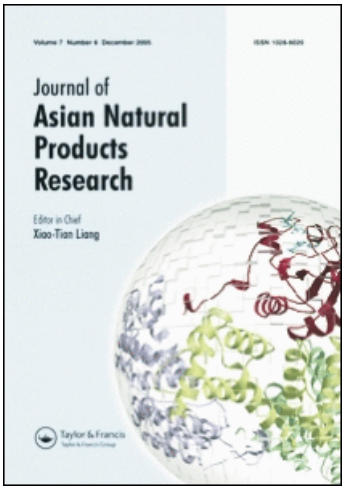

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FOUR NEW OLEANANE TYPE SAPONINS FROM *MORINA NEPALENSIS* VAR. *ALBA*

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Four new oleanane type saponins, monepalosides G–J (**1**–**4**), were isolated from the water-soluble part of the whole plant of *Morina nepalensis* var. *alba* Hand-Mazz. On the basis of chemical and spectroscopic evidence, their structures were determined as 3-*O*-α-L-arabinopyranosyl-(1 → 3)-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside (monepaloside G, **1**), 3-*O*-α-L-arabinopyranosyl-(1 → 3)-β-D-xylopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside (monepaloside H, **2**), 3-*O*-α-L-arabinopyranosyl-(1 → 3)-[β-D-glucopyranosyl-(1 → 2)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside (monepaloside I, **3**), 3-*O*-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranosy-(1 → 3)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside (monepaloside J, **4**), respectively. Two-dimensional NMR spectra, including H–H COSY, HMQC, 2D HMQC–TOCSY, HMBC and ROESY were utilized in the structure elucidation and complete assignments of ^{1}H and ^{13}C NMR spectra.

Keywords: *Morina nepalensis* var. *alba* Hand-Mazz; Dipsacaceae; Monepaloside G; Monepaloside H; Monepaloside I; Monepaloside J

INTRODUCTION

Morina nepalensis var. *alba* Hand-Mazz., belonging to the genus *Morina* of the family Dipsacaceae, is a well-known traditional Tibetan medicinal herb in China and has been used for the treatment of many diseases since ancient times [1,2]. We have reported six ursane type saponins monepalosides A–F, four caffeoylquinic acids, two new flavonoid glycosides monepalin A–B from the water-soluble fraction of the whole plant of *M. nepalensis* var. *alba* [3–6]. Further studies have led to the isolation and identification of another four new oleanane type triterpenoid saponins, monepalosides G–J. We report herein their structure elucidation by chemical and spectroscopic methods. Two-dimensional NMR spectra, including DQF H–H COSY, HMQC or HSQC, 2D HSQC–TOCSY or HMQC–TOCSY, HMBC and ROESY were utilized in the structure elucidation and complete assignments of ^{1}H and ^{13}C NMR spectra.

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RESULTS AND DISCUSSION

The *n*-butanol fraction of ethanol extracts of *M. nepalensis* var. *alba* Hand-Mazz. was repeatedly subjected to silica gel, Rp-8 and MCI gel CHP20 column chromatography to afford compounds **1**–**4**.

The aglycone of saponins **1**–**4** was determined to be oleanolic acid by comparing ^{13}C NMR data with similar saponins whose aglycone was oleanolic acid [7,8]. The ^{13}C signal assignments of the aglycone moiety of saponins **1**–**4** were thus achieved [7,8] and ^{1}H signal assignments were made by examination of the HMQC and H–H COSY spectra. The results were subsequently confirmed by the data from HMBC, ROESY and HMQC–TOCSY spectra and are summarized in Tables I and II.

Monepaloside G (**1**) was isolated as a white powder, mp 204–206°C, $[\alpha]_D^{24} + 0.59$ (*c* 0.43, MeOH). Its molecular formula was established as $C_{52}H_{84}O_{21}$ by combination of its negative ion HR-FABMS spectrum showing a quasi-molecular peak at *m/z* 1043.5340 $[M - H]^-$ (calcd for $C_{52}H_{83}O_{21}$: 1043.5427) and ^{13}C NMR (DEPT) spectra, which was also confirmed by the negative ion FABMS spectrum showing a molecular peak at *m/z* 1043 $[M - H]^-$.

