6,8-Di-*C*-glycosyl Flavonoids from *Dendrobium huoshanense*

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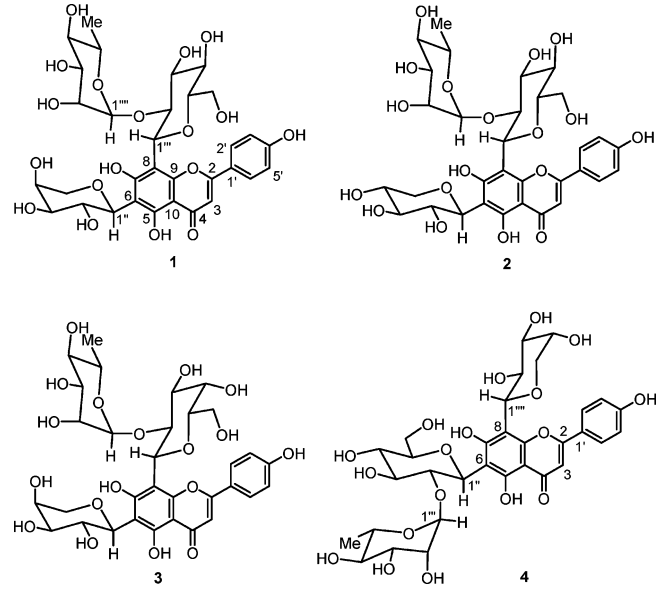
Dendrobium huoshanense is a valued herbal plant used in traditional Chinese medicine. Fractionation of the water-soluble part of *D. huoshanense* by repeated chromatography culminated in the isolation of four new 6,8-di-*C*-glycosyl flavones (**1**−**4**), in addition to seven known compounds, comprising malic acid, dimethyl malate, *N*-phenylacetamide, isopentyl butyrate, salicylic acid, shikimic acid, and isoschaftoside. By detailed spectroscopic analysis, the structures of **1**−**4** were determined to have a core of apigenin bearing pentoside (arabinoside or xyloside) and rhamnosyl-hexoside (glucoside or galactoside) substituents.

Dendrobium huoshanense C.Z. Tang et S.J. Cheng (Orchidaceae) is a valuable herbal plant used in traditional Chinese medicine.[1] Sections of the stems of this species have long been used to nourish the stomach, promote the secretion of body fluids, prevent ophthalmic disorders, relieve inflammation, and enhance immunity.[2] Biological studies have also indicated that *D. huoshanense* has antiaging, anticancer, and antidiabetes effects.[3] The plant has a slow growth rate, and excessive harvesting has left it critically endangered. Among the species in the polymorphic *Dendrobium* genus, most studies have focused on the bioactive small molecules present, which include the bibenzyl,[4] phenanthrene,[5] fluorene,[6] coumarin,[7] sesquiterpene,[8] flavanone,[9] and alkaloid[10] structural types. On the other hand, we have reported previously the structures of active polysaccharides extracted from the aerial parts of *D. huoshanense*.[11] The stem mucilage contains a glucomannan having β-(1→4)-Glc*p* and β-(1→4)-Man*p* linkages with partial acetylated mannosides at the 2- and 3-positions. Our earlier study revealed that the mucilage polysaccharide exhibits specific functions in activating murine splenocytes to produce several cytokines including IFN-γ, IL-10, IL-6, and IL-1α, as well as hematopoietic growth factors GM-CSF and G-CSF.[11] We report herein four di-*C*-glycosyl flavone constituents (**1**−**4**) of *D. huoshanense*.

Several methods were applied to separate the constituents of the water-soluble part of *D. huoshanense*. A typical flowchart is delineated in the Supporting Information. The aerial parts of *D. huoshanense* were extracted first with MeOH, and the concentrated extract was then taken up with water. The water-soluble portion was partitioned with organic solvents in sequence to give the hexane, EtOAc, *n*-BuOH, and water layers. The *n*-BuOH and water extracts were further separated by repeated chromatography on Sephadex LH-20, silica gel, and reversed-phase (RP-18) columns. By this means, seven known compounds, malic acid, dimethyl malate, *N*-phenylacetamide, isopentyl butyrate, salicylic acid, shikimic acid, and isoschaftoside,[12] as well as four new 6,8-di-*C*-glycosyl flavones (**1**−**4**) were isolated.

