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TRITERPENOID SAPONINS FROM *ASTER BATANGENSIS*

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Key Word Index—*Aster batangensis*; Compositae; triterpenoid saponins; asterbatanoside F, G, H and I; bayogenin; sedative activity; analgesic activity.

Abstract—Four novel triterpenoid saponins named asterbatanoside F, G, H and I were isolated from the roots of *Aster batangensis* and their strucutres elucidated as 3-*O*-*β*-D-glucopyranosyl-23-*O*-acetyl-bayogenin-28-*O*-*β*-D-glucopyranosyl-(1 → 6)-[α-L-rhamnopyranosyl-(1 → 2)]-*β*-D-glucopyranoside, 3-*O*-*β*-D-glucopyranosyl-bayogenin-28-*O*-*β*-D-glucopyranosyl-(1 → 6)-[α-L-rhamnopyranosyl-(1 → 2)]-*β*-D-glucopyranoside, 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-bayogenin-28-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranoside, and 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-23-*O*-acetyl-bayogenin-28-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranoside by means of spectral data, especially NMR including COSY, HETCOR, COLOC, HOHAHA, ROESY and selective INEPT techniques, and chemical evidence.

INTRODUCTION

Aster batangensis is used for the treatment of snake bite in Chinese folk medicine [1]. In the course of a search for novel bioactive compounds from medicinal plants, we found that the *n*-butanol extract from *A. batangensis* showed potent sedative activity. This encouraged us to study the glycosides of this plant, collected from Li-Jiang County, Yunnan Province, southwestern China.

Aster batangensis has not been chemically investigated before. In this paper, we report on the isolation and structural elucidation of four new triterpenoid saponins named asterbatanoside F (**1**), G (**2**), H (**3**) and I (**4**) from the *n*-butanol-soluble fraction of this plant.

RESULTS AND DISCUSSION

The *n*-butanol-soluble part of the 70% ethanol extract from the roots of *A. batangensis* was subjected to CC on highly porous resin (SIP-1300) and rechromatographed over silica gel, Sephadex LH-20 and reverse-phase C-8 columns to afford asterbatanoside F (**1**), G (**2**), H(**3**) and I (**4**).

Asterbatanoside F (**1**) was obtained as needles, $[\alpha]_D$ − 4.11° (MeOH; *c* 0.45). The FAB-mass spectral data (*m/z* 1185 $[M + Na]^+$, 1169 $[M + Li]^+$) in combination with the ^{13}C NMR spectral data (Tables 1 and 2) led to the molecular formula $C_{56}H_{90}O_{25}$. The IR spectrum of **1** showed the presence of OH (3400 cm^{-1}) and ester (1745 cm^{-1}) groups and a glycosidic linkage (1000–1100 cm^{-1}). The ^1H NMR spectrum contained the signals of six singlet groups at δ0.78, 0.79, 1.08, 1.19, 1.21 and 1.45, one trisubstituted olefinic proton at δ5.41, four anomeric protons at δ4.90 (2H, *d*, *J* = 8.0 Hz), 6.06 (*d*, *J* = 8.0 Hz) and 6.47 (*br s*), one ester carbonyl carbon at δ176.6, one sugar methyl at δ1.70 (*d*, *J* = 7.0 Hz) and a methyl of an acetyl group at δ1.98 (3H, *s*). The ^{13}C NMR data revealed the presence of six C-saturated quaternary carbons (δ42,2, 40.2, 37.1, 42.6, 47.3, 30.8), a pair of olefinic carbons (δ123.1, 144.2), one ester carbonyl carbon (δ176.6), one acetyl group (δ21.0, 170.8) and four anomeric carbons (δ94.9, 101.4, 105.4, 106.1). The numbers and chemical shifts of the tertiary methyl functions and quaternary carbons suggested that **1** was an oleanane-type triterpene tetraglycoside with an acetyl group. The ^1H signal at δ6.06 and the ^{13}C signal at δ94.9 indicated the presence of an ester-linked sugar moiety.

Upon acid hydrolysis, **1** gave glucose and rhamnose as sugar components which were identified by PC and TLC (direct comparison with authentic samples). The anomeric centres of the three glucosyl moieties were each determined to have *β*-configuration based on the large $J_{1,2}$ values (8.0 Hz). The C-5 of the rhamnosyl unit resonated at δ69.85 and thus had α-configuration [2].

