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Note

Two new acylated flavonoid glycosides from *Morina nepalensis* var. *alba* Hand.-Mazz.

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From the whole plant of *Morina nepalensis* var. *alba* Hand.-Mazz., two new acylated flavonoid glycosides (1 and 2), together with four known flavonoid glycosides (3–6), were isolated. Their structures were determined to be quercetin 3-*O*-[2‴-*O*-(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1→6)-β-D-galactopyranoside (monepalin A, 1), quercetin 3-*O*-[2‴-*O*-(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranoside (monepalin B, 2), quercetin 3-*O*-α-L-arabinopyranosyl-(1→6)-β-D-galactopyranoside (rumarin, 3), quercetin 3-*O*-β-D-galactopyranoside (4), quercetin 3-*O*-β-D-glucopyranoside (5) and apigenin 4′-*O*-β-D-glucopyranoside (6). Their structures were determined on the basis of chemical and spectroscopic evidence. Complete assignments of the ^{1}H and ^{13}C NMR spectra of all compounds were achieved from the 2D NMR spectra, including H–H COSY, HMQC, HMBC and 2D HMQC-TOCSY spectra. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; 2D NMR; *Morina nepalensis* var. *alba* Hand.-Mazz.; whole plant; monepalin A; monepalin B; flavonoid glycosides; Chinese medicinal herbs

INTRODUCTION

Morina nepalensis var. *alba* Hand.-Mazz., belonging to the family Dipsacaceae and the genus Morina, is not only a traditional Chinese medicinal herb but also a well known Tibetan medicinal herb and has been used for the treatment of many diseases since ancient times.[1,2] We have previously reported two new triterpenoid saponins and four caffeoylquinic acids from the water-soluble part of the whole plant.[3,4] Further studies led to the isolation of two new acylated flavonoid glycosides (**1** and **2**), together with four known flavonoid glycosides (**3–6**) (Fig. 1). We report here the structure elucidation of the new compounds **1** and **2** by chemical and spectroscopic methods and complete NMR assignments of all six compounds on the basis of 2D NMR techniques including H–H COSY, HMQC, HMBC and 2D HMQC-TOCSY spectroscopy.

RESULTS AND DISCUSSION

The ethanol extracts of the whole plants of *M. nepalensis* var. *alba* Hand.-Mazz. were partitioned between water and chloroform, then between water and *n*-butanol. The *n*-butanol fraction was subjected to silica gel, Sephadex LH-20, MCI gel CHP20 and reversed-phase (RP-8) column chromatography, which resulted in the isolation of compounds **1–6**.

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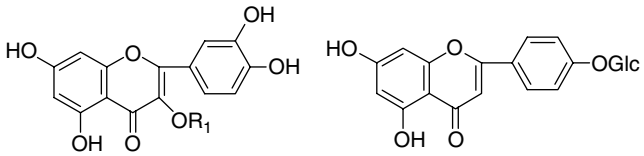
Compounds **3–6** were obtained as yellow powders and their structures were determined as quercetin 3-*O*-α-L-arabinopyranosyl-(1→6)-β-D-galactopyranoside (rumarin, **3**),[5–7] quercetin 3-*O*-β-D-galactopyranoside (hyperin, **4**),[7,8] quercetin 3-*O*-β-D-glucopyranoside (isoquercitrin, **5**)[7,9,10] and apigenin 4′-*O*-β-D-glucopyranoside (**6**),[7,10,11] by comparing their ^{13}C NMR and mass spectrometric (MS) data with those in the literature. The ^{13}C NMR assignments were further confirmed by 2D NMR spectra (Table 1). Unambiguous assignments of the ^{1}H NMR spectra were obtained by H–H COSY, HMQC and HMBC spectroscopy (Table 2). To the authors' knowledge, in this work the unambiguous and complete ^{1}H and ^{13}C NMR chemical shifts in DMSO of these four compounds were assigned by 2D NMR spectra for the first time.

