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 ¹H- and ¹³C-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 ¹H-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 ¹³C-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 ¹H-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 ¹H and ¹³C 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 occurring in flavone C-glycosides.

The anomeric protons in the ¹H-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 ¹³C-NMR spectral assignments at δ 70.4 and 74.1, respectively. Long-range correlations in the HMBC spectrum from δ 5.40 to ¹³C resonances at δ 104.5 (C-8) and 154.4 (C-9) and from δ 4.47 to ¹³C 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(¹H,¹³C) long-range correlations observed between δ 5.40 and the ¹³C resonance at δ 67.1 (5'''-CH₂) and between δ 4.47 and the ¹³C resonance at δ 69.6 (5''-CH₂). 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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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.

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, vicienin-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 pub-

lished 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). ¹H- and ¹³C-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 μ m 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–H₂O, 1:1) at room temperature. Each extraction was carried out twice. The MeOH fraction (49.5 g) was dissolved in 1 l H₂O, 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 H₂O and adsorbed onto an Amberlite XAD-2 column of 40 cm×12 cm (i.d.). Elution with H₂O 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=H₂O; 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*_f 10.5 min) gave **6** (0.7 mg), B.3.5 (*R*_f 14.1 min) **10** (3.0 mg), B.3.7 (*R*_f 17.9 min) **3** (3.5 mg), B.3.8 (*R*_f 19.7 min) **4** (6.3 mg), B.3.9 (*R*_f 21.9 min) **9** (1.5 mg), B.3.11 (*R*_f 26.2 min) **5** (4.0 mg), B.3.12 (*R*_f 27.9 min) **8** (0.5 mg), B.3.13 (*R*_f 29.7 min) **2** (9.3 mg), B.3.14 (*R*_f 31.6 min) **1** (5.0 mg) and B.3.16 (*R*_f 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=H₂O; 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; ¹H- and ¹³C-NMR: see Table 1. APCI-MS (positive mode) *m/z*: 535 [M+H]⁺. HR-ESI-MS *m/z*: 535.1445 [M+H]⁺ (Calcd for C₂₅H₂₇O₁₃, 535.1446).

Apigenin 6,8-Di-*C*- α -L-arabinopyranoside (**2**): UV λ_{max} (MeOH) nm 272, 338. ¹H-NMR (DMSO-*d*₆, 37 °C) δ : 13.76 (1H, brs, OH-5), 8.15 (2H, brs, 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, brm, H-2"), 3.44 (1H, m, H-3"), 3.79 (1H, m, H-4"), 3.83, 3.60 (2×1H, 2×m, 5"-CH₂); 8-*C*- α -Ara: 4.72 (1H, d, *J*=9.4 Hz, H-1"), 4.22 (1H, brm, H-2"), 3.48 (1H, m, H-3"), 3.85 (1H, m, H-4"), 3.90, 3.62 (2×1H, 2×m, 5"-CH₂); ¹³C-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; ¹H-NMR (DMSO-*d*₆, 37 °C) δ : 13.64 (1H, brs, 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, brs, H-3); 6-*C*- α -Ara: 4.62 (1H, d, *J*=9.4 Hz, H-1"), 4.00 (1H, brm, H-2"), 3.42 (1H, m, H-3"), 3.77 (1H, m, H-4"), 3.79, 3.57 (2×1H, 2×m, 5"-CH₂); 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"-CH₂); ¹³C-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; ¹H-NMR (DMSO-*d*₆, 60 °C) δ : 13.75 (1H, brs, OH-5), 8.07 (2H, brd, *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"-CH₂); 8-*C*- α -Ara: 4.80 (1H, d, *J*=9.5 Hz, H-1"), 4.09 (1H, brm, H-2"), 3.53 (1H, m, H-3"), 3.88 (1H, m, H-4"), 3.93, 3.69 (2×1H, 2×m, 5"-CH₂); ¹³C-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; ¹H-NMR (DMSO-*d*₆, 37 °C) δ : 13.58 (1H, brs, OH-5), 7.97 (2H, brd, *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"-CH₂); 8-*C*- β -Ara: 5.51 (1H, brs, 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"-CH₂); ¹³C-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; ¹H-NMR (DMSO-*d*₆, 37 °C) δ : 13.68 (1H, brs, 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, brs, 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"-CH₂); 8-*C*- β -Glc: 4.82 (1H, brd, *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"-CH₂); ¹³C-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; ¹H-NMR (DMSO-*d*₆, 60 °C) δ : 13.63 (1H, brs, 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, brs, 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"-CH₂); 8-*C*- β -Xyl: 4.75 (1H, brd, *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"-CH₂); ¹³C-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; ¹H-NMR (DMSO-*d*₆, 60 °C) δ : 13.71 (1H, brs, 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, brs, 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"-CH₂A), 3.10 (1H, m, 5"-CH₂B); 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"-CH₂); ¹³C-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, ¹H- and ¹³C-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 λ_{max} (MeOH) nm 271, 350; ¹H-NMR (DMSO-*d*₆, 60 °C) δ: 13.67 (1H, brs, OH-5), 7.46 (1H, brd, *J*=8.2 Hz, H-6'), 7.43 (1H, brs, H-2'), 6.87 (1H, brd, *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"-CH₂); 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""-CH₂); ¹³C-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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