On alkaline hydrolysis followed by treatment with diazomethane, **1** afforded a prosapogenin methyl ester (**1a**) which showed a $[M + Na]^+$ ion at *m/z* 687 and a $[M + Li]^+$ ion at *m/z* 671 in its FAB-mass spectrum. Methanolysis of **1a** yielded glucose and an aglycone methyl ester (**1b**) which was identified as bayogenin methyl ester by comparison of its physical data with those of an authentic sample and EI-mass, ^1H and ^{13}C NMR spec-

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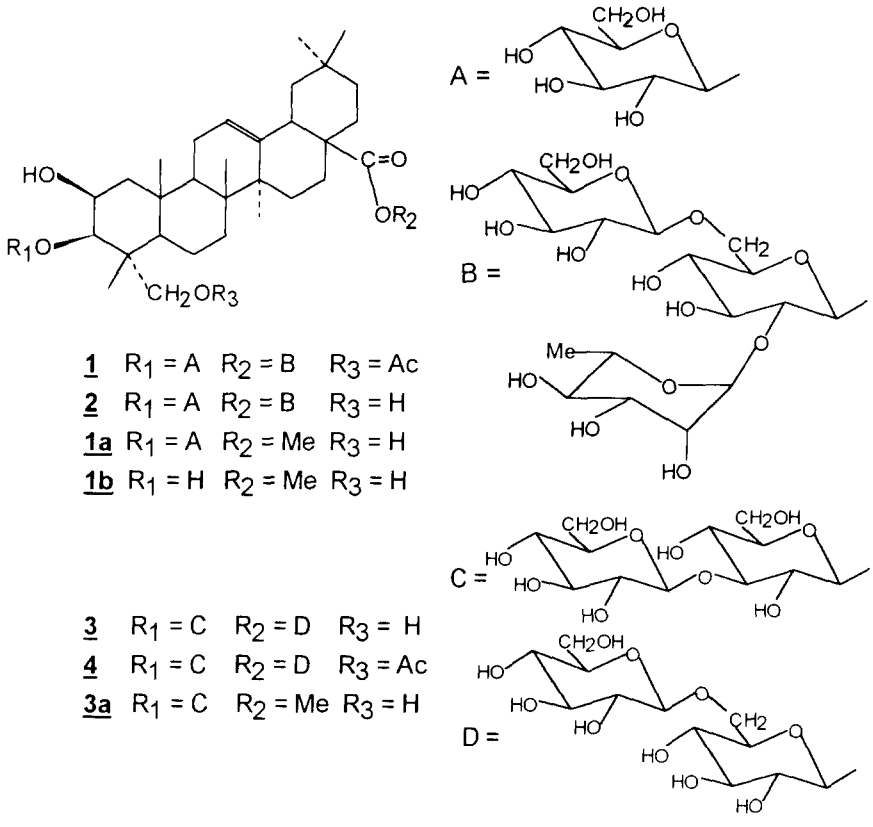

1 R_1 = A R_2 = B R_3 = Ac
2 R_1 = A R_2 = B R_3 = H
1a R_1 = A R_2 = Me R_3 = H
1b R_1 = H R_2 = Me R_3 = H

3 R_1 = C R_2 = D R_3 = H
4 R_1 = C R_2 = D R_3 = Ac
3a R_1 = C R_2 = Me R_3 = H

tral data with reference data [3]. A comparison of the ^{13}C NMR signals of the aglycone moiety in **1a** with those of **1b** indicated that the C-3 signal in **1a** appeared at lower field by + 9.86 ppm, indicating that the glycosylation took place at the C-3 position. The glucose H-1 signal at δ5.19 (*d*, J = 7.8 Hz) suggested that the glucosyl unit had β-configuration. Thus, **1a** was concluded to be 3-*O*-β-D-glucopyranosyl-bayogenin methyl ester. From this conclusion, the remaining 2 mol of glucosyl and 1 mol of rhamnosyl moieties were assignable to the C-28-*O*-sugar chain.

Comparison of the ^{1}H and ^{13}C NMR parameters of **1** with those of **1a** showed that they contained very similar signals for the aglycone parts, except that the C-23 signal of the glycone was deshielded by + 1.17 ppm to δ66.8 and the H-23 signals were shifted downfield by +0.46 ppm and +0.45 ppm to δ4.15 and 4.60 (each 1H, each *d*, J = 10.5 Hz), respectively. These shift resulted from the presence of an acetyl group at the C-23 position of the aglycone in **1** [4, 5]. This was confirmed by the COLOC spectrum which displayed a correlation contour between the H-23 signal and carbonyl carbon signal of the acetyl group. Therefore, the structure of the aglycone part of **1** was determined as 23-*O*-acetyl bayogenin.

The identity of the 28-*O*-trisaccharide was deduced by means of the 2D COSY, HOHAHA [6], HETCOR and ROESY [7] spectra. The 2D NMR data are summarized in Table 3. The 2D COSY and HOHAHA spectra allowed us to assign all of the proton signals in each monosaccharide, while the HETCOR spectrum enabled us to assign of all of the carbon signals of the sugar units. The assignment of ^{1}H and ^{13}C chemical shifts owing to the sugar moieties of **1** are listed in Table 2.

