Flavonoid Glycosides from *Ranunculus chinensis* BGE.

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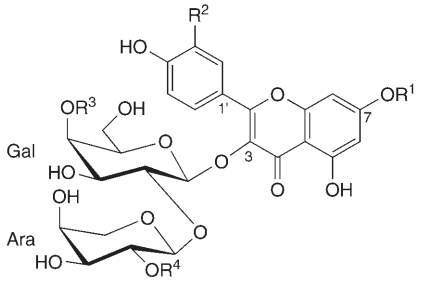
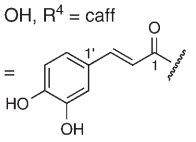
Four new flavonoid glycosides, 3-*O*-[α-L-arabinopyranosyl-(1→2)-β-D-galactopyranosyl]-7-*O*-β-D-glucopyranosylkaempferol (**1**), 3-*O*-(α-L-arabinopyranosyl-(1→2)-{4-*O*-[(*E*)-caffeoyl]-β-D-galactopyranosyl})-7-*O*-β-D-glucopyranosylquercetin (**2**), 3-*O*-{2-*O*-[(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1→2)-β-D-galactopyranosyl}-7-*O*-β-D-glucopyranosylkaemperfol (**3**), and 3-*O*-{2-*O*-[(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1→2)-β-D-galactopyranosyl}kaempferol (**4**), together with two known compounds were isolated from the aerial parts of *Ranunculus chinensis* BGE. The structures of the new glycosides were determined on the basis of spectroscopic analysis, including 1D- and 2D-NMR, and ESI-MS techniques, and chemical methods.

Introduction. – *Ranunculus chinensis* BGE. (Ranunculaceae), a perennial plant distributed widely in East Asia, is a Chinese folk medicine used for the treatment of acute and chronic hepatitis, and peritoneal dropsy [1]. Previous phytochemical studies of the genus *Ranunculus* revealed the presence of flavonoids [2][3], alkaloids [4], triterpene saponins [5], and lactones such as ranunculin and protoanemonin [6]. However, no report of biological or phytochemical investigation on this plant was found apart from a general study regarding its macroscopic and microscopic characteristics [7]. Flavonoids are widely distributed and recognized as taxonomic markers in the genus *Ranunculus*, and some acylated kaempferol and quercetin glycosides were found in some *Ranunculus* species [2][3][8][9]. To determine whether such derivatives are widespread in the genus *Ranunculus*, we conducted a chemical-constituents investigation on the 95% EtOH extract of *Ranunculus chinensis* BGE., resulting in the isolation of six flavonoid glycosides, including four new ones. In this paper, we describe the isolation and structural elucidation of the new glycosides **1**–**4**.



1 R^1 = β-D-Glc, R^2 = R^3 = R^4 = H
2 R^1 = β-D-Glc, R^2 = OH, R^3 = caff, R^4 = H
3 R^1 = β-D-Glc, R^2 = R^3 = H, R^4 = caff
4 R^1 = R^2 = R^3 = H, R^4 = caff
5 R^1 = β-D-Glc, R^2 = OH, R^3 = H, R^4 = caff
6 R^1 = R^3 = H, R^2 = OH, R^4 = caff

caff = (*E*)-caffeoyl =



Results and Discussion. – The dried aerial parts of *R. chinensis* were extracted with 95% EtOH. After concentration under reduced pressure, the extract was suspended in H_2O and partitioned successively with petroleum ether, AcOH, and BuOH. The BuOH-soluble fraction was separated by repeated chromatographic procedures to give new flavonoid glycosides **1**–**4**, along with two known ones: 3-*O*-{2-[(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1 → 2)-β-D-galactopyranosyl}-7-*O*-β-D-glucopyranosylquercetin (**5**) and 3-*O*-{2-[(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1 → 2)-β-D-galactopyranosyl}quercetin (**6**) [10].

Compound **1**, obtained as a yellow amorphous powder, possessed the molecular formula, $C_{32}H_{38}O_{20}$, as deduced from the HR-ESI-MS (*m/z* 765.1862 ($[M+Na]^+$)). The structure of **1** was established to be 3-*O*-[α-L-arabinopyranosyl-(1 → 2)-β-D-galactopyranosyl]-7-*O*-β-D-glucopyranosylkaempferol based on the ESI-MS, and 1D- and 2D-NMR data (*Tables 1* and *2*), as well as acidic hydrolysis and GC analysis.