The structures of **1**−**4** were elucidated by detailed spectroscopic analysis (UV, HRMS, ^{1}H and ^{13}C NMR). Compounds **1**−**4** were found to be structural isomers, giving, respectively, a molecular ion peak $[M + H]^+$ in their HRESIMS corresponding to the protonated molecular ion, $C_{32}H_{39}O_{18}$. Compound **1** existed as two rotamers (**1a** and **1b**) in methanol-d_4 solution, as shown by the ^{1}H and ^{13}C spectroscopic analysis (Tables 1 and 2). The proton and carbon signals were assigned according to the DEPT, COSY, HSQC, and HMBC NMR spectra. The proton signals at δ_H 7.90/8.03 (d, H-2′,6′), 6.92/6.96 (d, H-3′,5′), and 6.60/6.66 (s, H-3) were characteristics of an apigenin aglycone. The carbon signals at δ_C 182.8 (C=O), 159.1 (C-5), 162.1/162.4 (C-7), and 162.2/162.4 (C-4′) were in agreement with the apigenin skeleton bearing a carbonyl and three hydroxy groups. Substitution at C-6 and C-8 was inferred, as no corresponding aromatic protons were observed at these positions. Compound **1** was ascribed as having a core structure of apigenin bearing pentoside, hexoside, and deoxyhexoside substituents. The pentoside at C-6 showing the proton and carbon chemical shifts similar to those of isoschaftoside[12] was assigned as α-arabinopyranoside. Accordingly, the anomeric proton (Ara-1) on the axial position occurred at δ_H 4.87 as a doublet with a large coupling constant (J = 9.9 Hz). The $^3J_{H,C}$ correlation between δ_H 4.87 and δ_C 70.4 (Ara-5) supported a pyranose structure rather than a furanose structure.



The glucoside and rhamnoside also existed in the pyranose structures as shown by the $^3J_{H,C}$ correlations of δ_H 5.09/5.11 (Glc-1) with δ_C 81.7/81.6 (Glc-5) and δ_H 5.31/5.33 (Rha-1) with δ_C 68.1 (Rha-5). The large coupling constant (~10 Hz) of the Glc-1 proton indicated a β-glycoside linkage to the apigenin skeleton. A α-rhamnopyranoside unit was deduced from the small coupling constant (1.5 Hz) of the Rha-1 proton. The observed HMBC correlation of δ_H 5.31 (Rha-1) to δ_C 74.2 (Glc-2) was in agreement with a Rha(β1→2)Glc linkage. It was noted that the Rha-5 and Rha-6 protons appeared at the relatively high fields of δ_H 2.18/

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Table 1. ^{1}H NMR Data of Compounds **1**−**4** (CD_3OD, 600 MHz)