Comparison of the ^{13}C NMR data of the sugar part of **1** with those of methyl β-D-glucopyranoside and methyl α-L-rhamnopyranoside [2] indicated that two glucose units, a 3-*O*-glucose unit and one rhamnose unit, were in terminal locations. C-6 and C-2 of the inner glucose in the 28-*O*-sugar units resonated at δ69.5 and 75.3, respectively, which was more downfield than the corresponding carbon signals in methyl β-D-glucopyranoside. This suggested that glycosylation took place at the C-6 and C-2 positions of the inner glucose. In a selective INEPT experiment, irradiation of the anomeric proton signal of the rhamnose at δ6.47 enhanced the carbon resonance at δ75.3, suggesting (1 → 2) linkage between the rhamnose and the 28-*O*-inner glucose units. These conclusions were also unambiguously confirmed by a ROESY experiment, which showed NOE correlations between H-1 of the rhamnosyl unit with H-2 of the inner glucosyl unit, and between H-1 of the outer glucose unit with H-6 of the inner glucosyl unit, i.e. a (1 → 6) linkage between two glucose units was present in **1**. In addition, each glucose H-1 showed a NOE with H-3 and H-5, and rhamnose H-1 showed a NOE with H-4, which further confirmed the configuration of the sugar units.

Consequently, the structure of asterbatanoside F (**1**) was clarified as 3-*O*-β-D-glucopyranosyl-23-*O*-acetyl-bayogenin-28-*O*-β-D-glucopyranosyl-(1 → 6)-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranoside.

Table 1. ^{13}C NMR spectral data of the aglycone moieties of **1**, **2**, **1a**, **1b**, **3**, **4**, and **3a** (pyridine-d_5, 125 MHz for **1**, **3** and **4**, 75 MHz for **2**, **1a**, **1b**, and **3a**)

C	1	2	1a	1b	3	4	3a
1	44.0	44.3	44.2	44.9	44.3	43.9	44.3
2	70.2	70.6	70.6	71.6	70.8	69.7	70.9
3	83.2	83.2	83.1	73.3	83.0	83.3	83.0
4	42.2	42.8	42.2	42.2	42.4	41.7	42.3
5	48.8	48.6	48.5	48.5	48.6	48.7	48.6
6	18.3	18.0	18.1	18.4	18.1	18.2	18.1
7	33.1	33.2	32.9	32.8	33.0	32.9	33.0
8	40.2	40.2	39.9	39.9	40.1	40.0	40.0
9	48.5	47.9	47.8	48.3	47.7	48.4	47.7
10	37.1	37.1	37.1	37.2	37.0	37.0	37.1
11	23.8	24.1	24.1	24.0	24.1	23.9	24.1
12	123.1	122.8	122.9	123.0	122.9	122.9	123.2
13	144.2	144.3	144.3	144.2	144.2	144.2	144.3
14	42.6	42.6	42.9	42.4	42.9	42.2	43.0
15	28.7	28.8	28.2	28.1	28.3	28.1	28.2
16	23.5	23.7	23.5	23.5	23.5	23.4	23.6
17	47.3	47.3	47.1	47.0	47.1	47.0	47.1
18	41.7	42.1	42.0	41.9	41.8	41.7	42.0
19	46.5	46.2	46.1	46.2	46.3	46.1	46.2
20	30.8	30.7	30.9	30.8	30.8	30.7	30.9
21	34.2	34.2	34.1	34.0	34.1	33.9	34.1
22	32.4	32.4	32.9	32.9	32.6	32.5	33.0
23	66.8	66.0	65.6	67.9	65.2	66.6	65.3
24	14.8	15.1	15.2	14.5	15.0	14.6	15.1
25	17.6	17.6	17.4	17.3	17.4	17.1	17.4
26	17.3	17.6	17.4	17.3	17.7	17.6	17.4
27	25.8	26.0	26.3	26.2	26.2	26.0	26.4
28	176.6	176.6	178.2	178.1	176.5	176.6	178.1
29	33.3	33.2	33.2	33.1	33.1	33.1	33.2
30	24.1	23.8	23.8	23.7	23.7	23.6	23.8
Ac	21.0					20.9	
	170.8					170.9	
OMe			51.7	51.6			51.6

Asterbatanoside G (**2**) exhibited two quasimolecular ions at m/z 1143 $[M + Na]^+$ and 1127 $[M + Li]^+$ in its FAB-mass spectrum indicating its M_r to be 1120 for $C_{54}H_{88}O_{24}$. Acid hydrolysis of **2** afforded glucose and rhamnose which were identified by PC and TLC (direct comparison with authentic samples). Comparison of the ^{1}H and ^{13}C NMR spectral data (Tables 1 and 2) of **2** with those of asterbatanoside F (**1**) and **1a** indicated that it contained the same sugar moieties as **1** and the same aglycone unit as **1a**. Thus, **2** could be regarded as desacetyl **1**. This suggestion was confirmed by the conversion of **1** to **2** with 0.5% $NaHCO_3$. The fact that the M_r of **2** is 42 amu lower than that of **1** and the absence of acetyl group signals from the NMR spectra of **2** also favoured the above conclusion.