Compound **1** was isolated as a yellow powder, m.p. 197–199 °C. The molecular formula of **1** was established as $C_{35}H_{34}O_{19}$ by a combination of negative high-resolution fast atom bombardment (HR-FAB) MS, showing a quasi-molecular ion at m/z 757.1639, $[M-1]^-$ (calc. for $C_{35}H_{33}O_{19}$, 757.1616), and ^{13}C (DEPT) NMR spectroscopy. In the IR spectrum, signals of a conjugated ester carbonyl at 1696 cm^{-1}, in addition to those of a hydroxyl group at 3434 cm^{-1}, a double bond group at 1654 cm^{-1} and a phenyl group at 1605 and 1510 cm^{-1}, appeared. The ^{1}H and ^{13}C NMR spectra showed the presence of a quercetin moiety, two sugar residues and a caffeic acid moiety (Tables 1 and 2).[12–15] Two signals at δ 6.22 (brs) and 6.42 (brs) were due to H-6 and H-8, respectively; signals at δ 7.60 (brs), 6.83 (d,

MRC

J = 8.0 Hz) and 7.73 (d, J = 8.0 Hz) were characteristic of a 3,4-disubstituted B ring. Signals at δ 7.06 (brs), 6.82 (d, J = 7.6 Hz) and 6.97 (d, J = 7.6 Hz) were due to the 1,3,4-trisubstituted phenyl of the caffeic acid moiety; furthermore, signals at δ 7.42 (d, J = 15.8 Hz) and 6.04 (d, J = 15.8 Hz) were assigned to the *trans* double bond of caffeic acid.



1. R_1=Gal(6-1)Ara(2)Caff
2. R_1=Glc(6-1)Ara(2)Caff
3. R_1=Gal(6-1)Ara
4. R_1=Gal
5. R_1=Glc

6

Figure 1. Structures of compounds **1**–**6**.

The ^{1}H NMR spectrum also showed two anomeric protons at δ 4.22 (d, J = 7.2 Hz) and 5.53 (d, J = 7.2 Hz). In the HMQC-TOCSY spectrum (t_m = 100 ms), only four carbon signals at δ 100.07, 72.03, 70.52 and 67.90 were correlated with the anomeric proton H-1‴ (δ 4.22, d, J = 7.2 Hz); furthermore, another carbon signal at δ 65.50 was also assigned to this sugar in the 2D NMR spectra. The above evidence showed that this sugar was an α-L-arabinopyranosyl residue.[16–21] In the same way, only four carbon signals at δ 101.70, 76.00, 72.89 and 70.89 were correlated with the anomeric proton H-1″ (δ 5.53, d, J = 7.2 Hz) in the HMQC-TOCSY spectrum (t_m = 100 ms), in addition to another two carbon signals at δ 68.64 and 66.22 due to this sugar, which were diagnostic of a β-D-galactopyranosyl residue.[16–21] The presence of arabinose and galactose was further confirmed by GC–MS.

Table 1. ^{13}C NMR data for flavonoid glycosides **1**–**6** (125 MHz; DMSO-d_6)

C[a]	1	2	3	4	5	6
2	156.28	156.06	156.27	156.57[b]	156.31	163.03
3	133.39	133.01	133.24	133.77	133.43	103.17
4	177.49	177.27	177.24	177.74	177.54	182.08
5	161.28	161.21	161.09	161.45	161.34	157.02
6	98.93	98.47	98.68	98.97	98.87	99.63
7	164.42	164.48	164.47	164.37	164.45	164.37
8	93.57	93.92	93.47	93.82	93.70	94.96
9	156.36	156.50	156.55	156.57[b]	156.47	161.19
10	103.91	103.38	103.68	104.20	104.04	105.44
1′	120.99	120.65	120.92	121.39	121.28	121.12
2′	115.36	115.25	115.10	115.49	115.36	128.70
3′	144.98	146.03	144.75	145.03	144.94	116.11
4′	148.32	149.49	148.46	148.70	148.61	161.11
5′	115.89[b]	116.09[b]	115.80	116.33	116.33	116.11
6′	121.97	121.33	121.84	122.18	121.72	128.70
G-1″	101.70	100.89	101.73	102.16	101.02	100.02
G-2″	70.89	73.73	70.93	71.50	74.02	73.21
G-3″	72.89	78.62	72.90	73.44	77.63	77.25
G-4″	68.64	70.03	68.16	68.22	70.03	69.69
G-5″	76.00	76.29	74.24	76.04	76.61	76.51
G-6″	66.22	66.31	66.39	60.44	61.07	60.73
A-1‴	100.07	100.23	102.54			
A-2‴	72.03	72.23	72.39			
A-3‴	70.52	70.45	70.29			
A-4‴	67.90	67.89	67.29			
A-5‴	65.50	65.47	64.88			
C-1⁗	125.65	125.47				
C-2⁗	115.30	115.62				
C-3⁗	145.07	145.25				
C-4⁗	148.60	148.89				
C-5⁗	115.89[b]	116.09[b]				
C-6⁗	120.84	120.84				
C-7⁗	145.58	145.44				
C-8⁗	114.11	113.85				
C-9⁗	165.87	165.90				

