4 and A.5 contained flavone *C*-glycosides (recognised from their distinctive UV spectra recorded online by analytical HPLC coupled to diode-array detection). Fractions A.4 and A.5 were combined to give a new fraction (B), and passed through a Sephadex LH-20 column of 40 cm×2.5 cm (i.d.) with 80% aqueous MeOH as the mobile phase. Of the 3 fractions collected (B.1—B.3), HPLC analysis indicated flavone *C*-glycosides to be concentrated in B.3. These were separated by semi-preparative HPLC using a gradient method (solvent A=MeOH, solvent B=H_2O; A=28%, B=72% at t=0 min; A=30%, B=70% at t=15 min; A=40%, B=60% at t=30 min; A=50%, B=50% at t=35 min; A=100% at t=40 min; A=100% at t=45 min, followed by return to initial conditions) to give 18 fractions (B.3.1—B.3.18). Of these, 10 were selected for final purification by either semi-preparative HPLC or Sephadex LH-20 and processed to give sufficient material for spectroscopic characterisation. Fraction B.3.4 (R_t 10.5 min) gave **6** (0.7 mg), B.3.5 (R_t 14.1 min) **10** (3.0 mg), B.3.7 (R_t 17.9 min) **3** (3.5 mg), B.3.8 (R_t 19.7 min) **4** (6.3 mg), B.3.9 (R_t 21.9 min) **9** (1.5 mg), B.3.11 (R_t 26.2 min) **5** (4.0 mg), B.3.12 (R_t 27.9 min) **8** (0.5 mg), B.3.13 (R_t 29.7 min) **2** (9.3 mg), B.3.14 (R_t 31.6 min) **1** (5.0 mg) and B.3.16 (R_t 36.6 min) **7** (2.6 mg).

Quantitative Determination of Flavone *C*-Glycosides Ground plant material (100 mg) was extracted with 2 ml 80% aqueous MeOH for 12 h at 25 °C then sonicated for 20 min. Analytical HPLC of the filtered extract was carried out using a gradient method (solvent A=MeOH, solvent B=H_2O; A=25%, B=75% at t=0 min; A=50%, B=50% at t=35 min; A=100% at t=36 min; A=100% at t=40 min; A=25%, B=75% at t=41 min) to separate **1**—**10**. The percentage amount of each compound in the whole plant of *V. yedoensis* was evaluated using HPLC chromatograms extracted at 335 nm and standard curves determined with the purified compounds. This gave the flavone *C*-glycoside content as 0.03% (**1**), 0.16% (**2**), 0.07% (**3**), 0.08% (**4**), <0.02% (**5**), <0.02% (**6**), 0.04% (**7**), 0.02% (**8**), <0.02% (**9**) and 0.12% (**10**).

Apigenin 6-*C*-α-L-Arabinopyranosyl-8-*C*-β-L-arabinopyranoside (**1**): UV λ_{max} (MeOH) nm 271, 338; ^{1}H- and ^{13}C-NMR: see Table 1. APCI-MS (positive mode) *m/z*: 535 [M+H]$^+$. HR-ESI-MS *m/z*: 535.1445 [M+H]$^+$ (Calcd for $C_{25}H_{27}O_{13}$, 535.1446).

Apigenin 6,8-Di-*C*-α-L-arabinopyranoside (**2**): UV λ_{max} (MeOH) nm 272, 338. ^{1}H-NMR (DMSO-d_6, 37 °C) δ: 13.76 (1H, br s, OH-5), 8.15 (2H, br s, H-2′,6′), 6.91 (2H, d, J=8.8 Hz, H-3′,5′), 6.78 (1H, s, H-3); 6-*C*-α-Ara: 4.66 (1H, d, J=9.5 Hz, H-1″), 4.00 (1H, br m, H-2″), 3.44 (1H, m, H-3″), 3.79 (1H, m, H-4″), 3.83, 3.60 (2×1H, 2×m, 5″-CH_2); 8-*C*-α-Ara: 4.72 (1H, d, J=9.4 Hz, H-1‴), 4.22 (1H, br m, H-2‴), 3.48 (1H, m, H-3‴), 3.85 (1H, m, H-4‴), 3.90, 3.62 (2×1H, 2×m, 5‴-CH_2); ^{13}C-NMR (DMSO-d_6, 37 °C) δ: 128.8 (C-2′,6′), 115.5 (C-3′,5′), 101.7 (C-3); 6-*C*-α-Ara: 73.8 (C-1″), 68.8 (C-2″), 73.9 (C-3″), 68.3 (C-4″), 69.8 (C-5″); 8-*C*-α-Ara: 74.3 (C-1‴), 68.2 (C-2‴), 74.5 (C-3‴), 68.6 (C-4‴), 70.6 (C-5‴). APCI-MS (positive mode) *m/z*: 535 [M+H]$^+$.