The acidic hydrolysis of **1** gave D-glucose, D-galactose, and L-arabinose as the sugar moieties, which were in agreement with the ESI-MS fragments at *m/z* 611 ($[M+H-132]^+$), 449 ($[M+H-132-162]^+$), and 287 ($[M+H-132-162-162]^+$). The ^{1}H-NMR spectrum (*Table 1*) displayed signals for three anomeric H-atoms (δ 5.68 (*d*, *J* = 7.6), 5.07 (*d*, *J* = 7.2), and 4.56 (*d*, *J* = 7.2)), and a kaempferol skeleton [11], which was characterized by a pair of *meta*-coupled *doublet*s at δ 6.79 and 6.43 (*d*, *J* = 2.4, each 1 H), and an *AA′BB′* aromatic system signals at δ 8.15 and 6.90 (*d*, *J* = 8.7, each 2 H). These assignments were also consistent with the signals of 15 sp^2 (6 CH and 9 C) and 17 sp^3 (14 CH and 3 CH_2) C-atoms in the ^{13}C-NMR spectrum (*Table 2*) of **1**. The glycosidic linkages C(3)-*O*-β-D-Gal-(2 → 1)-α-L-Ara and C(7)-*O*-β-D-Glc were detected from the HMBC cross-peaks of H–C(1)(Gal)/C(3), H–C(1)(Ara)/C(2)(Gal), and H–C(1)(Glc)/C(7).

Compound **2** had the molecular formula $C_{41}H_{44}O_{24}$ determined by the HR-ESI-MS (*m/z* 943.2085 ($[M+Na]^+$)). The acidic hydrolysis and GC analysis, together with ^{1}H- and ^{13}C-NMR spectra revealed one α-L-arabinopyranosyl, one β-D-galactopyranosyl, and one β-D-glucopyranosyl moiety in the molecule of **2**. The detailed analysis of the 1D- and 2D-NMR data revealed the structure of **2** as 3-*O*-(α-L-arabinopyranosyl-(1 → 2)-{4-*O*-[(*E*)-caffeoyl]-β-D-galactopyranosyl})-7-*O*-β-D-glucopyranosylquercetin.

The ^{1}H-NMR spectrum (*Table 1*) of **2** exhibited H-atom signals for a quercetin, and three monosaccharide and one (*E*)-caffeoyl (caff) moieties. Quercetin was revealed by a pair of *doublet*s at δ 6.43 and 6.76 (*d*, *J* = 1.6, each 1 H), and signals of a 1,2,4-trisubstituted aromatic ring (7.78 (*dd*, *J* = 8.4, 1.8), 7.58 (*d*, *J* = 1.8), and 6.88 (*d*, *J* = 8.6)). A 1,2,4-trisubstituted benzene ring (7.06 (br. *s*), 7.02 (br. *d*, *J* = 8.3), and 6.78 (*d*, *J* = 8.5)) and an (*E*)-double bond (7.49 and 6.31 (*d*, *J* = 15.9, each 1 H)) accounted for the caffeoyl residue. In the ^{13}C-NMR spectrum of **2**, signals attributed to C(3), C(4), and C(5) of the galactosyl residue were shifted −6.0, +7.7, and −4.2 ppm, respectively, compared to those of **1**, suggesting the (*E*)-caffeoyl to be at C(4) of the galactosyl moiety, which was supported by the HMBC correlation between H–C(4)(Gal) and C(1)(caff). Furthermore, the HMBC correlations of H–C(1)(Gal)/C(3), H–C(1)(Ara)/C(2)(Gal), and H–C(1)(Glc)/C(7) confirmed the same positions of attachment of the sugars as in **1**.

Compounds **3** and **4** were also isolated as yellow amorphous powders. Both **3** and **4** had a kaempferol unit as aglycone inferred by comparing their ^{1}H- and ^{13}C-NMR data

Table 1. *^{1}H-NMR Data* (400 Hz) *of* **1**–**4**. δ in ppm, J in Hz.