[a] G = glucose or galactose, A = arabinose, C = caffeoyl.
[b] Signals in the same column.

Table 2. ^{1}H NMR data for flavonoid glycosides **1–6** (500 MHz; DMSO-d_6; J in Hz)

H[a]	1	2	3	4	5	6
3						6.81
6	6.22 (brs)	6.16 (brs)	6.16 (d, 2.0)	6.19 (brs)	6.19 (brs)	6.43 (brs)
8	6.42 (brs)	6.42 (brs)	6.38 (d, 2.0)	6.41 (brs)	6.39 (brs)	6.81 (brs)
2′	7.60 (brs)	7.64 (d, 2.0)	7.55 (d, 2.0)	7.57 (d, 2.0)	7.57	7.92 (d, 7.7)
3′						6.92 (d, 7.5)
5′	6.83 (d, 8.0)	6.83 (d, 8.5)	6.81 (d, 8.3)	6.83 (d, 8.5)	6.83 (d, 8.0)	6.92 (d, 7.5)
6′	7.73 (d, 8.0)	7.55 (dd, 2.0, 8.5)	7.62 (dd, 2.0, 8.3)	7.64 (d, 8.5)	7.56	7.92 (d, 7.7)
G-1″	5.53 (d, 7.2)	5.33 (d, 7.8)	5.25 (d, 7.8)	5.37 (d, 7.5)	5.44 (d, 5.8)	5.06 (d, 7.1)
G-2″	3.60	3.28 (t, 8.1)	3.55	3.59 (t, 8.2)	3.22	3.29
G-3″	3.31 (dd, 2.3, 8.7)	3.07 (t, 9.0)	3.02	3.40 (dd, 2.7, 8.6)	3.07	3.33
G-4″	3.57	2.93 (t, 9.2)	3.64	3.67	3.08	3.20
G-5″	3.41 (t, 5.0)	3.12	3.53	3.36	3.21	3.46
G-6″a	3.58	3.65	3.65	3.48 (dd, 5.5, 10.5)	3.56	3.73 (brd, 10.3)
G-6″b	3.46	3.41	3.40	3.32	3.32	3.50
A-1‴	4.22 (d, 7.2)	4.13 (d, 7.7)	3.94 (d, 6.9)			
A-2‴	4.71 (t, 8.3)	4.59 (dd, 7.7, 9.5)	3.36			
A-3‴	2.98 (dd, 2.9, 9.0)	2.77 (dd, 3.3, 9.5)	3.13			
A-4‴	3.47	3.38	3.43			
A-5‴a	3.57	3.45	3.51			
A-5‴b	2.86 (brd, 12.2)	2.62 (brd, 12.1)	3.01			
C-2⁗	7.06 (brs)	7.04 (d, 1.5)				
C-5⁗	6.82 (d, 7.6)	6.80 (d, 8.0)				
C-6⁗	6.97 (d, 7.6)	6.86 (dd, 1.5, 8.0)				
C-7⁗	7.42 (d, 15.8)	7.38 (d, 15.8)				
C-8⁗	6.04 (d, 15.8)	5.92 (d, 15.8)				

[a] G = glucose or galactose, A = arabinose, C = caffeoyl.