The ^{1}H and ^{13}C NMR spectra showed four anomeric proton signals at δ 4.75 (d, $J = 7.1$ Hz), 5.24 (d, $J = 6.8$ Hz), 6.23 (d, $J = 8.1$ Hz) and 5.00 (d, $J = 7.7$ Hz) and four anomeric carbon signals at δ 107.44, 106.55, 95.75 and 105.30. Consequently **1** was assumed to have four sugar units. Sugar analysis by GC–MS spectrum revealed that **1** contained D-glucose and L-arabinose.

The ^{13}C NMR data of the sugar part of **1** were very similar with those of monepaloside A (**5**) [4], which indicated **1** had the same sugar linkage pattern as **5**. The structure of **1** was different from saponin **5** only in the aglycone. As discussed above, the aglycone of **1** was oleanolic acid.

The linkage positions between the sugar units and between the sugar and the aglycone were further confirmed by HMBC spectrum. In the HMBC spectrum, the following long range correlations between ^{1}H and ^{13}C signals were observed: external arabinosyl H-1 (δ 5.24, d, $J = 6.8$ Hz) and inner arabinosyl C-3 (δ 83.17); inner arabinosyl H-1 (δ 4.75, d, $J = 7.1$ Hz) and C-3 (δ 88.86) of aglycone; external glucosyl H-1 (δ 5.00, d, $J = 7.7$ Hz) and inner glucosyl C-6 (δ 69.41); inner glucosyl H-1 (δ 6.23, d, $J = 8.1$ Hz) and C-28 (δ 176.84) of aglycone. So the structure of **1** was elucidated as 3-*O*-α-L-arabinopyranosyl-(1 → 3)-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside and named monepaloside G.

Monepaloside H (**2**) was isolated as a white powder, mp 198.5–200°C. Its molecular formula was established as $C_{52}H_{83}O_{21}$ by combination of its negative ion HR-FABMS spectrum showing a quasi-molecular peak at *m/z* 1043.5435 $[M - H]^-$ (calcd for $C_{52}H_{83}O_{21}$: 1043.5427) and ^{13}C NMR (DEPT) spectrum, which was also confirmed by its negative ion FABMS spectrum showing a molecular peak at *m/z* 1044 $[M]^-$.

The ^{1}H and ^{13}C NMR spectra of compound **2** showed four anomeric proton signals at δ 4.75 (d, $J = 7.3$ Hz), 5.24 (d, $J = 6.9$ Hz), 6.24 (d, $J = 8.2$ Hz), 5.01 (d, $J = 7.9$ Hz) and four anomeric carbon signals at δ 107.24, 105.98, 95.74 and 105.30. Consequently **2** was assumed to contain four sugar units. Sugar analysis by GC–MS spectra revealed that **2** contained D-glucose, D-xylose and L-arabinose.

The ^{13}C NMR data of sugar moiety of **2** were very similar with those of monepaloside B (**6**) [4], which indicated that **2** had the same sugar linkage pattern as saponin **6** [4]. The linkage sites between the sugar units and between the sugar and aglycone were further confirmed by HMBC spectra showing the following long range correlations: arabinosyl H-1 (δ 5.24, d, $J = 6.9$ Hz) and xylosyl C-3 (δ 86.93); xylosyl H-1 (δ 4.75, d, $J = 7.3$ Hz) and

TABLE I ^{13}C NMR data of saponins **1**–**4** (125 MHz, pyridine-d_5)