	1 ((D$_6$)DMSO)	**2** ((D$_6$)DMSO)	**3** (CD$_3$OD)	**4** (CD$_3$OD)
H–C(6)	6.43 (*d*, *J* = 2.4)	6.43 (*d*, *J* = 1.6)	6.44 (*d*, *J* = 2.1)	6.17 (br. *s*)
H–C(8)	6.79 (*d*, *J* = 2.4)	6.76 (*d*, *J* = 1.6)	6.59 (*d*, *J* = 2.1)	6.31 (br. *s*)
H–C(2′)	8.15 (*d*, *J* = 8.7)	7.58 (*d*, *J* = 1.8)	8.03 (*d*, *J* = 8.7)	8.03 (*d*, *J* = 8.5)
H–C(3′)	6.90 (*d*, *J* = 8.7)		6.90 (*d*, *J* = 8.7)	6.90 (*d*, *J* = 8.5)
H–C(5′)	6.90 (*d*, *J* = 8.7)	6.88 (*d*, *J* = 8.6)	6.90 (*d*, *J* = 8.7)	6.90 (*d*, *J* = 8.5)
H–C(6′)	8.15 (*d*, *J* = 8.7)	7.78 (*dd*, *J* = 8.4, 1.8)	8.03 (*d*, *J* = 8.7)	8.03 (*d*, *J* = 8.5)
Gal				
H–C(1)	5.68 (*d*, *J* = 7.6)	5.73 (*d*, *J* = 7.6)	5.73 (*d*, *J* = 7.8)	5.52 (*d*, *J* = 7.7)
H–C(2)	3.70–3.78 (*m*)	3.79–3.88 (*m*)	3.89–3.95 (*m*)	3.96 (*dd*, *J* = 9.4, 8.0)
H–C(3)	3.63 (*dd*, *J* = 9.6, 3.2)	3.49–3.55 (*m*)	3.75 (*dd*, *J* = 7.2, 3.4)	3.68 (*dd*, *J* = 9.6, 3.2)
H–C(4)	3.24–3.34 (*m*)	4.86–4.90 (*m*)	3.82 (*d*, *J* = 3.2)	3.78 (*d*, *J* = 2.5)
H–C(5)	3.25–3.34 (*m*)	3.24–3.32 (*m*)	3.45–3.48 (*m*)	3.42–3.47 (*m*)
CH$_2$(6)	3.36–3.43 (*m*),	3.33–3.42 (*m*),	3.54–3.61 (*m*),	3.56–3.63 (*m*),
	3.24–3.32 (*m*)	3.28–3.32 (*m*)	3.37–3.42 (*m*)	3.36–3.43 (*m*)
Ara				
H–C(1)	4.56 (*d*, *J* = 7.2)	4.72 (*d*, *J* = 7.4)	5.13 (*d*, *J* = 7.2)	5.12 (*d*, *J* = 7.0)
H–C(2)	3.63 (*dd*, *J* = 9.6, 3.2)	3.58–3.66 (*m*)	4.90 (*dd*, *J* = 8.7, 3.2)	4.86–4.93 (*m*)
H–C(3)	3.33–3.41 (*m*)	3.31–3.41 (*m*)	3.60–3.65 (*m*)	3.59–3.64 (*m*)
H–C(4)	3.64–3.71 (*m*)	3.63–3.71 (*m*)	3.62–3.64 (*m*)	3.60–3.67 (*m*)
CH$_2$(5)	3.64–3.75 (*m*),	3.74–3.81 (*m*),	4.03 (*dd*, *J* = 11.4, 3.8),	4.05 (*dd*, *J* = 12.1, 4.0),
	3.01–3.09 (*m*)	3.18–3.24 (*m*)	3.32–3.38 (*m*)	3.32–3.36 (*m*)
Glc				
H–C(1)	5.07 (*d*, *J* = 7.2)	5.08 (*d*, *J* = 7.4)	5.08 (*d*, *J* = 7.2)	
H–C(2)	3.03–3.11 (*m*)	3.22–3.32 (*m*)	3.47–3.52 (*m*)	
H–C(3)	3.09–3.18 (*m*)	3.26–3.31 (*m*)	3.49–3.52 (*m*)	
H–C(4)	3.12–3.21 (*m*)	3.15–3.23 (*m*)	3.42 (*t*, *J* = 9.0)	
H–C(5)	3.41–3.48 (*m*)	3.40–3.49 (*m*)	3.52–3.57 (*m*)	
CH$_2$(6)	3.65–3.72 (*m*),	3.63–3.75 (*m*),	3.90–3.94 (*m*),	
	3.43–3.51 (*m*)	3.41–3.52 (*m*)	3.71 (*dd*, *J* = 12.0, 6.0)	
(*E*)-Caffeoyl				
H–C(2′)		7.06 (br. *s*)	6.79 (*d*, *J* = 1.8)	6.89 (br. *s*)
H–C(5′)		6.78 (*d*, *J* = 8.5)	6.60 (*d*, *J* = 8.1)	6.67 (*d*, *J* = 7.5)
H–C(6′)		7.02 (br. *d*, *J* = 8.3)	6.68 (*dd*, *J* = 8.2, 1.8)	6.78 (br. *d*, *J* = 7.2)
H–C(3)		7.49 (*d*, *J* = 15.9)	7.44 (*d*, *J* = 15.9)	7.51 (*d*, *J* = 15.8)
H–C(2)		6.31 (*d*, *J* = 15.9)	6.18 (*d*, *J* = 15.9)	6.25 (*d*, *J* = 15.8)