From the above evidence, the structure of asterbatanoside G (**2**) was proved to be 3-*O*-β-D-glucopyranosylbayogenin-28-*O*-β-D-glucopyranosyl-(1 → 6)-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranoside.

Asterbatanoside H (**3**) showed quasimolecular ion peaks at m/z 1159 $[M + Na]^+$ and 1143 $[M + Li]^+$ in its FAB-mass spectrum, corresponding to the molecular formula $C_{54}H_{88}O_{25}$. On acid hydrolysis, **3** gave glucose and an aglycone which was identified as bayogenin by comparison with an authentic sample.

The ^{1}H and ^{13}C NMR spectral data (Tables 1 and 2) showed four anomeric signals (δ4.98, 5.07, 5.18, 6.20 and 95.7, 105.3, 105.5, 106.0). This indicated that **3** consisted of 1 mol of aglycone and 4 mol of glucose. The β-configurations at the anomeric centres of the glucose units were suggested by the chemical shifts and the $J_{1,2}$ couplings (8.5 Hz) of the anomeric protons in the ^{1}H NMR spectrum, and by the ^{13}C NMR data for the four sugar residues. Because the C-3 chemical shift in the aglycone was shifted to downfield by +10.63 ppm and the C-28 shift was moved upfield by −3.5 ppm, two saccharide chains linked separately to C-3 and C-28 were suggested.

Alkaline hydrolysis of **3** provided a prosapogenin which was treated with diazomethane to give its methyl ester (**3a**). Compound **3a** showed two quasimolecular ion peaks at m/z 849 $[M + Na]^+$ and 833 $[M + Li]^+$. The molecular formula, $C_{43}H_{70}O_{15}$, was deduced from the FAB-mass spectrum and the ^{13}C NMR data (Tables 1 and 2). In the ^{1}H and ^{13}C NMR spectra the presence of

Table 2. NMR spectral data of the sugar moieties of **1**, **2**, **1a**, **3**, **4** and **3a** (pyridine-d_5 500 MHz for δ_H of **1**, **3** and **4** 300 MHz for δ_H of **2**, **1a** and **3a**, 125 MHz for δ_C of **1**, **3** and **4**, 75 MHz for δ_C of **2**, **1a** and **3a**)

	1		**2**		**1a**		**3**		**4**		**3a**	
Position	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
3-*O*-*Sugar*												
Inner Glc												
1	106.1	4.90	105.8	4.98	105.8	5.19	105.3	5.07	105.7	5.03	105.6	5.10
2	75.3[a]	3.93	75.5		75.6		74.1	3.97	74.0	4.03	74.2	
3	78.5[b]	4.13	78.7		78.7		88.9	4.01	88.7	4.08	89.0	
4	71.6[c]	4.14	71.7		71.7		69.7	4.00	69.7	4.06	69.9	
5	78.6	3.93	78.3		78.4		78.0	3.85	78.0	3.86	78.0	
6a	62.7	4.27	62.7		62.8		62.6	4.16	62.4	4.20	62.4	
6b		4.45						4.30		4.36		
Outer Glc												
1							106.0	5.18	105.9	5.23	106.1	5.19
2							75.6	3.99	75.5	4.06	75.6	
3							78.8	4.17	78.7	4.20	78.8	
4							71.7	4.14	71.5	4.18	71.8	
5							78.5	3.96	78.4	3.99	78.4	
6a							62.7	4.22	62.5	4.26	62.7	
6b								4.47		4.49		
28-*O*-Sugar												
Inner Glc												
1	94.9	6.06	94.9	6.11			95.7	6.20	95.7	6.25		
2	75.3	4.32	75.2				74.0	4.08	73.9	4.12		
3	79.6	4.21	79.6				78.8	4.12	78.7	4.18		
4	71.2	4.24	71.3				71.6	4.25	71.5	4.34		
5	77.8	4.01	77.8				77.9	4.05	78.0	4.11		
6a	69.5	4.23	69.5				69.5	4.32	69.4	4.35		
6b		4.60						4.67		4.67		
Outer Glc												
1	105.4	4.90	105.4	5.18			105.3	4.98	105.3	4.97		
2	75.3[a]	3.93	75.5				75.2	3.95	75.1	3.99		
3	78.4[b]	4.13	78.7				78.0	4.19	78.0	4.22		
4	71.5[c]	4.14	71.6				71.6	4.15	71.4	4.20		
5	78.6	3.79	78.3				78.7	3.83	78.6	3.95		
6a	62.6	4.27	62.7				62.3	4.24	62.3	4.35		
6b		4.40						4.42		4.45		
Rham												
1	101.4	6.47	101.5	6.60								
2	72.3	4.71	72.3									
3	72.7	4.47	72.6									
4	73.9	4.25	73.9									
5	69.9	4.47	69.8									
6	18.9	1.70	18.8	1.78								

[a-c]Assignments may be interchangeable.