C	**1**	**2**	**3**	**4**
1	38.88	38.83	38.86	38.94
2	26.67	26.74	26.65	26.79
3	88.86	88.88	89.01	88.84
4	39.69	39.63	39.73	39.92
5	55.95	55.91	55.91	56.01
6	18.66	18.58	18.58	18.83
7	32.61	32.60	32.59	32.63
8	39.99	39.98	39.95	40.03
9	48.16	48.14	48.12	48.19
10	37.12	37.10	37.06	37.15
11	23.88	23.87	23.87	23.80
12	122.95	122.89	122.93	122.97
13	144.24	144.23	144.21	144.26
14	42.22	42.21	42.20	42.25
15	28.37	28.35	28.34	28.40
16	23.48	23.46	23.45	23.50
17	47.13	47.12	47.11	47.16
18	41.78	41.76	41.75	41.80
19	46.34	46.35	46.32	46.38
20	30.86	30.82	30.83	30.86
21	34.08	34.06	34.05	34.10
22	33.24*	33.19*	33.21*	33.25*
23	28.23	28.16	28.34	28.26
24	17.07	17.02	16.82	17.10
25	15.74	15.68	15.67	15.75
26	17.60	17.58	17.57	17.63
27	26.18	26.13	26.14	26.19
28	176.84	176.61	176.60	176.65
29	33.24*	33.19*	33.21*	33.25*
30	23.77	23.75	23.75	23.79
3-*O*-Ara (or xyl)-1	107.44	107.24	105.40*	107.42
2	71.85	74.56	77.27	71.97
3	83.17	86.93	82.30	84.27
4	69.36*	69.46*	68.77	69.44*
5	66.86*	66.61	65.88	67.10
Ara (or glc′)-1	106.55	105.98	105.32	106.03
2	72.89	72.88	72.68	75.25
3	74.45	74.56	74.55	76.72
4	69.36*	69.46*	69.42	81.18
5	67.00	67.39*	67.15	76.62
6				62.03
Glc″-1			104.44	105.01
2			76.18	74.86
3			78.78*	78.49*
4			72.33	71.60*
5			77.44	78.28*
6			63.13	62.52
28-*O*-glc-1	95.75	95.74	95.74	95.76
2	73.93	73.93	73.95	73.96
3	78.53	78.77*	78.51*	78.49*
4	70.92	70.97	70.93	70.98
5	78.03	78.02	78.04	78.03
6	69.41	69.46*	69.51	69.44*
glc-1	105.30	105.30	105.40*	105.29
2	75.21	75.20	75.21	75.25*
3	78.78	78.77*	78.78	78.78
4	71.54	71.59	71.52	71.60*
5	78.43	78.48	78.44	78.49*
6	62.73	62.69	62.64	62.71

∗ Signals in the same column.

TABLE II ^{1}H NMR data of saponins **1**–**4** (500 MHz, pyridine-d_5, *J*/Hz)