with those of **1**. The glycone moieties were shown to be 3-*O*-{2-[(*E*)-caffeoyl)]-α-L-arabinopyranosyl-(1 → 2)-β-D-galactopyranosyl} and 7-*O*-β-D-glucopyranosyl in **3**, and 3-*O*-{2-*O*-[(*E*)-caffeoyl)]-α-L-arabinopyranosyl-(1 → 2)-β-D-galactopyranosyl} in **4**, the same as in **5** and **6**, respectively, based on the ^{1}H- and ^{13}C-NMR data. The above conclusions were further supported by the ESI-MS molecular ion peaks at 927 ([*M* + Na]$^+$) and 903 ([*M* − H]$^-$) for **3**, and 765 ([*M* + Na]$^+$) and 741 ([*M* − H]$^-$) for **4**, as well as acidic hydrolysis experiments. Therefore, their structures were elucidated to be 3-*O*-{2-*O*-[(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1 → 2)-β-D-galactopyranosyl}-7-*O*-β-D-glucopyranosylkaempferol (**3**) and 3-*O*-{2-*O*-[(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1 → 2)-β-D-galactopyranosyl}kaempferol (**4**).

Table 2. *^{13}C-NMR Data* (100 MHz) *of* **1**–**4**[a])

	1	**2**	**3**	**4**
C(2)	156.0	156.0	158.6	158.6
C(3)	133.3	133.4	135.4	135.2
C(4)	177.7	177.6	180.0	180.0
C(5)	160.6	160.5	162.9	163.3
C(6)	99.3	99.3	101.1	100.4
C(7)	162.8	162.8	164.7	165.9
C(8)	94.5	94.4	95.9	94.9
C(9)	155.9	155.9	158.1	158.2
C(10)	105.6	105.6	107.9	106.1
C(1′)	120.9	125.8	127.9	128.0
C(2′)	131.2	116.1	132.7	132.6
C(3′)	115.2	144.9	116.5	116.6
C(4′)	160.0	148.7	161.8	161.7
C(5′)	115.2	115.3	116.5	116.6
C(6′)	131.2	122.4	132.7	132.6
Gal				
C(1)	98.3	98.3	99.6	101.9
C(2)	79.7	79.4	79.4	79.2
C(3)	73.5	67.5	74.1	74.9
C(4)	69.5	77.2	70.7	70.9
C(5)	76.1	71.9	77.3	77.2
C(6)	60.1	60.0	62.3	62.3
Ara				
C(1)	104.7	104.3	101.2	100.0
C(2)	73.1	73.6	75.1	75.1
C(3)	76.0	76.0	75.9	75.8
C(4)	67.8	67.9	71.3	71.3
C(5)	65.8	65.7	66.8	66.6
Glc				
C(1)	99.9	99.9	101.9	
C(2)	73.9	73.1	75.1	
C(3)	76.3	76.3	78.1	
C(4)	69.6	69.6	71.6	
C(5)	77.2	77.2	78.6	
C(6)	60.7	60.6	62.7	
(*E*)-Caffeoyl				
C(1′)		121.4	123.0	123.1
C(2′)		114.8	115.3	115.5
C(3′)		144.9	146.8	146.9
C(4′)		148.2	149.5	149.7
C(5′)		115.9	116.6	116.6
C(6′)		121.2	122.7	123.0
C(3)		145.5	147.1	147.3
C(2)		114.8	115.6	115.6
C(1)		166.2	168.8	168.9

[a]) **1** and **2** dissolved in (D_6)DMSO, **3** and **4** in CD_3OD.