Apigenin 6-*C*-α-L-Arabinopyranosyl-8-*C*-β-D-glucopyranoside (Isoschaftoside) (**3**): UV λ_{max} (MeOH) nm 271, 338; ^{1}H-NMR (DMSO-d_6, 37 °C) δ: 13.64 (1H, br s, OH-5), 7.97 (2H, d, J=8.4 Hz, H-2′,6′), 6.89 (2H, d, J=8.7 Hz, H-3′,5′), 6.66 (1H, br s, H-3); 6-*C*-α-Ara: 4.62 (1H, d, J=9.4 Hz, H-1″), 4.00 (1H, br m, H-2″), 3.42 (1H, m, H-3″), 3.77 (1H, m, H-4″), 3.79, 3.57 (2×1H, 2×m, 5″-CH_2); 8-*C*-β-Glc: 4.81 (1H, d, J=9.9 Hz, H-1‴), 3.89 (1H, m, H-2‴), 3.30 (1H, m, H-3‴), 3.36 (1H, m, H-4‴), 3.27 (1H, m, H-5‴), 3.74, 3.52 (2×1H, 2×m, 6‴-CH_2); ^{13}C-NMR (DMSO-d_6, 37 °C) δ: 128.7 (C-2′,6′), 115.7 (C-3′,5′), 102.0 (C-3); 6-*C*-α-Ara: 74.1 (C-1″), 69.0 (C-2″), 74.0 (C-3″), 68.5 (C-4″), 69.7 (C-5″); 8-*C*-β-Glc: 73.8 (C-1‴), 71.0 (C-2‴), 78.8 (C-3‴), 70.4 (C-4‴), 81.5 (C-5‴), 61.0 (C-6‴). APCI-MS (positive mode) *m/z*: 565 [M+H]$^+$.

Apigenin 6-*C*-β-D-Glucopyranosyl-8-*C*-α-L-arabinopyranoside (Schaftoside) (**4**): UV λ_{max} (MeOH) nm 271, 338; ^{1}H-NMR (DMSO-d_6, 60 °C) δ: 13.75 (1H, br s, OH-5), 8.07 (2H, br d, J=8.2 Hz, H-2′,6′), 6.92 (2H, d, J=8.2 Hz, H-3′,5′), 6.73 (1H, s, H-3); 6-*C*-β-Glc: 4.74 (1H, d, J=9.8 Hz, H-1″), 3.89 (1H, m, H-2″), 3.28 (1H, m, H-3″), 3.28 (1H, m, H-4″), 3.28 (1H, m, H-5″), 3.70, 3.54 (2×1H, 2×m, 6″-CH_2); 8-*C*-α-Ara: 4.80 (1H, d, J=9.5 Hz, H-1‴), 4.09 (1H, br m, H-2‴), 3.53 (1H, m, H-3‴), 3.88 (1H, m, H-4‴), 3.93, 3.69 (2×1H, 2×m, 5‴-CH_2); ^{13}C-NMR (DMSO-d_6, 60 °C) δ: 128.6 (C-2′,6′), 115.6 (C-3′,5′), 101.9 (C-3); 6-*C*-β-Glc: 73.1 (C-1″), 70.7 (C-2″), 78.2 (C-3″), 69.7 (C-4″), 80.8 (C-5″), 60.5 (C-6″); 8-*C*-α-Ara: 74.6 (C-1‴), 68.7 (C-2‴), 74.0 (C-3‴), 68.3 (C-4‴), 70.2 (C-5‴). APCI-MS (positive mode) *m/z*: 565 [M+H]$^+$.

