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TRITERPENE SAPONINS FROM *ASTER YUNNANENSIS*

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Key Word Index—*Aster yunnanensis*; Compositae; triterpene saponins; asteryunnanosides A, B, C, D; arjunolic acid; maslinic acid.

Abstract—Four new triterpene saponins, asteryunnanosides A, B, C and D, have been isolated from *Aster yunnanensis* and their structures deduced as 2α,3β,23-trihydroxyolean-12-en-28-oic acid-28-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranoside, 2α,3β,23-trihydroxyolean-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside, 2α,3β-dihydroxyolean-12-en-28-oic acid-28-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranoside and 2α,3β-dihydroxyolean-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside, respectively, by means of spectral and chemical data.

INTRODUCTION

The plants of genus *Aster* have been used as drugs for the treatment of fevers, colds, tonsillitis, snake bites and bee stings in Chinese folk medicine [1]. During a search for novel bioactive compounds from medicinal plants, we found *n*-butanol extracts from *Aster yunnanensis* showed potent analgesic and sedative activities. It encouraged us to study the glycosides of this plant, collected from Li-Jiang County, Yunnan Province, southwestern China. *Aster yunnanensis* has not been chemically investigated before as far as we know and in this paper we report on the isolation and structural elucidation of four new oleane-type saponins (**1**–**4**) from the roots of this plant by a combination of ^1H–^1H COSY, HETCOR [2], HOHAHA [3, 4] and ROESY [5–7] techniques.

RESULTS AND DISCUSSION

The *n*-butanol-soluble part of the 70% ethanol extract from the roots of *A. yunnanensis* was chromatographed on a column of highly porous resin (SIP-1300) and rechromatographed on silica gel, Sephadex LH-20 and C-8 reversed-phase columns to afford asteryunnanoside A (**1**), B (**2**), C (**3**) and D (**4**).

Asteryunnanoside A (**1**) was obtained as needles, mp 238–239°. $[\alpha]_D$ − 3.16° (pyridine; *c* 0.12), and showed positive to the Liebermann–Burchard and Molish tests. Its molecular formula was calculated as $C_{42}H_{68}O_{14}\cdot 3H_2O$ by combination of its elemental analysis (Anal. Calcd: C, 59.29; H, 8.71. Found: C, 59.51; H, 8.36%) and FAB-mass spectrometry (*m/z*: 819 $[M + Na]^+$ and 803 $[M + Li]^+$). The IR spectrum of **1** showed the presence of hydroxyl (3400 cm^{-1}), ester group (1750 cm^{-1}) and glycosidic linkage (1000–1100 cm^{-1}). The ^1H NMR spectrum showed the signals of six singlet methyl groups (δ0.75, 0.82, 1.03, 1.08, 1.12 and 1.14), one trisubstituted olefinic proton (δ5.43), two anomeric sugar protons (δ6.21, *d*, *J* = 8.0 Hz and 6.65, *br s*) and one methyl at δ1.77 (*d*, *J* = 6.1 Hz) in one sugar moiety which indicated the presence of one deoxy sugar. The ^{13}C NMR spectrum revealed the presence of six quaternary carbons (δ30.8, 38.6, 40.2, 42.5, 43.6 and 47.2), a pair of olefinic carbons (δ122.4 and 144.3), one ester carbonyl carbon (δ176.4), two anomeric carbons (δ94.9 and 101.5) and one sugar methyl at δ18.8. These data suggested **1** was an oleane-type triterpene carboxylic acid diglycoside. When it was hydrolysed with mineral acid, compound **1** afforded an aglycone (**1a**) and D-glucose, L-rhamnose as sugar components which were determined by PC and TLC in direct comparison with standard sugars.

Compound **1a**, $C_{30}H_{48}O_5$, showed IR absorption bands of hydroxy and carboxyl groups. The mass spectrum of **1a** contained characteristic fragment ions at *m/z* 248 and 203 owing to retro-Diels–Alder-type fragmentation of an olean-12-en-28-oic acid without any substitution on the C, D and E rings [8]. The ^1H NMR spectrum of the peracetate (**1b**) of **1a** showed six tertiary methyls, three acetoxyl signals and an AB-type coupling at δ3.88 and 3.99 (2H, *J* = 11.8 Hz) for 23-methylene protons [9], one proton at δ5.41 (*d*, *J* = 10 Hz) for H-3α and 5.45 (*m*) for H-2β. These observations indicated that three oxygen atoms were attached to the C-2, C-3 and C-23 positions. These spectral properties suggested **1a** was 2α,3β,23-trihydroxyolean-12-en-28-oic acid (arjunolic acid). The ^{13}C NMR spectral data (Table 1) of the aglycone **1a** were