position	**1a/1b**[a]	**2**	**3**	**4**
3	6.60, s/6.66, s	6.56, s	6.69, s	6.60, s
2′, 6′	7.90, d (8.7)/8.03, d (8.8)	7.91, d (8.1)	8.04, d (8.6)	7.91, d (8.6)
3′, 5′	6.92, d (8.7)/6.96, d (8.8)	6.92, d (8.8)	6.98, d (8.6)	6.92, d (8.9)
4′				
1″	4.87, d (9.9)/4.87, d (9.9)	5.02, d (9.2)	4.88, d (8.0)	4.96, d (9.2)
2″	4.00, dd (9.9, 9.2)/4.02, dd (9.9, 9.2)	4.08, t (9.2)	4.07, dd (8.5, 8.0)	4.53, t (9.2)
3″	3.62, dd (9.2, 3.0)/3.64, dd (9.2, 3.1)	3.71, t (9.2)	3.65, dd (8.5, 1.5)	3.60, t (9.2)
4″	3.47, dd (3.0, 2.0)/3.48, dd (3.1, 2.0)	4.03, dt (9.2, 2.5)	3.77, dt (2,0, 1.5)	3.43, t (9.2)
5″	4.04, dd (12.3, 2.0); 3.74, d (12.3)/ 4.06, dd (12.0, 2.0); 3.76, d (12.0)	3.85, dd (12.0, 2.5); 4.08, dd (12.0, 9.2)	3.65, dd (12.3, 2.0); 3.86, dd (12.3, 2.0)	3.37, dt (9.2, 3.0)
6″				3.71, dd (12.2, 3.0); 3.84, d (12.2, 3.0)
1‴	5.09, d (9.9)/5.11, d (10.1)	5.00, d (9.2)	5.07, d (8.6)	5.41, d (1.0)
2‴	4.30, dd (9.9, 8.7)/4.33, dd (10.1, 8.9)	4.55, dd (9.2, 9.0)	4.33, t (8.6)	3.84, dd (2.6, 1.0)
3‴	3.68, t (8.7)/3.70, t (8.9)	3.62, t (9.0)	3.65, t (8.5)	3.35, dd (8.0, 2.6)
4‴	3.64, t (8.7)/3.66, t (8.9)	3.47, t (9.0)	3.36, br s	3.15, t (8.0)
5‴	3.45, ddd (8.7, 5.6, 2.1)/ 3.48, ddd (8.9, 6.0, 2.3)	3.37, ddd (9.0, 6.0, 1.6)	3.45, br d (5.3)	2.15, dd (8.0, 6.0)
6‴	3.78, dd (12.2, 5.6); 3.96, dd (12.2, 2.1)/ 3.80, dd (12.0, 6.0); 3.98, d (12.0, 2.3)	3.73, dd (12.0, 6.0); 3.89, dd (12.0, 1.6)	3.80, dd (12.0, 5.3); 3.97, d (12.0)	0.70, d (6.0)
1⁗	5.31, d (1.5)/5.33, d (1.5)	5.40, s	5.33, s	5.01, d (9.6)
2⁗	3.84, dd (3.0, 1.5)/3.86, dd (2.9, 1.5)	3.85, m	3.86, br s	4.03, t (9.6)
3⁗	3.35, dd (9.6, 3.0)/3.36, dd (9.7, 2.9)	3.37, m	3.34, m	3.70, dd (9.6, 1.7)
4⁗	3.14, t (9.6)/3.16, t (9.7)	3.15, t (9.6)	3.16, t (9.6)	3.70, td (2.0, 1.7)
5⁗	2.18, dd (9.6, 6.0)/2.15, dd (9.7, 6.2)	2.20, br s	2.12, dd (9.6, 5.4)	4.07, dd (12.2, 2.0); 3.88, dd (12.2, 2.0)
6⁗	0.68, d (6.0)/0.65, d (6.2)	0.71, d (5.9)	0.65, d (5.4)	

[a] Compound **1** existed as two rotamers (**1a** and **1b**) in methanol-d_4 solution.

Table 2. ^{13}C NMR Data of Compounds **1**−**4** (CD_3OD, 150 MHz)

position	**1a/1b**[a]	**2**	**3**	**4**
2	165.5/165.4	164.9	167.9	165.0
3	102.0/101.9	101.8	102.2	102.1
4	182.8/182.8	182.8	182.9	182.7
5	159.1/159.1	160.3	161.7	161.7
6	107.6/107.6	110.0	107.4	109.8
7	162.1/162.4	160.3	161.2	160.4
8	105.1/105.1	103.5	104.5	103.3
9	155.8/155.8	154.7	157.2	154.4
10	105.1/105.1	101.8	104.5	104.5
1′	121.6/121.5	121.2	122.0	121.6
2′, 6′	128.8/128.8	128.5	128.9	128.5
3′, 5′	115.8/115.9	116.1	115.6	115.9
4′	162.2/162.4	162.0	162.0	162.0
1″	75.0/75.0	76.1	75.1	72.4
2″	69.2/69.0	70.5	70.5	73.2
3″	74.1/74.1	74.5	74.1	80.7
4″	71.1/71.1	69.1	70.5	70.8
5″	70.4/70.4	70.4	71.0	81.3
6″				61.9
1‴	72.1/72.1	72.2	72.0	100.0
2‴	74.2/74.2	73.3	74.1	71.1
3‴	80.6/80.6	80.7	80.5	70.6
4‴	71.1/71.1	70.7	70.5	72.0
5‴	81.7/81.6	81.2	81.4	68.1
6‴	61.7/61.7	61.8	61.5	16.8
1⁗	100.1/100.1	99.8	100.1	76.0
2⁗	71.0/71.0	71.1	70.5	69.0
3⁗	70.5/70.5	70.5	70.5	74.2
4⁗	72.1/72.1	72.3	72.0	69.3
5⁗	68.1/68.1	68.2	68.1	70.5
6⁗	16.6/16.6	16.6	16.6	

[a] Compound **1** existed as two rotamers (**1a** and **1b**) in methanol-d_4 solution.