H	**1**	**2**	**3**	**4**
1	1.52	1.50	1.47	1.51
	0.92	0.89	0.86	0.92
2	2.11	2.05	2.02	2.12
	1.84	1.82	1.82	1.85
3	3.33 (dd, 4.3, 11.0)	3.30 (dd, 4.1, 11.0)	3.22	3.32 (dd, 3.9, 12.0)
5	0.80	0.78	0.73	0.78 (d, 11.8)
6	1.46	1.44	1.44	1.46
	1.30	1.29	1.28	1.29
7	1.89	1.87	1.88	1.88
	1.76	1.74	1.75	1.76
9	1.63	1.60	1.58	1.61 (d, 8.4)
11	1.91	1.89	1.88	1.90
12	5.40 (t-like)	5.41 (t-like)	5.39 (t-like)	5.41 (t-like)
15	2.29 (m)	2.31 (brt, 12.9)	2.29 (brt, 12.7)	2.30 (brt, 12.3)
	1.15	1.16	1.15	1.16
16	2.07	2.04	2.07	2.06
	1.95	1.92	1.95	1.94
18	3.17 (brd, 13.4)	3.18 (dd, 3.8, 13.9)	3.17 (brd, 13.1)	3.17 (dd, 4.1, 13.5)
19	1.76	1.72	1.73	1.74
	1.24	1.21	1.23	1.23
21	1.34	1.32	1.33	1.33
	1.11	1.09	1.10	1.10
22	1.46	1.44	1.43	1.45
	1.32	1.31	1.31	1.31
23	1.27 (s)	1.28 (s)	1.20 (s)	1.28 (s)
24	0.95 (s)	0.97 (s)	1.05 (s)	0.97 (s)
25	0.86 (s)	0.87 (s)*	0.82 (s)	0.86 (s)*
26	1.08 (s)	1.09 (s)	1.06 (s)	1.08 (s)
27	1.24 (s)	1.24 (s)	1.22 (s)	1.24 (s)
29	0.88 (s)	0.88 (s)	0.87 (s)	0.87 (s)
30	0.86 (s)	0.87 (s)*	0.85 (s)	0.86 (s)*
3-*O*-ara (or xyl)-1	4.75 (d, 7.1)	4.75 (d, 7.3)	4.84 (d, 5.9)	4.73 (d, 7.3)
2	4.52	3.98	4.73 (t, 7.2)	4.55
3	4.19	4.09	4.32	4.16
4	4.44	4.05	4.48 (brd, 6.2)	4.39
5	4.26	4.28	4.25	4.20
	3.79	3.68 (brd, 11.0)	3.74 (brd, 10.4)	3.74 (brd, 11.7)
Ara (or glc′)-1	5.24	5.24 (d, 6.9)	5.19 (d, 7.2)	5.33 (d, 7.9)
2	4.47	4.48 (t, 7.9)	4.47	4.00
3	4.17	4.12	4.13	4.26
4	4.32	4.25	4.32	4.28
5	4.26	4.30	4.28	3.91
	3.98	3.78 (brd, 12.3)	3.73 (brd, 10.8)	
6				4.50
				4.45
Glc″-1			5.44 (d, 7.8)	5.16 (d, 7.9)
2			4.00	4.05
3			4.13	4.14
4			4.13	4.18
5			3.60	3.97
6			4.34	4.49
			4.24	4.25
28-*O*-glc-1	6.23 (d, 8.1)	6.24 (d, 8.2)	6.25 (d, 7.7)	6.23 (d, 8.2)
2	4.10	4.09	4.12	4.11
3	4.20	4.20	4.20	4.21
4	4.29	4.28	4.31	4.30
5	4.07	4.06	4.08	4.07
6	4.68 (brd, 10.4)	4.69 (brd, 11.4)	4.68 (brd, 10.4)	4.69 (d, 10.7)
	4.31	4.30	4.31	4.32
Glc-1	5.00 (d. 7.7)	5.01 (d, 7.9)	5.02 (d, 7.8)	5.01 (d, 7.6)
2	3.96	3.96	3.97	3.97
3	4.15	4.15	4.15	4.15

TABLE II – *continued*

H	1	2	3	4
4	4.16	4.17	4.16	4.17
5	3.85	3.87	3.85	3.86
6	4.43	4.43 (brd, 11.0)	4.44 (brd, 11.4)	4.44
	4.31	4.31	4.32	4.31

∗ Signals in the same column.

C-3 (δ 88.88) of the aglycone; external glucosyl H-1 (δ 5.01, d, $J = 7.9$ Hz) and inner glucosyl C-6 (δ 69.46); inner glucosyl H-1 (δ 6.24, d, $J = 8.2$ Hz) and C-28 (δ 176.61) of the aglycone. So the structure of **2** was determined to be 3-*O*-α-L-arabinopyranosyl-(1 → 3)-β-D-xylopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside and named monepaloside H.

Monepaloside I (**3**) was isolated as a white powder, mp 217–219.5°C, $[\alpha]_D^{25}$ + 8.96 (*c* 0.43, MeOH). Its negative ion FABMS spectrum showed a quasi-molecular peak at *m/z* 1205 $[M - H]^-$. Furthermore, its negative ion HR-FABMS spectrum showed a quasi-molecular peak at *m/z* 1205.6001 $[M - 1]^-$, so the molecular formula was established as $C_{58}H_{94}O_{26}$ (calcd for $C_{58}H_{94}O_{26}$: 1205.5955) by combination with ^{13}C NMR (DEPT) spectrum.