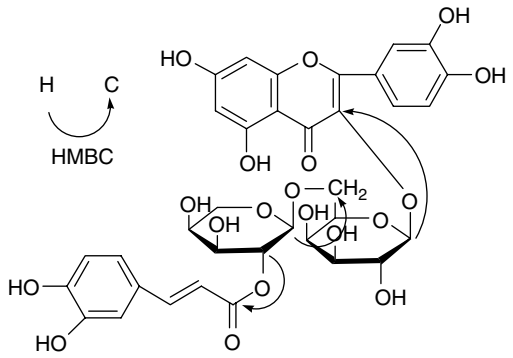


Figure 2. Key long-range information between ^{1}H and ^{13}C from HMBC spectrum of **1**.

Compared with compound **3**, C-6″ of galactose in **1** shows a downfield shift to 66.20 ppm, suggesting that the α-L-arabinopyranosyl residue is connected to C-6″ of the β-D-galactopyranosyl residue. Attachment of the caffeic acid moiety through an ester linkage at C-2″ of arabinose was suggested by the downfield of H-2‴ at δ 4.71. These linkages were further confirmed by the HMBC spectrum, showing long-range correlations between the following proton and carbon signals (Fig. 2, Table 3): Gal H-1″ (δ 5.53, d, J = 7.2 Hz) and C-3 (δ 133.39) of the quercetin moiety, Ara H-1‴ (δ 4.22, d, J = 7.2 Hz) and Gal C-6″ (δ 66.22), Ara H-2‴ (δ 4.71, t, J = 8.3 Hz) and C-9⁗ (δ 165.87) of the caffeic acid moiety. Therefore, the structure of **1** was determined as quercetin 3-*O*-[2‴-*O*-(*E*)-caffeoyl]-α-L-arapyranosyl-(1→6)-β-D-galactopyranoside and named monepalin A.

Compound **2** was also a yellow powder and its HR-FABMS, FABMS, IR and NMR spectra were closely similar to those of **1**. HR-FABMS also established the same molecular formula, $C_{35}H_{34}O_{19}$. The ^{1}H and ^{13}C NMR spectra of **2** suggested that it was also a flavonoid glycoside composed of a quercetin moiety, two sugar residues and a caffeic acid moiety. Comparison of the ^{13}C NMR data of **2** with those of **1** showed that 2 differs only in the inner sugar residue linked at C-3 of the quercetin moiety. In the HMQC-TOCSY spectrum, six carbon signals at δ 100.89, 78.62, 76.29, 73.73, 70.03 and 66.31 correlated with the anomeric proton signal of this sugar H-1″ (δ 5.33, d, J = 7.8 Hz), which was characteristic of a β-D-glucopyranosyl residue.[16–21] The coupling constant ^3J(H-1, H − 2) = 7.8 Hz (>5 Hz) also confirmed the β-configuration. The linkages between the moieties were also confirmed by the HMBC spectrum, showing long-range correlations between the following ^{1}H and ^{13}C signals (Fig. 3): Glc H-1″ (δ 5.33, d, J = 7.8 Hz) and C-3 (δ 133.01) of the quercetin moiety, Ara H-1‴ (δ 4.13, d, J = 7.7 Hz) and Glc C-6″ (δ 66.31), Ara H-2‴ (δ 4.59, dd, J = 7.7 Hz, 9.5 Hz) and C-9⁗ (δ 165.90) of the caffeic acid moiety. Hence the structure of **2** was determined as quercetin 3-*O*-[2‴-*O*-(*E*)-caffeoyl]-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranoside and named monepalin B.

The isolation of the two new compounds **1** and **2** required repeated column chromatography on silica gel, Sephadex

Table 3. 2D NMR data for compound **1** (δ in pyridine-d_5; J in Hz)