2.15 and 0.68/0.65, presumably due to the shielding effects of the apigenin aglycone. In comparison, the anomeric proton of the *O*-glycoside occurred at lower fields of δ_H 5.31/5.33 (Rha-1), whereas the corresponding protons in the *C*-glycosides appeared at the higher fields of δ_H 4.87 (Ara-1) and 5.09/5.11 (Glc-1). The Rha-1, at δ_C 100.1 (an acetal), the Ara-1, at δ_C 75.0 (an ether), and the Glc-1, at δ_C 72.1 (an ether), were deduced by exhibiting correlations to δ_H 5.31/5.33 (Rha-1), 4.87 (Ara-1), and 5.09/5.11 (Glc-1), respectively, in their HSQC spectra. Long-range correlations in the HMBC spectrum from δ_H 4.87 to δ_C 107.6 (C-6) and 159.1 (C-5) and from δ_H 5.09 to δ_C 105.1 (C-8) and 155.8 (C-9) indicated that the C-6 and C-8 positions of the apigenin unit carried arabinoside and glucoside substituents, respectively. Thus, the structure of compound **1** is assigned as 6-*C*-(α-arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-*β*-glucopyranosyl]apigenin. However, further work on acid hydrolysis and comparison of the sugar units with standards by chiral chromatography could not be performed due to lack of sufficient sample.

The disaccharide moiety Rha(α1→2)Glc of compound **2** showed ^{1}H and ^{13}C NMR chemical shifts (Tables 1 and 2) similar to those of compound **1**. The Glc-1 proton at δ_H 5.00 exhibited a large coupling constant of 9.2 Hz, and the HMBC correlations indicated a *β*-glucopyranoside located at the C-8 position of apigenin. The pentose substituent at C-6 of **2** was assigned as *β*-xylopyranoside because it displayed HMBC correlations of the Xyl-1 proton (at δ_H 5.02) with C-6 (at δ_C 110.0) and C-5 (at δ_C 160.3). The Xyl-1 proton showed a large coupling constant of 9.2 Hz and a $^3J_{H,C}$ correlation with the Xyl-5 carbon (at δ_C 70.4), in agreement with a *β*-configuration of the xylopyranoside. The signals at δ_C 74.5 and 69.1 were typical of Xyl-3 and Xyl-4 carbons. The Xyl-1 carbon in **2** occurred at δ_C 76.1, about 1.1 ppm further downfield than the Ara-1 carbon in **1**. Thus, the structure of compound **2** was assigned as 6-*C*-(*β*-xylopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-*β*-glucopyranosyl]apigenin. The absolute configurations of the sugar units were not determined by hydrolysis/chiral chromatography due to insufficient amount of sample.

Compound **3** showed MS and ^{1}H and ^{13}C NMR spectra typical of a 6,8-di-*C*-glycosyl apigenin derivative containing mono- and disaccharide moieties. The structure was similar to **1**, except that **3** exhibited a galactoside moiety in lieu of the glucoside unit of **1** according to ^{1}H and ^{13}C NMR spectroscopic analysis (Tables 1 and 2). The Gal-4 proton occurred at δ_H 3.36 with a small coupling constant (<2 Hz), indicating its equatorial disposition. The Gal-4 carbon (at δ_C 70.5) of **3** was 0.6 ppm upfield when compared with the Glc-4 of **1**. Observation of the HMBC correlation between δ_H 5.33 (Rha-1) and δ_C 74.1 (Gal-2) was in agreement with a Rha(α1→2)Gal linkage. Like compounds **1** and **2**, the Rha-5 and Rha-6 protons in **3** appeared at relatively upfield shifts of δ_H 2.12 and 0.65, respectively. The HMBC correlations of the Ara-1 proton (at δ_H 4.88) with C-6 (at δ_C 107.4) supported the arabinosyl substituent being attached to the C-6 position of the apigenin unit. The α-configuration for the arabinopyranoside portion was inferred from the axially oriented Ara-2 proton, which was displayed at δ_H

4.07 as a doublet of doublets with large coupling constants ($J_{1,2}$ = 8.0 Hz and $J_{2,3}$ = 8.5 Hz). Accordingly, the structure of compound **3** was assigned as 6-*C*-(α-arabinopyranosyl)-8-*C*-[(2-*O*-α-rhamnopyranosyl)-β-galactopyranosyl]apigenin. The absolute configurations of sugar units were not determined by further work due to insufficient amount of sample.