two anomeric proton signals at δ5.29 (*d*, J = 7.8 Hz) and 5.20 (*d*, J = 7.9 Hz), and two anomeric carbon signals at δ105.6 and 106.1 suggested that **3a** contained two β-D-glucopyranosyl units. By comparison of the ^{13}C NMR data of **3a** with those of methyl β-D-glucopyranoside, it was found that for one glucose unit the C-3 resonance (δ89.0) was shifted downfield by + 10.85 ppm and the C-2 (δ74.22), C-4 (δ69.9) signals shifted upfield by −0.58, −1.55 ppm, respectively, owing to the glycosylation effect and that the other glucose unit had almost identical ^{13}C NMR data. This showed that one terminal glucose unit was connected to the C-3 hydroxyl group of the other glucose unit. Compound **3a**, thus, was elucidated as the methyl ester of bayogenin-3-*O*-β-D-glucopyranosyl-(1 → 3) β-D-glucopyranoside. This conclusion indicated that the 28-*O*-sugar chain consisted of two glucosyl units.

The ^{13}C NMR data of the remaining two glucose units of **3** showed that the C-6 signal of the 28-*O*-inner glucosyl unit resonated at δ69.5, which was shifted more downfield than that of methyl β-D-glucopyranoside. This observation indicated that the other glucose unit must be connected to the C-6 hydroxyl group of this glucose unit. Therefore, the 28-*O*-sugar chain was identified as β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl.

Table 3. Summary of the 2D-NMR correlations of **1**

H	COSY (^{1}H)	HETCOR (^{13}C)	HOHAHA (^{1}H)	ROESY (^{1}H)
3-*O*-Glc				
1′	2′	1′	2′, 3′	3, 3′, 5′
2′	1′, 3′	2′	1′, 3′, 4′	4′
3′	2′, 4′	3′	1′, 2′, 4′, 5′	1′, 5′
4′	3′, 5′	4′	2′, 3′, 5′, 6′a	2′
5′	4′, 6′a, 6′b	5′	2′, 3′, 4′, 6′a, 6′b	1′, 3′, 6′a
6′a	5′, 6′b	6′	4′, 5′, 6′b	6′b, 5′
6′b	5′, 6′a	6′	4′, 5′, 6′a	6′a
28-Sugar				
Inner Glc				
1″	2″	1″	2″, 3″	3″, 5″
2″	1″, 3″	2″	1″, 3″, 4″	4″, 1‴
3″	2″, 4″	3″	1″, 2″, 4″, 5″	1″, 5″
4″	3″, 5″	4″	2″, 3″, 5″, 6″a	2″
5″	4″, 6″,	5″	2″, 3″, 4″, 6″a, 6″b	1″, 3″, 6″a
6″a	5″, 6″a, 6″b	6″	4″, 5″, 6″b	5″, 6″b, 1‴
6″b	5″, 6″a	6″	5″, 6″a	6″a, 1‴
Outer Glc				
1‴	2‴	1‴	2‴, 3‴	3‴, 5‴, 6″a, 6″b
2‴	1‴, 3‴	2‴	1‴, 3‴, 4‴	4‴
3‴	2‴, 4‴	3‴	1‴, 2‴, 4‴, 5‴	1‴, 5‴
4‴	3‴, 5‴	4‴	2‴, 3‴, 5‴, 6‴a	1‴, 3‴, 6‴a
5‴	4‴, 6‴a, 6‴b	5‴	2‴, 3‴, 4‴, 6‴a, 6‴b	1‴, 3‴, 6‴a
6‴a	5‴, 6‴b	6‴	4‴, 5‴, 6‴b	5‴, 6‴b
6‴b	5‴, 6‴a	6‴	4‴, 5‴, 6‴a	6‴a
Rham				
1⁗	2⁗	1⁗	2⁗	2″, 2‴, 4‴
2⁗	1⁗, 3⁗	2⁗	1⁗, 3⁗, 4⁗	1⁗
3⁗	2⁗, 4⁗	3⁗	2⁗, 4⁗, 5⁗	5⁗
4⁗	3⁗, 5⁗	4⁗	2⁗, 3⁗, 5⁗, 6⁗	1⁗
5⁗	4⁗, 6⁗	5⁗	3⁗, 4⁗, 6⁗	3⁗, 6⁗
6⁗	5⁗	6⁗	4⁗, 5⁗	5⁗

However, since the signals of the sugar units overlapped, it was difficult to assign the ^{1}H and ^{13}C NMR data. By using the 2D COSY, HOHAHA and HMQC spectra (Table 4), the ^{1}H and ^{13}C NMR data could be more precisely assigned. The complete assignments of chemical shifts of the sugar moieties are given in Table 2. Furthermore, the ROESY spectrum where four correlation contours were observed between aglycone–H-3 and 3-*O*-inner Glc–H-1, 3-*O*-inner Glc–H-3 and 3-*O*-outer Glc–H-1; and between 28-*O*-inner Glc–H-6 and 28-*O*-outer Glc–H-1 (Table 4) confirmed the interlinkage locations obtained by ^{13}C NMR.