Atom No.[a]	δ_C	$^{13}C \times {}^{1}H$ HMQC (^{1}H)	$^{1}H \times {}^{1}H$ COSY (^{1}H)	$^{1}H \times {}^{13}C$ HMBC (^{13}C)	$^{1}H \times {}^{13}C$ HMQC-TOCSY (^{13}C)
2	156.28				
3	133.39				
4	177.49				
5	161.28				
6	98.93	6.22 (brs)	8	5, 7, 8, 10	6, 8
7	164.42				
8	93.57	6.42 (brs)	6	6, 7, 9, 10	6, 8
9	156.36				
10	103.91				
1′	120.99				
2′	115.36	7.60 (brs)	6′	2, 3′, 4′, 6′	2, 5, 6
3′	144.98				
4′	148.32				
5′	115.89	6.83 (d, 8.0)	6′	1′, 3′, 4′	2, 5, 6
6′	121.97	7.73 (d, 8.0)	2′, 5′	2, 2′, 4′	2, 5, 6
G-1	101.70	5.53 (d, 7.2)	G-2	3, G-5	G-1, G-2, G-3, G-4
G-2	70.89	3.60 (m)	G-1, G-3		
G-3	72.89	3.31 (dd, 2.3, 8.7)	G-2, G-4	G-2, G-4	G-1, G-2, G-3, G-4
G-4	68.64	3.57 (m)	G-3, G-5		
G-5	76.00	3.41 (t, 5.0)	G-4, G-6a		G-5, G-6
G-6a	66.22	3.58 (m)	G-5, G-6a		G-5, G-6
G-6b		3.46 (m)	G-6b		G-5, G-6
A-1	100.07	4.22 (d, 7.2)	A-2	A-3, A-5	A-1, A-2, A-3, A-4
A-2	72.03	4.71 (t, 8.3)	A-1, A-3	C-9, A-1, A-3	A-1, A-2, A-3, A-4
A-3	70.52	2.98 (dd, 2.9, 9.0)	A-2	A-2	A-1, A-2, A-3, A-4, A-5
A-4	67.90	3.47 (m)	A-5a		A-1, A-2, A-3, A-4, A-5
A-5a	65.50	3.57 (m)	A-4, A-5b		
A-5b		2.86 (brd, 12.2)	A-5a	A-1, A-4	A-3, A-4, A-5
C-1	125.65				
C-2	115.30	7.06 (brs)	C-6	C-4, C-6, C-7	C-2, C-5, C-6
C-3	145.07				
C-4	148.60				
C-5	115.89	6.82 (d, 7.6)	C-6	C-1, C-3, C-4	C-2, C-5, C-6
C-6	120.84	6.97 (d, 7.6)	C-2, C-5	C-2, C-4, C-7	C-2, C-5, C-6
C-7	145.58	7.42 (d, 15.8)	C-8	C-1, C-2, C-6, C-9	C-7, C-8
C-8	114.11	6.04 (d, 15.8)	C-7	C-1, C-9	C-7, C-8
C-9	165.87				

[a] G = galactose; A = arabinose; C = caffeoyl.

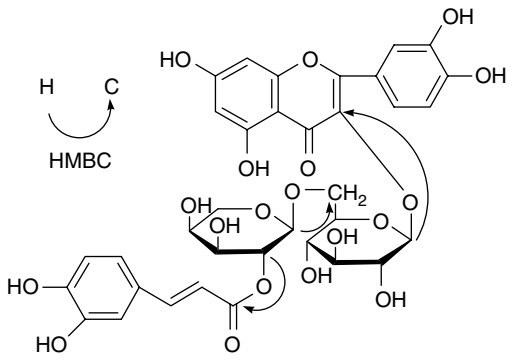


Figure 3. Key long-range information between ^{1}H and ^{13}C from HMBC spectrum of **2**.

LH-20 and MCI gel CHP-20, and only small quantities of samples were obtained, especially for **2** (3 mg). It is interesting that the H-2 of the α-L-arabinopyranosyl residue is found downfield from the anomeric proton when C-2 of the α-L-arabinopyranosyl residue was acylated by caffeic acid. At the same time, C-2 (α-C) of the α-L-arabinopyranosyl residue was shifted upfield by <1 ppm, but C-1 (β-C) and C-3 (β-C) shifted downfield by >2 ppm and <1 ppm, respectively.

EXPERIMENTAL

General

Melting-points (uncorrected) were recorded on an XRC-I instrument produced by Sichuan University (China). UV and

IR spectra were recorded on Shimadzu UV-210A and Bio-Rad FTS-135 spectrophotometers, respectively. FAB mass spectra were measured out on a VG Autospect 3000 spectrometer. All NMR experiments were recorded on a Bruker DRX-500 spectrometer operating at 500 and 125 MHz for ^{1}H and ^{13}C, respectively and equipped with an inverse-detection 5 mm probe (BBI probe, ^{1}H 90° pulse width = 9.5 μs, ^{13}C 90°pulse width =18.5 μs) operating at room temperature. Samples **1** (30 mg), **2** (3 mg), **3** (50 mg), **4** (30 mg), **5** (40 mg) and **6** (30 mg) were dissolved in DMSO-d_6 (0.4 ml) to record the ^{1}H and ^{13}C NMR spectra using TMS as an internal reference.