Investigation of compound **4** by 2D NMR (COSY, HSQC, and HMBC) indicated that the monosaccharide moiety is α-arabinopyranoside, and the disaccharide is α-rhamnopyranosyl-β-glucopyranoside. The long-range correlations in the HMBC spectrum of **4** suggested that the arabinosyl substituent is located at C-8, whereas the disaccharide substituent could be positioned at C-6 of the apigenin unit. Similar to compounds **1**−**3**, the Rha-5 and Rha-6 protons in **4** were shielded by the apigenin aglycone to occur at relatively upfield chemical shifts of δ_H 2.15 and 0.70, respectively. Thus, compound **4** was assigned as 6-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]-8-*C*-(α-arabinopyranosyl)apigenin and as a positional isomer of **1**.

The constituents of *C*-glycosyl flavones are rich in Rutaceous,[13] Compositous,[14] and Fabaceous[15] plants. Nearly 60 apigenin *C*-glycosides have been isolated from natural sources.[13,16,17] Most glycosyl apigenins contain monosaccharides of D-Glc, D-Gal, D-Ara, L-Ara, D-Xyl, and L-Rha at the C-6 and C-8 positions. The glycosyl apigenins bearing disaccharide substituents are rarely found. In this study, we have isolated four 6,8-di-*C*-glycosyl apigenins (**1**−**4**) bearing the substituents of a pentoside (arabinoside or xyloside) and a rhamnosyl-hexoside (glucoside or galactoside) from the medicinal plant *D. huoshanense*. A number of *C*-glycosyl flavones have been reported to possess biological activities, such as antioxidative,[18] hepatoprotective,[19] antihypertensive,[20] antimicrobial,[21] cytotoxic, and cytokine-inducing effects.[22]

Experimental Section

General Experimental Procedures. Optical rotations were measured on a JASCO DIP-1000 polarimeter; $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. UV−vis spectra were recorded on a Molecular Devices SpectraMax M5 spectrometer. Circular dichroism (CD) spectra were recorded on a JASCO J815 CD spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AVANCE (600 MHz) spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to δ_H 3.31/δ_C 48.2 for CD_3OD. The splitting patterns are reported as s (singlet), d (doublet), t (triplet), m (multiplet), dd (double of doublets) dt (double of triplets), td (triple of doublets), and br (broad). Coupling constants (J) are given in Hz. Electrospray ionization mass spectra (ESIMS) were recorded on a Bruker Daltonics BioTOF III high-resolution mass spectrometer. Merck silica gel 60 F254 plates (0.25 mm) were used for thin-layer chromatography. Merck silica gel 60 (0.040−0.063 mm), GE Healthcare Sephadex LH-20 (0.03−0.10 mm), and LiChroprep RP-18 (0.040−0.063 mm) were used for column chromatography. RP-HPLC was conducted on C_{18} columns (250 × 4.6 mm for analysis or 200 × 10 mm for semipreparative) using a Waters 2795 separations module and a 2996 photodiode array detector.

Plant Material. The leaves and stems of *Dendrobium huoshanense* were obtained from Yuen-Foong-Yu Biotech Co., Taipei, Taiwan, in March 2006. The plant was identified by Kai-Young Kang, Institute of Botany, Chinese Academy of Sciences. A voucher specimen (acquisition number CCTCC P200503) has been deposited in the China Center for Type Culture Collection, Wuhan University.

Extraction and Isolation. The freeze-dried leaves and stems of *D. huoshanense* (175 g) were extracted with methanol at 4 °C. The concentrated extract (19.35 g) was further partitioned in a sequence into four layers: a hexane layer (3.93 g), an ethyl acetate layer (1.34 g), an *n*-butanol layer (4.51 g), and a water layer (10.92 g). The *n*-butanol layer was chromatographed over a Sephadex LH-20 column (50 × 5 cm) by elution with gradients of MeOH−$CHCl_3$ (9:1 to 1:0) to yield malic acid (40.8 mg), *N*-phenylacetamide (24.6 mg), and salicylic acid (437.2 mg). Another *n*-butanol fraction was separated on a silica gel column (MeOH−$CHCl_3$, 2:8 to 1:0), followed by MPLC and semipreparative HPLC, using an isocratic mixture of MeOH−H_2O as elution system, to give dimethyl malate (36.7 mg), isopentyl butyrate (6.4 mg), shikimic acid (239.7 mg), **1** [0.9 mg; MeOH−H_2O (32:68, 1.2 mL/min), t_R 42.5 min], **3** [1.0 mg; MeOH−H_2O containing 0.1% TFA (25:75, 1.5 mL/min), t_R 66.3 min], and **4** [1.8 mg, MeOH−H_2O (32:68, 1.2 mL/min), t_R 57.2 min]. The water layer (10.92 g) was fractionated on a Sephadex LH-20 column (MeOH−H_2O, 1:9 to 1:0), followed by MPLC and HPLC, using an isocratic mixture of MeOH−H_2O as elution system, to give isoschaftoside (2.4 mg), **1** [1.3 mg; MeOH−H_2O (28:72, 1.5 mL/min), t_R 56.7 min], and **2** [1.4 mg, MeOH−H_2O (30:70, 1.2 mL/min), t_R 56.6 min].