The ^1H NMR spectrum of compound **3** showed five anomeric proton signals at δ 4.84 (d, $J = 5.9$ Hz), 5.19 (d, $J = 7.2$ Hz), 5.44 (d, $J = 7.8$ Hz), 6.25 (d, $J = 7.7$ Hz) and 5.02 (d, $J = 7.8$ Hz). The ^{13}C NMR spectrum also revealed five anomeric carbon signals at δ 105.40 (2C), 105.32, 104.44, 95.74. So **3** contained five sugar units. Sugar analysis by GC–MS spectrum revealed that **3** contained D-glucose and L-arabinose.

The ^{13}C NMR spectra of sugar moiety of **3** were assigned by two-dimensional NMR spectra including HMQC–TOCSY, HSQC, H–H COSY spectra. The assigned ^{13}C NMR data closely resembled those of monepaloside E (**7**) [6], which indicated **3** had the same sugar linkage pattern as saponin **7**, but they are different in the aglycone moiety. So the structure of **3** was elucidated as 3-*O*-α-L-arabinopyranosyl-(1 → 3)-[β-D-glucopyranosy-(1 → 2)]-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside and named monepaloside I.

Monepaloside J (**4**) was isolated as a white powder, mp 212–215°C, $[\alpha]_D^{22}$ + 16.52 (*c* 0.47, MeOH). Its negative ion FABMS spectrum showing a molecular peak at *m/z* 1236 $[M]^-$. Furthermore, its negative ion HR-FABMS spectrum showed a quasi-molecular peak at *m/z* 1235.6055 $[M - H]^-$, so the molecular formula was established as $C_{59}H_{96}O_{27}$ (calcd for $C_{59}H_{95}O_{27}$: 1235.6061) by FABMS and ^{13}C NMR (DEPT) spectra.

The ^1H NMR spectrum of compound **4** showed five anomeric proton signals at δ 4.73 (d, $J = 7.3$ Hz), 5.33 (d, $J = 7.9$ Hz), 5.16 (d, $J = 7.9$ Hz), 6.23 (d, $J = 8.2$ Hz) and 5.01 (d, $J = 7.6$ Hz). The ^{13}C NMR spectra also revealed five anomeric carbon signals at δ 107.42, 106.03, 105.01, 95.76, 105.29. So **4** was assumed to contain five sugar units. Sugar analysis by GC–MS spectrum revealed that **4** contained D-glucose and L-arabinose.

Comparison of the ^{13}C NMR data of the sugar moiety of **4** with known saponin mazusaponin II (**8**) indicated that **4** had three similar sugar units as **8**, but two more glucosyl units than **8** [9]. Like saponin **8**, compound **4** had an inner arabinopyranosyl unit linked at C-3 of the aglycone and a gentiobiosyl unit linked at C-28 of the aglycone. Another two β-D-glucopyranosyl units were assigned from NMR spectra. From the HMQC–TOCSY spectrum, six carbon signals at δ 106.03, 81.18, 76.72, 76.62, 75.25 and 62.03 correlated with the anomeric proton signal H-1 (δ 5.33, d, $J = 7.9$ Hz); and six carbon signals at δ 105.01, 78.49, 78.28, 74.86, 71.60 and 62.52 correlated with another anomeric proton signal H-1

(δ 5.16, d, $J = 7.9$ Hz). With the aid of other two-dimensional NMR spectra like HMQC, H–H COSY and HMBC, the carbon signals were assigned to be C-1, C-4, C-3, C-5, C-2 and C-6 for the first glucose and C-1, C-3, C-5, C-2, C-4 and C-6 for the second glucose [10–14]. The chemical shifts of two glucosyl units were characteristic of β-D-glucopyranosyl units. The coupling constants $^3J_{\text{H-1,H-2}}$ (>5 Hz) also supported the β-configuration [10–14].