Apigenin 6-*C*-β-D-Glucopyranosyl-8-*C*-β-L-arabinopyranoside (Neoschaftoside) (**5**): UV λ_{max} (MeOH) nm 273, 338; ^{1}H-NMR (DMSO-d_6, 37 °C) δ: 13.58 (1H, br s, OH-5), 7.97 (2H, br d, J=8.8 Hz, H-2′,6′), 6.90 (2H, d, J=8.8 Hz, H-3′,5′), 6.77 (1H, s, H-3); 6-*C*-β-Glc: 4.61 (1H, d, J=9.8 Hz, H-1″), 4.12 (1H, m, H-2″), 3.20 (1H, m, H-3″), 3.11 (1H, m, H-4″), 3.15 (1H, m, H-5″), 3.68, 3.40 (2×1H, 2×m, 6″-CH_2); 8-*C*-β-Ara: 5.51 (1H, br s, H-1‴), 3.78 (1H, m, H-2‴), 3.88 (1H, m, H-3‴), 4.01 (1H, m, H-4‴), 3.74, 3.64 (2×1H, 2×m, 5‴-CH_2); ^{13}C-NMR (DMSO-d_6, 37 °C) δ: 128.0 (C-2′,6′), 115.5 (C-3′,5′), 101.9 (C-3); 6-*C*-β-Glc: 72.8 (C-1″), 69.7 (C-2″), 78.7 (C-3″), 70.5 (C-4″), 81.2 (C-5″), 61.3 (C-6″); 8-*C*-β-Ara: 71.0 (C-1‴), 72.1 (C-2‴), 69.6 (C-3‴), 62.8 (C-4‴), 66.7 (C-5‴). APCI-MS (positive mode) *m/z*: 565 [M+H]$^+$.

Apigenin 6,8-Di-*C*-β-D-glucopyranoside (Vicenin-2) (**6**): UV λ_{max} (MeOH) nm 273, 338; ^{1}H-NMR (DMSO-d_6, 37 °C) δ: 13.68 (1H, br s, OH-5), 7.90 (2H, d, J=8.7 Hz, H-2′,6′), 6.85 (2H, d, J=8.7 Hz, H-3′,5′), 6.41 (1H, br s, H-3); 6-*C*-β-Glc: 4.62 (1H, d, J=9.8 Hz, H-1″), 4.05 (1H, m, H-2″), 3.21 (1H, m, H-3″), 3.21 (1H, m, H-4″), 3.16 (1H, m, H-5″), 3.63, 3.48 (2×1H, 2×m, 6″-CH_2); 8-*C*-β-Glc: 4.82 (1H, br d, J=9.6 Hz, H-1‴), 3.84 (1H, m, H-2‴), 3.28 (1H, m, H-3‴), 3.30 (1H, m, H-4‴), 3.24 (1H, m, H-5‴), 3.73, 3.50 (2×1H, 2×m, 6‴-CH_2); ^{13}C-NMR (DMSO-d_6, 37 °C) δ: 127.9 (C-2′,6′), 115.4 (C-3′,5′), 101.2 (C-3); 6-*C*-β-Glc: 74.2 (C-1″), 70.7 (C-2″), 78.8 (C-3″), 70.3 (C-4″), 80.5 (C-5″), 61.0 (C-6″); 8-*C*-β-Glc: 74.4 (C-1‴), 71.8 (C-2‴), 79.0 (C-3‴), 70.7 (C-4‴), 81.3 (C-5‴), 61.3 (C-6‴). APCI-MS (positive mode) *m/z*: 595 [M+H]$^+$.

Apigenin 6-*C*-α-L-Arabinopyranosyl-8-*C*-β-D-xylopyranoside (**7**): UV λ_{max} (MeOH) nm 273, 338; ^{1}H-NMR (DMSO-d_6, 60 °C) δ: 13.63 (1H, br s, OH-5), 7.89 (2H, d, J=8.8 Hz, H-2′,6′), 6.92 (2H, d, J=8.8 Hz, H-3′,5′), 6.63 (1H, br s, H-3); 6-*C*-α-Ara: 4.65 (1H, d, J=9.3 Hz, H-1″), 4.01 (1H, m, H-2″), 3.44 (1H, m, H-3″), 3.79 (1H, m, H-4″), 3.82, 3.58 (2×1H, 2×m, 5″-CH_2); 8-*C*-β-Xyl: 4.75 (1H, br d, J=9.8 Hz, H-1‴), 3.95 (1H, m, H-2‴), 3.27 (1H, m, H-3‴), 3.57 (1H, m, H-4‴), 3.90, 3.21 (2×1H, 2×m, 5‴-CH_2); ^{13}C-NMR (DMSO-d_6, 60 °C) δ: 128.6 (C-2′,6′), 115.6 (C-3′,5′), 102.0 (C-3); 6-*C*-α-Ara: 73.9 (C-1″), 68.9 (C-2″), 73.8 (C-3″), 68.2 (C-4″), 69.4 (C-5″); 8-*C*-β-Xyl: 74.4 (C-1‴), 70.8 (C-2‴), 78.8 (C-3‴), 69.9 (C-4‴), 70.0 (C-5‴). APCI-MS (positive mode) *m/z*: 535 [M+H]$^+$.