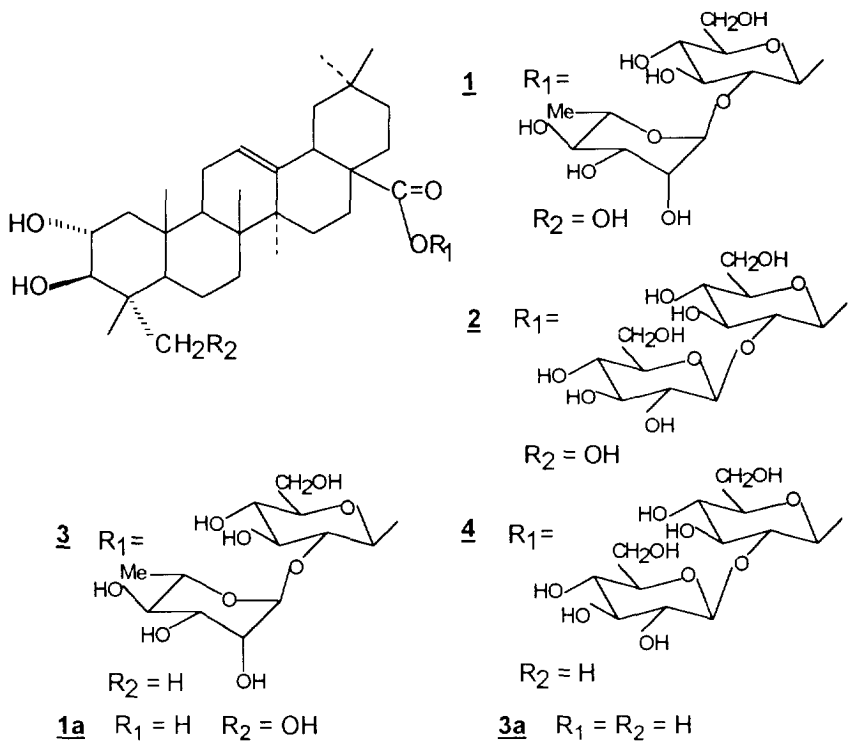

Table 1. ^{13}C NMR spectral data of aglycone moieties of compounds **1**, **2**, **1a**, **3**, **3a** and **4** (pyridine-d_5, 100 MHz for δ_C, ppm)

C	1	2	1a	3	4	3a
1	47.9	47.7	47.7	46.4	46.4	46.0
2	69.0	68.9	68.9	68.6	68.7	69.0
3	78.7	78.0	78.6	83.8	83.9	84.0
4	43.6	43.6	43.6	39.8	39.9	39.2
5	48.3	48.0	48.3	56.0	56.1	55.4
6	18.8	18.6	18.7	18.9	19.0	18.4
7	33.2	33.0	33.3	33.3	33.4	33.1
8	40.2	40.1	40.0	40.0	39.9	39.5
9	48.4	48.2	48.3	48.2	48.3	47.7
10	38.6	38.4	38.6	38.6	38.6	38.4
11	21.4	24.0	24.1	23.4	23.3	23.2
12	122.4	122.5	122.6	122.5	122.6	122.2
13	144.3	144.4	144.9	144.3	144.5	143.9
14	42.5	42.2	42.4	42.4	42.3	41.8
15	28.7	29.1	30.0	28.7	29.1	29.7
16	23.6	23.2	23.9	24.0	24.0	23.7
17	47.2	47.0	46.8	47.1	47.1	46.6
18	42.2	41.9	42.1	42.1	42.0	41.4
19	46.5	46.3	46.6	47.9	47.9	46.8
20	30.8	30.7	31.0	30.7	30.8	30.7
21	34.2	34.1	34.4	34.1	34.2	34.0
22	32.4	32.3	33.1	32.2	32.4	32.5
23	67.2	66.6	67.1	29.3	29.4	29.9
24	14.3	14.2	14.2	17.5	17.7	16.7
25	17.7	17.6	17.6	17.0	17.0	16.6
26	17.6	17.1	17.1	17.7	17.7	17.0
27	26.0	26.2	26.2	25.9	26.3	26.0
28	176.4	176.4	180.1	176.4	176.5	178.2
29	33.2	33.1	33.3	33.1	33.2	32.7
30	23.8	23.8	23.9	23.7	23.9	23.6
OMe						51.4

virtually coincident with those of arjunolic acid reported in the literature [10]. The 2D NMR spectra of **1** provided further insights into the structure of the aglycone. The ^1H-^1H COSY spectrum of **1** showed a coupling interaction between the proton δ4.23 (H-2) and δ4.20 (H-3) which assigned two hydroxyl groups to the C-2 and C-3 positions, and the HETCOR spectrum showed a strong counter at δ69.0/4.23 which indicated that the proton at δ4.23 (H-2) was attached to the carbon at δ69.0. Another strong peak linkage of the signal of H-3 at δ4.20 with the signal of C-3 at δ78.7 was observed, which confirmed the assignment of the C-2 and C-3 hydroxyl groups.