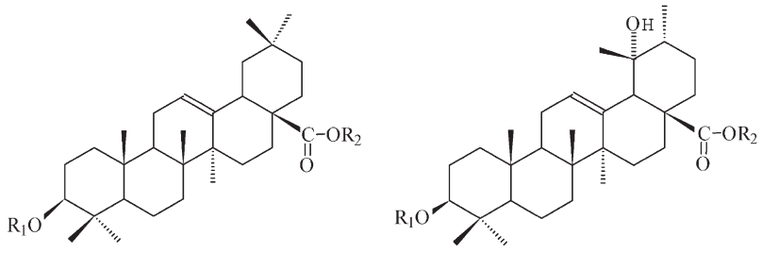
The C-4 of the glucosyl unit was shifted downfield to δ 81.84, which suggested another glucopyranosyl unit was linked at C-4 of this glucose. This deduction was supported by HMBC spectrum showing long range correlations between external glucosyl H-1 (δ 5.16, d, $J = 7.9$ Hz) and inner glucosyl C-4 (δ 81.18). Other linkage sites were also confirmed by ^{1}H and ^{13}C long correlations from HMBC spectrum. They were glucosyl H-1 (δ 5.33, d, $J = 7.9$ Hz) and arabinosyl C-3 (δ 84.27); arabinosyl H-1 (δ 4.73, d, $J = 7.3$ Hz) and C-3 (δ 88.84) of aglycone; external glucosyl H-1 (δ 5.01, d, $J = 7.6$ Hz) and inner glucosyl C-6 (δ 69.44), inner glucosyl H-1 (δ 6.23, d, $J = 8.2$ Hz) and C-28 (δ 176.65 of the aglycone. So the structure of **4** was determined to be 3-*O*-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 3)-α-L-arabinopyranosyl oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside) and named monepaloside J (Fig. 1).

EXPERIMENTAL

General Experimental Procedures

Optical rotations were measured on a HORIBA SEPA-300 polarimeter using a sodium lamp. Melting points were measured on a melting point apparatus produced by Sichuan University, China, and are uncorrected. FABMS spectra were recorded on a VG Autospect 3000 spectrometer. All NMR spectra were recorded on a Bruker DRX-500 MHz spectrometer operating 500 and 100 MHz for ^{1}H and ^{13}C, respectively, equipped with an inverse detection 5 mm probe (BBI) operating at room temperature. About 30 mg of samples were dissolved in pyridine-d_5 (0.4 ml) to record NMR spectra using the lowest field signals of pyridine-d_5 (^{1}H: δ 8.71; ^{13}C: δ 149.9) as internal reference.

HMQC–TOCSY or HSQC–TOCSY experiments utilized a spin-lock of 100 ms as the mixing time. The HMBC experiment used 62 ms as the mixing time to obtain ^{1}H and ^{13}C long range correlation. Z-PFG was used to obtain HMQC, HSQC, HMBC and



	R_1	R_2		R_1	R_2
1	ara(3-1)ara	glc(6-1)glc	5	ara(3-1)ara	glc(6-1)glc
2	xyl(3-1)ara	glc(6-1)glc	6	xyl(3-1)ara	glc(6-1)glc
3	ara(2-1)glc(3-1)ara	glc(6-1)glc	7	ara(2-1)glc(3-1)ara	glc(6-1)glc
4	ara(3-1)glc(4-1)glc	glc(6-1)glc	8	ara	glc(6-1)glc

FIGURE 1 Structures of saponins **1**–**8**.

DQF H–H COSY spectra. Data processing was carried out on an HP computer with Bruker XWINNMR programs.

Plant Material

Plant material of *M. nepalensis* var. *alba* Hand-Mazz. was collected in July, 1999 from Xiao-Zhong-Dian, Zhong-Dian County of Yunnan province, China and identified by Dr Zheng-Dong Fang. A voucher specimen (Qing-Zhang Group No. 1238) was deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences, Kunming, China.

Extraction and Isolation

The ethanol extracts of whole plants of *M. nepalensis* var. *alba* Hand-Mazz. (3.4 kg) were partitioned between water and chloroform firstly then between water and *n*-BuOH. The *n*-BuOH fraction (250 g) was subjected to Si gel column chromatography with EtOAc–acetone–H_2O (9:10:1) to give six fractions (Fr I–VI).