Consequently, the structure of asterbatanoside H (**3**) was established as 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-bayogenin-28-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranoside.

Asterbatanoside I (**4**) showed spectroscopic (IR, NMR) properties similar to those of asterbatanoside H (**3**). The molecular formula, $C_{56}H_{90}O_{26}$, was established by FAB-mass spectrometry which showed two quasimolecular ion peaks at *m/z* 1227 $[M + Na]^+$ and 1211 $[M + Li]^+$. This was 42 mass units more than that of **3** and indicated the presence of one acetyl group in **4**. The NMR spectral data of **4** showed the presence of one acetyl group [δ2.05 (3H, *s*) and δ_H20.9 (*q*), 170.7 (*s*)]. A careful comparison of the NMR parameters of **4** with those of **3** indicated that the C-23 signal (δ66.6) in **4** was shifted downfield by +1.45 ppm and the H-23 signals [δ4.22 and 4.63 (each 1H, each *d*, J = 11 Hz)] by +0.61, +0.3 ppm due to acylation-induced shifts (AIS), respectively. This suggested that the acetyl group was attached to the C-23 oxygen atom of the aglycone.

The NMR parameters of the sugar moieties of **4** were superimposable on those of **3**. Therefore, **4** was regarded as the acetate of **3**. This suggestion was confirmed by the conversion of **4** to **3** with 0.5% $NaHCO_3$.

From the above data, asterbatanoside I (**4**) was elucidated as 3-*O*-*β*-D-glucopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-23-*O*-acetyl-bayogenin-28-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranoside.

Asterbatanoside F showed inhibitory activities against the writhing of mice (16%) induced by acetic acid at a dose of 25 mg kg^{-1} and against spontaneous activity of mice (18%) at a dose of 25 mg kg^{-1} s.c.

EXPERIMENTAL

Mp: uncorr; $[\alpha]_D$: 28°. FAB-MS: direct-inlet on a VG ZAB-HS mass spectrometer using glycerin as matrix; EI-MS: MAT-95 mass spectrometer; ^{1}H and ^{13}C NMR: 500

Table 4. Summary of the 2D-NMR correlations of **3**

H	COSY (^{1}H)	HETCOR (^{13}C)	HOHAHA (^{1}H)	ROESY (^{1}H)
3-*O*-Glc				
Inner Glc				
1′	2′	1′	2′, 3′	3, 3′, 5′
2′	1′, 3′	2′	1′, 3′, 4′	4′
3′	2′, 4′	3′	1′, 2′, 4′, 5′	1′, 5′, 1″
4′	3′, 5′	4′	2′, 3′, 5′, 6′a	2′
5′	4′, 6′a, 6′b	5′	2′, 3′, 4, 6′a, 6′b	1′, 3′, 6′a
6′a	5′, 6′b	6′	4′, 5′, 6′b	6′b, 5′
6′b	5′, 6′a	6′	5′, 6′a	6′a
Outer Glc				
1″	2″	1″	2″, 3″	3′, 3″, 5″
2″	1″, 3″	2″	1″, 3″, 4″	4″
3″	2″, 4″	3″	1″, 2″, 4″, 5″	1″, 5″
4″	3″, 5″	4″	2″, 3″, 5″, 6″a	2″
5″	4″, 6″a, 6″b	5″	2″, 3″, 4″, 6″a, 6″b	1″, 3″, 6″a
6″a	5″, 6″b	6″	4″, 5″, 6″b	6″b, 5″
6″b	5″, 6″a	6″	5″, 6″a	6″a
28-*O*-Sugar				
Inner Glc				
1‴	2‴	1‴	2‴, 3‴	3‴, 5‴
2‴	1‴, 3‴	2‴	1‴, 3‴, 4‴	4‴
3‴	2‴, 4‴	3‴	1‴, 2‴, 4‴, 5‴	1‴, 5‴
4‴	3‴, 5‴	4‴	2‴, 3‴, 5‴, 6‴a	2‴
5‴	4‴, 6‴a, 6‴b	5‴	3‴, 4‴, 6‴a, 6‴b	1‴, 3‴, 6‴a
6‴a	5‴, 6‴b	6‴	4‴, 5‴, 6‴b	5‴, 6‴b, 1⁗
6‴b	5‴, 6‴a	6‴	5‴, 6‴a	6‴a, 1⁗
Outer Glc				
1⁗	2⁗	1⁗	2⁗, 3⁗	3⁗, 5⁗, 6⁗a, 6⁗b
2⁗	1⁗, 3⁗	2⁗	1⁗, 3⁗, 4⁗	4⁗
3⁗	2⁗, 4⁗	3⁗	1⁗, 2⁗, 4⁗, 5⁗	1⁗, 5⁗
4⁗	3⁗, 5⁗	4⁗	2⁗, 3⁗, 5⁗, 6⁗a	2⁗
5⁗	4⁗, 6⁗a, 6⁗b	5⁗	2⁗, 3⁗, 4⁗, 6⁗a, 6⁗b	1⁗, 3⁗, 6⁗a
6⁗a	5⁗, 6⁗b	6⁗	4⁗, 5⁗, 6⁗b	5⁗, 6⁗b
6⁗b	5⁗, 6⁗a	6⁗	5⁗, 6⁗a	6⁗a