Experimental Part

General. Column chromatography (CC): silica gel (200–300 or 400 mesh; *Qingdao Haiyang, Co.*, China), *ODS-A* gel (*Greenherbs Science & Technology Development Co., Ltd.*, Beijing, China), *D-1400* macroporous resin (*Yangzhou Pharmaceutical Factory*, China), and *Sephadex LH-20* (*Pharmacia Biotech AB*, S-Uppsala). Optical rotation: *Perkin-Elmer 341* polarimeter. UV Spectra: *Varian CARY 300 Bio* spectrometer; λ_{max} in nm (log ε). IR Spectra: *Nicolet Magna-750-FTIR* spectrometer, KBr pellets; in cm^{-1}. NMR Spectra: *Bruker DRX-400* (400 (^{1}H) or 100 MHz (^{13}C)) instrument; in CD_3OD or (D_6)DMSO; δ in ppm rel. to Me_4Si, *J* in Hz. ESI- and HR-ESI-MS: *LCQ Deca* and *Q-Tof Ultima* mass spectrometers, resp. GC Analyses: *Perkin-Elmer Sigma-115* gas chromatograph.

Plant Material. The aerial parts of *Ranunculus chinensis* BGE. were collected from Dali of Yunnan Province, P. R. China, in March 2005, and was authenticated by Dr. *J. Huang* of Shanghai Institute of Materia Medica, Chinese Academy of Sciences. A voucher specimen (No. 20050303) was deposited at the Herbarium of Shanghai Institute of Materia Medica.

Extraction and Isolation. The aerial parts of *Ranunculus chinensis* BGE. (13 kg) were extracted with 50 l of 95% EtOH for three times. After evaporation of the solvent, the extract was suspended in 4 l of H_2O and then partitioned successively with 4 l of petroleum ether, 4 l of AcOEt, and 4 l of BuOH. The BuOH-soluble part (250 g) was subjected to CC (macroporous resin (i.d. 10 × 80 cm); EtOH/H_2O 0:100, 10:90, 30:70, 50:50, 70:30, 95:5 (*v*/*v*)): *Fr. A–F. Fr. C* (30% EtOH, 30 g) was separated by CC (SiO_2, $CHCl_3$/MeOH 100:0 → 0:100): *Fr. C.1–C.10*. *Fr. C.7* afforded **4** (12 mg) and **6** (55 mg) after two CC (1. *Sephadex*; MeOH/H_2O 70:30; 2. *ODS*; MeOH/H_2O 30:70 for **6**, 40:60 for **4**). *Fr. C.9* (8.2 g) was separated by CC (SiO_2; $CHCl_3$/MeOH 5:2) into *Fr. C.9.1–C.9.6*. *Fr. C.9.3* gave **3** (105 mg) by two CC (1. *Sephadex*; MeOH/H_2O 80:20; 2. *ODS*; MeOH/H_2O 15:85). Compounds **1** (43 mg), **2** (21 mg), and **5** (57 mg) were obtained from *Fr. C.9.5* after two CC (1. *Sephadex*; MeOH/H_2O 70:30; 2. *ODS*; MeOH/H_2O 10:90 for **1**, 15:85 for **5**, and 25:75 for **2**).

3-O-*[α*-L-*Arabinopyranosyl-(1 → 2)-β*-D-*galactopyranosyl]-7*-O-*β*-D-*glucopyranosylkaempferol* (= *3-[2*-O-*(α*-L-*Arabinopyranosyl)-β*-D-*galactopyranosyloxy]-7-(β*-D-*glucopyranosyloxy)-5-hydroxy-2-(4-hydroxyphenyl)-4*H-*1-benzopyran-4-one*; **1**). Yellow amorphous powder. $[\alpha]_D^{22} = -39.5$ ($c = 0.425$, H_2O). UV (H_2O): 265 (4.10), 345 (3.96). IR: 3386, 2923, 1654, 1602, 1492. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS (pos.; neg.): 765 ($[M+Na]^+$), 743 ($[M+H]^+$), 611 ($[M+H-132]^+$), 449 ($[M+H-132-162]^+$), 287 ($[M+H-132-162-162]^+$); 741 ($[M-H]^-$). HR-ESI-MS: 765.1862 ($[M+Na]^+$, $C_{32}H_{38}NaO_{20}^+$; calc. 765.1854).