Fr IV (40 g) was subjected to Diaion HP-20 column chromatography followed by silica gel with $CHCl_3$–MeOH–H_2O and Rp-8 column chromatography with aqueous methanol repeatedly to afford **1** (220 mg), **2** (10 mg), **3** (320 mg), **4** (190 mg).

Acid Hydrolysis and GC–MS Analysis

A solution of 2 mg of compound **1**, or **2**, **3**, **4** in 2 M HCl–dioxane (1:1, 1 ml) was heated at 95°C for about 6 h. The reaction mixture was blown to dryness with a N_2 stream. The residue was dissolved with pyridine (0.5 ml) then added with $(CH_3)_3SiNHSi(CH_3)_3$ (0.5 ml). After 10 min at room temperature, the reaction mixture was blown to dryness with a N_2 stream. The residue was dissolved with ethyl ester then directly subjected to GC–MS analysis.

GC–MS experiment was carried out on a MD 800 instrument. Trimethylsilyl ether derivatives were separated using a HP Ac-5 capillary column (0.25 m × 30 m). Nitrogen was used as carrier gas. The initial column oven temperature was 180°C; the temperature was increased at 5°C min^{-1} to a final value of 240°C. The sugar units were determined by comparing the retention times and MS behavior with authentic sugars. R_f (s) (MS:*m*/*z*) = Glc (685) (482 $[M]^+$), Ara (419) (438 $[M]^+$), Xyl (506) (438 $[M]^+$). The presence of arabinose, glucose in **1**, **3** and **4**, arabinose, xylose and glucose in **2** were detected.

Spectral Data

Monepaloside G (**1**): White powder, mp 204–206°C, $[\alpha]_D^{24}$ + 0.59 (*c* 0.43, MeOH). Negative ion FABMS: *m*/*z* 1043 $[M - H]^-$, 911 $[1043 - 132]^-$, 881 $[1043 - 162]^-$, 719 $[881 - 162]^-$, 615 $[881 - 133 \times 2]^-$, 587$[719 - 132]^-$, 455 $[587 - 132]^-$. Negative ion HR-FABMS: *m*/*z* 1043.5340 $[M - H]^-$, calcd for $C_{52}H_{83}O_{21}$: 1043.5427.

Monepaloside H (**2**): White powder, mp 198.5–200°C. Negative ion FABMS: *m*/*z* 1043 $[M - H]^-$, 912 $[M - 132]^-$, 881 $[1043 - 162]^-$, 719 $[881 - 162]^-$, 617 $[881 - 132 \times 2]^-$, 587 $[719 - 132]^-$, 455 $[587 - 132]^-$. Negative ion HR-FABMS: *m*/*z* 1043.5435 $[M - H]^-$, calcd for $C_{52}H_{83}O_{21}$: 1043.5427.

Monepaloside I (**3**): White powder, mp 217–219.5°C, $[\alpha]_D^{25}$ + 8.96 (*c* 0.43, MeOH). Negative ion FABMS: *m*/*z* 1205 $[M - H]^-$, 1074 $[M - 132]^-$, 911 $[1074 - 162 - H]^-$, 881 $[1205 - 162 \times 2]^-$, 749 $[881 - 132]^-$, 587 $[749 - 162]^-$, 455 $[587 - 132]^-$. Negative ion HR-FABMS: *m*/*z* 1205.6001 $[M - H]^-$, calcd for $C_{58}H_{94}O_{26}$: 1205.5955.

Monepaloside J (**4**): White powder, mp 212–215°C, $[\alpha]_D^{22}$ + 16.52 (*c* 0.47, MeOH). Negative ion FABMS: *m/z* 1236 $[M]^-$, 1073 $[M - 162 - H]^-$, 911 $[1073 - 162]^-$, 749 $[911 - 162]^-$, 587 $[749 - 162]^-$, 455 $[587 - 132]^-$. Negative ion HR-FABMS: *m/z* 1235.6055 $[M - H]^-$, calcd for $C_{59}H_{95}O_{27}$: 1235.6061.

^1H and ^{13}C NMR data of compounds **1**–**4** are listed in Tables I and II.

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