and 300 MHz for δ_H, and 125 and 75 MHz for δ_C; COSY, HOHAHA and ROESY: GE OMEGA-500 spectrometer; selective INEPT and HETCOR: Nicolet NT-360 spectrometer; PC: Whatman No. 1 using the solvent systems *n*-BuOH–pyridine–H_2O (6:4:3) and *n*-BuOH–HOAc–H_2O (4:1:5, upper layer), respectively, detection with aniline phthalate.

Plant material. Roots of *Aster batangensis* were collected in August 1992 from Li-Jiang County, Yunnan Province, southwestern China. A voucher specimen was identified by Prof. Z. W. Lu and is deposited in the Herbarium of Kunming Institute of Botany, Academia Sinica, China.

Extraction and separation. The dried roots (14 kg) of *A. batangensis* were extracted (× 5) with 70% EtOH at room temp. After concn *in vacuo*, the residue (2496 g) was suspended in H_2O and then extracted with petrol, EtOAc and *n*-BuOH, successively. The *n*-BuOH extract (543 g) was subjected to CC over highly porous resin (SIP-1300) eluting initially with H_2O, followed by EtOH. The EtOH eluent (368.9 g) was chromatographed on a column of silica gel (1.8 kg, 200–300 u) eluted with a $CHCl_3$–MeOH–H_2O (80:10:1–10:10:1) gradient to give five crude fractions (frs 1–5). Fr. 4 was intially chromatographed on Sephadex LH-20 with MeOH and the fraction containing triterpene saponins was further rechromatographed over Lichroprep RP-8 eluted with a MeOH–H_2O (5:5–7:3) gradient. This afforded 1.8 g asterbatanoside F (**1**), 65 mg asterbatanoside G (**2**), 101 mg asterbatanoside H (**3**) and 57 mg asterbatanoside I (**4**).

Asterbatanoside F (**1**). Needles from MeOH, mp 218–220°, $[\alpha]_D$ −4.11° (MeOH; *c* 0.45), $C_{56}H_{90}O_{25}$. FAB-MS *m/z*: 1185 $[M + Na]^+$ and $[M + Li]^+$; ^{1}H NMR: aglycone moiety: δ0.78, 0.79, 1.08, 1.19, 1.21 and 1.45 (each 3H, each *s*, tert-Me × 6), 1.98 (3H, *s*, Ac), 4.15 and 4.60 (each 1H, each *d*, *J* = 10.5 Hz, H-23), 3.07 (1H, *dd*, *J* = 13.5, 3.5 Hz, H-18), 5.41 (*br s*, H-12); sugar moiety: Table 2; ^{13}C NMR: Tables 1 and 2.

Alkaline hydrolysis of compound **1**. A soln of **1** (25 mg) in 5% KOH–MeOH (5 ml) was heated at 100° for 4 hr. The reaction mixture was cooled to room temp. and neutralized to pH6 with dilute HCl. After removal of MeOH, the remaining mixture was passed through a column of highly porous resin eluted with H_2O and then MeOH. The MeOH eluent was treated with CH_2N_2 and evapd to dryness. The residue was subjected to CC over silica gel to

afford the methyl ester of prosapogenin (**1a**) which was identified as 3-*O*-β-D-glucopyranosyl bayogenin methyl ester by comparison of its ^1H and ^{13}C NMR data (Tables 1 and 2) with an authentic sample.

Acid hydrolysis of compound **1**. A soln of **1** (50 mg) in 2 M HCl–MeOH (6 ml) was heated at 100° for 4 hr. After cooling to room temp., the reaction mixture was neutralized with Ag_2CO_3 and filtered. The filtrate was evapd *in vacuo*. The residue was dissolved in H_2O and extracted with Et_2O. From the aq. layer, glucose and rhamnose were identified by PC and TLC (direct comparison with authentic samples). The Et_2O soln was washed with H_2O and evapd to dryness. The residue was dissolved in MeOH and treated with CH_2N_2. After removal of MeOH, the residue was recrystallized with MeOH to afford bayogenin methyl ester (12 mg) which was identified by direct comparison (co-TLC, co-mp, ^1H and ^{13}C NMR) (Table 1) with an authentic sample.

Asterbatanoside G (**2**). Amorphous powder, mp 232–234°, $[\alpha]_D$ −7.7° (MeOH; *c* 0.43). FAB-MS *m/z*: 1143 $[M + Na]^+$ and 1127 $[M + Li]^+$ ^1H NMR: aglycone moiety: δ0.80, 0.82, 1.14, 1.19, 1.31 and 1.47 (each 3H, each *s*, tert-Me × 6), 3.58 and 4.34 (each 1H, each *d*, *J* = 10.3 Hz, H-23), 5.45 (1H, *br s*, H-12); sugar moiety: Table 2; ^{13}C NMR: Tables 1 and 2.