3-O-(α-L-*Arabinopyranosyl-(1 → 2)-{4*-O-*[(*E*)-caffeoyl]-β*-D-*galactopyranosyl})-7-O-β*-D-*glucopyranosylquercetin* (= *3-{2*-O-*(α*-L-*Arabinopyranosyl)-4*-O-*[(*E*)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]-β*-D-*galactopyranosyloxy}-2-(3,4-dihydroxyphenyl)-7-(β*-D-*glucopyranosyloxy)-5-hydroxy-4*H-*1-benzopyran-4-one*; **2**). Yellow amorphous powder. $[\alpha]_D^{22} = -108.3$ ($c = 0.430$, H_2O). UV (H_2O): 252 (4.40), 331 (4.37). IR: 3405, 2940, 1693, 1654, 1600, 1492. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS (pos.; neg.): 943 ($[M+Na]^+$), 921 ($[M+H]^+$), 759 ($[M+H-162]^+$), 627 ($[M+H-162-132]^+$), 465 ($[M+H-162-132-162]^+$); 919 ($[M-H]^-$). HR-ESI-MS: 943.2085 ($[M+Na]^+$, $C_{41}H_{44}NaO_{24}^+$; calc. 943.2120).

3-O-*{2*-O-*[(*E*)-Caffeoyl]-α*-L-*arabinopyranosyl-(1 → 2)-β*-D-*galactopyranosyl}-7*-O-*β*-D-*glucopyranosylkaempferol* (= *3-(2*-O-*{2*-O-*[(*E*)-3-(3,4-Dihydroxyphenyl)prop-2-enoyl]-α*-L-*arabinopyranosyloxy}-β*-D-*galactopyranosyloxy)-7-(β*-D-*glucopyranosyloxy)-5-hydroxy-2-(4-hydroxyphenyl)-4*H-*1-benzopyran-4-one*; **3**). Yellow amorphous powder. $[\alpha]_D^{22} = -87.6$ ($c = 0.555$, MeOH). UV (MeOH): 268 (4.38), 331 (4.45). IR: 3400, 2925, 1697, 1654, 1600, 1492. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS (pos.; neg.): 927 ($[M+Na]^+$), 743 ($[M+H-162]^+$), 611 ($[M+H-162-132]^+$), 449 ($[M+H-162-132-162]^+$); 903 ($[M-H]^-$). HR-ESI-MS: 927.2198 ($[M+Na]^+$, $C_{41}H_{44}NaO_{23}^+$; calc. 927.2171).

3-O-*{2*-O-*[(*E*)-Caffeoyl)-α*-L-*arabinopyranosyl-(1 → 2)-β*-D-*galactopyranosyl}kaempferol* (= *3-(2*-O-*{2*-O-*[(*E*)-3-(3,4-Dihydroxyphenyl)prop-2-enoyl]-α*-L-*arabinofuranosyl}-β*-D-*galactopyranosyloxy)-5,7-dihydroxy-2-(4-hydroxyphenyl)-4*H-*1-benzopyran-4-one*; **4**). Yellow amorphous powder. $[\alpha]_D^{22} = -69.2$ ($c = 0.390$, MeOH). UV (MeOH): 267 (4.68), 333 (4.76). IR: 3415, 2927, 1697, 1652, 1606, 1510. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. ESI-MS (pos.; neg.): 765 ($[M+Na]^+$); 741 ($[M-H]^-$). HR-ESI-MS: 765.1600 ($[M+Na]^+$, $C_{35}H_{34}NaO_{18}^+$; calc. 765.1643).

Acid Hydrolysis of **1**–**4**. Acid hydrolysis of **1**–**4** and sugar identification was conducted according to our standard procedure [12]. In brief, each glycoside (*ca.* 2.0 mg) in 2N HCl/dioxane 1:1 (*v*/*v*; 2 ml) was refluxed for 2 h. On cooling, the mixture was neutralized with $NaHCO_3$. After extraction with AcOEt, the aq. layer was concentrated by blowing with N_2. The residue was purified by CC (*Sephadex LH-20*; MeOH/H_2O 1:1) to give the sugar mixture. The purified sugars and standard D-galactose, D-glucose, and L-arabinose (*Sigma*, USA) were treated with L-cysteine methyl ester hydrochloride (2 mg) in pyridine (1 ml) at 60° for 1 h. Then, the soln. was treated *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (0.02 ml) at 60° for 1 h. The supernatant was applied to GLC analysis (*Supelco*; 230°, N_2). D-Glucose (t_R 24.1 min) was detected from **1**–**3**, and D-galactose (t_R 13.8 min) and L-arabinose (t_R 12.1 min) were detected from **1**–**4** by comparing their retention times with those of authentic samples.

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