6-*C*-(α-Arabinopyranosyl)-1-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]apigenin (1): amorphous, colorless solid; $[\alpha]^{20}_D$ +12.0 (*c* 0.1, MeOH); UV (MeOH) λ_{max} (log ε) 220 (2.70), 270 (2.38), 331 (2.70) nm; CD (*c* 1.0 × 10^{-4}, MeOH) $\Delta\varepsilon$ +21.99 (302 nm), −5.36 (286 nm), +9.80 (273 nm); ^{1}H and ^{13}C NMR data, see Tables 1 and 2; ESIMS (positive mode) *m*/*z* 711 (29), 437 (7), 381 (30), 289 (22), 288 (62); HRESIMS (positive mode) *m*/*z* 711.2133 [M + H]$^+$ (calcd for $C_{32}H_{39}O_{18}$, 711.2131).

6-*C*-(β-Xylopyranosyl)-1-*C*-[(2-*O*-α-rhamnopyranosyl)-β-glucopyranosyl]apigenin (2): amorphous, colorless solid; $[\alpha]^{20}_D$ +48.0 (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ε) 216 (2.45), 270 (1.76), 332 (3.00) nm; CD (*c* 1.0 × 10^{-4}, MeOH) $\Delta\varepsilon$ +21.99 (320 nm), −21.22 (272 nm); ^{1}H and ^{13}C NMR data, see Tables 1 and 2; ESIMS (positive mode) *m*/*z* 711 (37), 557 (12), 453 (10), 437 (40), 413 (22), 381 (10), 337 (19), 330 (31), 309 (9), 289 (32); HRESIMS (positive mode) *m*/*z* 711.2131 [M + H]$^+$ (calcd for $C_{32}H_{39}O_{18}$, 711.2131).

6-*C*-(α-Arabinopyranosyl)-1-*C*-[(2-*O*-α-rhamnopyranosyl)-β-galactopyranosyl]apigenin (3): amorphous, colorless solid; $[\alpha]^{20}_D$ +12.0 (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ε) 209 (1.60), 270 (0.93), 334 (0.98) nm; CD (*c* 1.0 × 10^{-4}, MeOH) $\Delta\varepsilon$ −0.04 (302 nm), −4.41 (286 nm), +0.82 (270 nm); ^{1}H and ^{13}C NMR data, see Tables 1 and 2; ESIMS (positive mode) *m*/*z* 709 (100), 413 (98), 337 (100), 212 (52), 98 (59); HRESIMS (positive mode) *m*/*z* 711.2121 [M + H]$^+$ (calcd for $C_{32}H_{39}O_{18}$, 711.2131).

6-*C*-[(2-*O*-α-Rhamnopyranosyl)-β-glucopyranosyl]-1-*C*-(α-arabinopyranosyl)apigenin (4): amorphous, colorless solid; $[\alpha]^{20}_D$ +96.0 (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ε) 220 (2.70), 270 (2.10), 334 (2.51) nm; CD (*c* 1.0 × 10^{-4}, MeOH) $\Delta\varepsilon$ +18.11 (317 nm), −32.78 (269 nm), +4.57 (241 nm); ^{1}H and ^{13}C NMR data, see Tables 1 and 2; ESIMS (positive mode) *m*/*z* 711 (52), 659 (6), 437 (35), 413 (25), 381 (100), 337 (30), 289 (70), 288 (48); HRESIMS (positive mode) *m*/*z* 711.2142 [M + H]$^+$ (calcd for $C_{32}H_{39}O_{18}$, 711.2131).

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Supporting Information Available: Flowchart for isolation of constituents, ^{1}H, ^{13}C, and 2D NMR spectra, and HMBC correlations of compounds **1**−**4** are available free of charge via the Internet at http://pubs.acs.org.

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