Conversion of compound **1** *to* **2**. A soln of **1** (9 mg) in 1% $NaHCO_3$–EtOH (1:1, 5 ml) was heated at 100° for 40 min. The reaction mixture was neutralized with Dowex 50W-X 8 (H^+ form) and evapd to dryness. The residue was subjected to CC over silica gel eluted with $CHCl_3$–MeOH–H_2O (18:6:1) to give the desacyl glycoside (6 mg) which was identical to **2** (direct comparison of ^1H NMR and other physical data).

Acid hydrolysis of compound **2**. A soln of **2** (5 mg) in 2M HCl–MeOH (2 ml) was allowed to stand at 100° for 4 hr, and the precipitates formed were collected. The filtrate was evapd repeatedly at 40° until the soln showed a neutral reaction. The residue was identified as glucose and rhamnose by PC and TLC (direct comparison with standard sugars).

Asterbatanoside H (**3**). Amorphous powder, mp 229–231°, $[\alpha]_D$ +8.31° (MeOH; *c* 0.11), $C_{54}H_{88}O_{25}$. FAB-MS *m/z*: 1159 $[M + Na]^+$ and 1143 $[M + Li]^+$ ^1H NMR: aglycone moiety: δ0.79, 0.80, 1.13, 1.18, 1.28 and 1.52 (each 3H, each *s*, tert-Me × 6), 3.11 (*dd*, *J* = 13.5, 5 Hz, H-18), 3.61 and 4.33 (each 1H, each *d*, *J* = 10.0 Hz, H-23), 5.36 (1H, *br s*, H-12); sugar moiety: Table 2; ^{13}C NMR: Tables 1 and 2.

Alkaline hydrolysis of compound **3**. A soln of **3** (30 mg) in 5% KOH–MeOH (5 ml) was heated at 100° for 4 hr. The reaction mixture was cooled to room temp. and adjusted to pH6 with dilute HCl. After removal of MeOH, the remaining mixture was passed through a column of highly porous resin eluted with H_2O and then MeOH. The MeOH eluent was treated with CH_2N_2 and evapd to dryness. The residue was subjected to CC over silica gel to afford the methyl ester of prosapogenin (**3a**, 12 mg). Compound **3a**: amorphous powder, mp 157–159°. ^1H NMR: aglycone moiety: δ0.88, 0.89, 1.02, 1.16, 1.33, 1.56 (each 3H, each *s*, tert-Me × 6), 3.08 (1H, *dd*, *J* = 12.4, 4.0 Hz, H-18), 3.69 (3H, *s*, OMe), 5.38 (1H, *br s*, H-12); sugar moiety: Table 2. ^{13}C NMR: Tables 1 and 2.

Acid hydrolysis of compound **3**. A soln of **3** (5 mg) in 2M HCl–MeOH (2 ml) was heated at 100° for 4 hr, and the ppts formed were collected. The filtrate was evapd repeatedly at 40° until the soln showed a neutral reaction. The residue was identified as glucose by PC and TLC (direct comparison with an authentic sample).

Asterbatanoside I (**4**). Amorphous powder, mp 225–227°, $[\alpha]_D$ +23.66° (MeOH; *c* 0.29), $C_{56}H_{90}O_{26}$. FAB-MS *m/z*: 1227 $[M + Na]^+$ and 1211 $[M + Li]^+$ ^1H NMR: aglycone moiety: δ0.82, 0.83, 1.12, 1.26, 1.30, 1.50 (each 3H, each *s*, tert-Me × 6), 2.05 (3H, *s*, CH_3CO), 3.17 (1H, *dd*, *J* = 12.3, 4.5 Hz, H-18), 4.22 and 4.63 (each 1H, each *d*, *J* = 11.0 Hz, H-23), 5.41 (1H, *br s*, H-12); sugar moiety: Table 2; ^{13}C NMR: Tables 1 and 2.

Conversion of compound **4** *to* **3**. A soln of **4** (7 mg) in 1% $NaHCO_3$–EtOH (1:1, 5 ml) was heated at 100° for 40 min. The reaction mixture was neutralized with Dowex 50W-X8 (H^+ form) and evapd to dryness. The residue was subjected to CC over silica gel eluted with $CHCl_3$–MeOH–H_2O (18:6:1) to give the desacyl glycoside (5 mg) which was identical to **3** (comparison of ^1H NMR and physical data).

Acid hydrolysis of compound **4**. A soln of **4** (5 mg) in 2M HCl–MeOH (2 ml) was heated at 100° for 4 hr, and the ppts formed were collected. The filtrate was evapd repeatedly at 40° until the soln showed a neutral reaction. The residue was identified as glucose by PC and TLC (direct comparison with standard sugars).

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