One-dimensional ^{1}H and ^{13}C NMR spectra were acquired under standard conditions. The NMR conditions for all compounds were as follows: 1D spectra were acquired using 64 K data points and spectral widths of 7500 Hz (or 5000 Hz) and 27 500 Hz (or 25 000 Hz) for ^{1}H and ^{13}C, respectively. 32 K data points were used for the processing with no window function for ^{1}H and an exponential function (LB = 4) for the ^{13}C spectrum.

Standard pulse sequences were used for the 2D spectra. Spectral widths of 7500 Hz (or 5000 Hz) and 27 500 Hz (or 25 000 Hz) were used for ^{1}H and ^{13}C, respectively. Relaxation delays of 1.5 s were used for all 2D NMR experiments except H–H COSY (2 s). The 2D spectra used 1024 × 256 (COSY, HMQC, HSQC and HMQC-TOCSY) and 2048 × 256 (HMBC) data point matrices which were then zero filled to 1024 × 512 and 2048 × 512, respectively. A non-shifted sine-bell window function was used along the F_1 and F_2 axes for H–H COSY, HMQC, HSQC and HMBC and a 90° shifted sine-bell window function was used along the F_1 and F_2 axes for HMQC-TOCSY. The HMQC-TOCSY experiment utilized 100 ms as the spin-lock mixing time. The HMBC experiment used 62 ms as the delay time to obtain ^{1}H and ^{13}C long-range correlations. Z-PFGs were used to obtain HMQC, HSQC, HMBC and DQF H–H COSY spectra. Data processing was carried out on an HP computer with Bruker XWINNMR programs.

Silica gel (160–200 or 200–300 mesh) (Qingdao Marine Chemical Products Industry) and RP-8, Sephadex LH-20 and MCI gel CHP20 (Merck) were used for column chromatography.

Plant material

Morina nepalensis var. *alba* Hand.-Mazz. was collected in northwest Yunnan province, China, in July 1999. A voucher specimen is deposited in the Department of Ethnobotany, Kunming Institute of Botany, Chinese Academy of Sciences.[3,4]

Extraction and isolation:

Ethanol extracts of *Morina nepalensis* var. *alba* Hand.-Mazz. (3.4 kg) were partitioned first between water and chloroform and then between water and *n*-butanol. The *n*-butanol fraction (250 g) was subjected to silica gel column chromatography with ethyl acetate–acetone–water (9 : 10 : 1) to give six fractions (Fr I–VI).

Fr III (22 g) was repeatedly subjected to silica gel column chromatography, eluting with ethyl acetate–acetone–water (6 : 2 : 0.5) or chloroform–methanol–water (8 : 2 : 0.2), and then to MCI gel CHP20 or Sephadex LH-20 column chromatography, eluting with aqueous methanol (10–100%) to afford **1** (40 mg), **2** (3 mg), **4** (50 mg), **5** (80 mg) and **6** (300 mg).

A 2.5 g amount of Fr IV (40 g) was subjected to Sephadex LH-20 column chromatography with aqueous methanol (40–100%) and then to RP-8 column chromatography, eluting with aqueous methanol (10–40%), to afford **3** (2 g).

Acid hydrolysis and GC–MS analysis of 1

A solution of **1** (2 mg) in 2M HCl–dioxane (1 : 1, 1 ml) was heated at 95 °C for about 6 h. The reaction mixture was blowed to dryness with a stream of N_2. The residue was dissolved in pyridine (0.5 ml) and $(CH_3)_3SiNHSi(CH_3)_3$ (0.5 ml). After 10 min at room temperature, the reaction mixture was blown to dryness with a stream of N_2. The residue was dissolved in diethyl ether then subjected directly to GC–MS analysis.