Apigenin 6-*C*-β-D-Xylopyranosyl-8-*C*-α-L-arabinopyranoside (**8**): UV λ_{max} (MeOH) nm 271, 338; ^{1}H-NMR (DMSO-d_6, 60 °C) δ: 13.71 (1H, br s, OH-5), 7.99 (2H, d, J=8.6 Hz, H-2′,6′), 6.90 (2H, d, J=8.6 Hz, H-3′,5′), 6.56 (1H, br s, H-3); 6-*C*-β-Xyl: 4.57 (1H, d, J=9.8 Hz, H-1″), 4.08 (1H, m, H-2″), 3.19 (1H, m, H-3″), 3.42 (1H, m, H-4″), 3.77 (1H, dd, J=10.9, 5.3 Hz, 5″-CH_2A), 3.10 (1H, m, 5″-CH_2B); 8-*C*-α-Ara: 4.77 (1H, d, J=9.6 Hz, H-1‴), 4.05 (1H, m, H-2‴), 3.50 (1H, m, H-3‴), 3.84 (1H, m, H-

4‴), 3.89, 3.65 (2×1H, 2×m, 5‴-CH$_2$); ^{13}C-NMR (DMSO-d_6, 60 °C) δ: 127.8 (C-2′,6′), 115.3 (C-3′,5′), 101.6 (C-3); 6-*C*-β-Xyl: 74.2 (C-1″), 70.1 (C-2″), 78.9 (C-3″), 69.6 (C-4″), 69.7 (C-5″); 8-*C*-α-Ara: 75.0 (C-1‴), 69.4 (C-2‴), 74.2 (C-3‴), 68.3 (C-4‴), 70.0 (C-5‴). APCI-MS (positive mode) *m*/*z*: 535 [M+H]$^+$.

Luteolin 6-*C*-β-D-Glucopyranoside (Isoorientin) (**9**): UV, ^{1}H- and ^{13}C-NMR and MS data in agreement with published data.[7,8,10]

Luteolin 6-*C*-α-L-Arabinopyranosyl-8-*C*-β-D-glucopyranoside (Isocarlinoside) (**10**): UV $\lambda_{\max}$ (MeOH) nm 271, 350; ^{1}H-NMR (DMSO-d_6, 60 °C) δ: 13.67 (1H, br s, OH-5), 7.46 (1H, br d, J=8.2 Hz, H-6′), 7.43 (1H, br s, H-2′), 6.87 (1H, br d, J=8.2 Hz, H-5′), 6.56 (1H, s, H-3); 6-*C*-α-Ara: 4.68 (1H, d, J=9.6 Hz, H-1″), 3.97 (1H, m, H-2″), 3.47 (1H, m, H-3″), 3.82 (1H, m, H-4″), 3.85, 3.62 (2×1H, 2×m, 5″-CH$_2$); 8-*C*-β-Glc: 4.84 (1H, d, J=9.8 Hz, H-1‴), 3.92 (1H, m, H-2‴), 3.35 (1H, m, H-3‴), 3.39 (1H, m, H-4‴), 3.33 (1H, m, H-5‴), 3.78, 3.58 (2×1H, 2×m, 6‴-CH$_2$); ^{13}C-NMR (DMSO-d_6, 60 °C) δ: 118.5 (C-6′), 115.2 (C-5′), 113.1 (C-2′), 101.7 (C-3); 6-*C*-α-Ara: 73.8 (C-1″), 68.8 (C-2″), 73.8 (C-3″), 68.3 (C-4″), 69.8 (C-5″); 8-*C*-β-Glc: 73.5 (C-1‴), 70.8 (C-2‴), 78.5 (C-3‴), 70.4 (C-4‴), 81.4 (C-5‴), 61.2 (C-6‴). APCI-MS (positive mode) *m*/*z*: 581 [M+H]$^+$.

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