The GC–MS experiment was carried out on an MD 800 instrument. Trimethylsilyl ether derivatives were separated using an HP Ac-5 capillary column (30 × 0.25 m i.d.). Nitrogen was used as the carrier gas. The initial column oven temperature was 180 °C, then increased at 5 °C min^{-1} to 240 °C. The sugars were determined by comparison of their retention times and MS data with those for standard sugars: t_R(min) Glc 6.85 (*m/z* 482), Ara 4.19 (*m/z* 438), Gal 6.50 (*m/z* 482).

Spectral data

Compound **1**

Yellow powder, m.p. 197–199 °C. Negative-ion FABMS: *m/z* 757 ([M − H]$^-$), 735, 603, 463, 339, 300, 276, 183, 91. Negative-ion HR-FABMS: *m/z* 757.1639 [M − H]$^-$; calc. for $C_{35}H_{33}O_{19}$, 757.1616. IR (cm^{-1}). ν_{max}^{KBr} 3434 (br), 2918, 1696, 1654, 1605, 1510, 1445, 1359, 1263, 1166, 1067, 812, 595. UV, λ_{max}^{MeOH} (nm) (log ε): 208.5 (4.51), 257 (4.28), 344.5 (4.28).

Compound **2**

Yellow powder. Negative-ion FABMS: *m/z* 757 ([M − H]$^-$), 709, 627, 595, 463, 389, 339, 325, 300, 297, 183, 97, 79. Negative-ion HR-FABMS: *m/z* 757.1545 [M − H]$^-$; calc. for $C_{35}H_{33}O_{19}$, 757.1616. IR (cm^{-1}): ν_{max}^{KBr} 3413 (br), 2923, 1700, 1653, 1603, 1509, 1448, 1361, 1271, 1199, 1170, 1074, 813, 650, 598. UV, λ_{max}^{MeOH} (nm) (log ε): 209 (4.52), 264.5 (4.26), 365 (4.26).

Compound **3**

Yellow powder, m.p. 249–251.5 °C. Negative-ion FABMS: *m/z* 595 ([M − H]$^-$), 538, 463, 339, 325, 304, 300, 275, 256, 219, 165, 89. IR (cm^{-1}): ν_{max}^{KBr} 3495 (br), 3373, 2918, 1654, 1606, 1509, 1364, 1277, 1203, 1167, 1087, 1068, 943, 781, 705, 602. UV, λ_{max}^{MeOH} (nm) (log ε): 207.5 (4.52), 257.5 (4.29), 363.5 (4.23).

Compound **4**

Yellow powder, m.p. 230–232 °C. Negative-ion FABMS: *m/z* 463 ([M − H]$^-$), 447, 423, 389, 297, 204, 188, 158, 125, 97, 79. IR (cm^{-1}): ν_{max}^{KBr} 3400 (br), 2919, 1656, 1606, 1508, 1447, 1363, 1303, 1271, 1199, 1172, 1118, 1062, 1012, 847, 801, 655, 593. UV, λ_{max}^{MeOH} (nm) (log ε): 207 (4.54), 256.5 (4.31), 361.5 (4.23).

Compound **5**

Yellow powder, m.p. 235–238 °C. Negative-ion FABMS: m/z 463 ([M − H]$^-$), 447, 431, 389, 339, 325, 301, 247, 171, 155, 125, 97, 81. IR (cm^{-1}): γ_{max}^{KBr} 3461 (br), 3373, 2898, 1655, 1606, 1555, 1503, 1443, 1364, 1256, 1205, 1172, 1089, 1055, 887, 798, 601. UV, λ_{max}^{MeOH} (nm) (log ε): 207 (4.48), 261 (4.22), 357.5 (4.15).

Compound **6**

Yellow powder, m.p. 231–233 °C. Negative-ion FABMS: m/z 431 ([M − H]$^-$), 299, 269, 129, 113, 97, 81. IR (cm^{-1}): γ_{max}^{KBr} 3407 (br), 2905, 1659, 1607, 1497, 1449, 1345, 1299, 1207, 1178, 1075, 1047, 836, 627. UV, λ_{max}^{MeOH} (nm) (log ε): 206 (4.57), 267.5 (4.28), 334.5 (4.34).

For the ^{1}H and ^{13}C NMR data for **1–6**, see Tables 1 and 2.

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