When the ^{13}C NMR spectrum of **1** was compared with that of **1a**, the upfield shift by -3.7 ppm was observed only at the C-28 signal, i.e. the glycosylation took place at C-28. The fragment ions at *m/z* 273 $[Rham(OAc)_3]^+$ and 561 $[Rham(OAc)_3 + Glc(OAc)_3]^+$ indicated the sequence of sugar moieties. In order to establish the connection between glucose and rhamnose units, the complete assignment of ^1H and ^{13}C NMR data of sugar units was performed by using ^1H–^1H COSY and ^{13}C–^1H COSY spectra (Table 2).

The anomeric proton signal at δ6.21 (*d*) was easily designated as the H-1′ of the inner glucose and the anomeric broad singlet at δ6.65 as H-1″ of the rhamnosyl moiety. From the ^1H–^1H COSY spectrum, the anomeric proton signal for H-1′ at δ6.21 was coupled to the H-2′ proton signal at δ4.51 and continuing this *J*-connectivity path, it was possible to locate H-3′ at δ4.38, H-4′ at δ4.36, H-5′ at δ4.00 and H-6′ at δ4.41. Similarly, from the second anomeric singlet H-1″ at δ6.65, the *J*-connectivity pathway can be traced out from the ^1H–^1H COSY spectrum identifying all the couplings belong to the

Table 2. NMR spectral data of sugar moieties of compounds **1**–**4** (400 MHz for δ_H, 100 MHz for δ_C, ppm, J = Hz)

	1		**2**		**3**		**4**	
Position	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
inner Glc								
1′	6.21 (*d*, 8.0)	94.9	6.20 (*d*, 8.2)	93.6	6.21 (*d*, 7.9)	94.9	6.22 (*d*, 8.3)	93.7
2′	4.51 (*dd*, 8.0, 8.3)	76.1	4.48 (*dd*, 8.2, 8.4)	78.2	4.52	75.5	4.52 (*dd*, 8.3, 8.4)	74.0
3′	4.38	79.7	4.28	78.7	4.40	79.9	4.29	79.0
4′	4.36	71.6	4.24	70.8	4.36	71.3	4.26	70.9
5′	4.00	78.9	3.91	80.0	3.99	79.0	3.92	79.1
6′	4.41	62.4	4.36	62.1	4.41	62.0	4.38	62.2
Rham								
1″	6.65 (*br s*)	101.5			6.67 (*br s*)	101.4		
2″	4.83	72.3			4.82	72.3		
3″	4.58	72.6			4.59	72.6		
4″	4.34	74.0			4.35	73.9		
5″	4.58	69.9			4.59	69.8		
6″	1.77 (*d*, 6.1)	18.8			1.77 (*d*, 5.5)	18.7		
outer Glc							5.76 (*d*, 7.7)	104.7
1″			5.74 (*d*, 7.6)	104.6			4.12	76.0
2″			4.09	75.9			4.28	78.2
3″			4.26	78.2			4.14	72.9
4″			4.07	72.8			4.06	78.2
5″			4.02	78.0			4.69	63.9
6″			4.39, 4.66	63.8			4.42	

rhamnose spin system. The ^{13}C–^{1}H COSY spectrum revealed the direct correlation between the carbons and their attached protons which allowed the ^{13}C NMR data of the oligosaccharide portion to be completely assigned.

The C-2′ signal of the glucose moiety in the ^{13}C NMR spectrum was at lower field by + 1.33 ppm than that of methyl β-D-glucopyranoside [11]. This observation implied that the rhamnosyl moiety was bound through the glycoside linkage to the C-2′ hydroxyl group of the glucosyl moiety. The low-field resonance of the H-2′ signal at δ4.51 also supported this proposal. The configuration of the glucosyl group was easily confirmed as β based on $J_{1,2}$ = 8.0 Hz. The C-5″ signal of the rhamnosyl unit was at δ69.9 showing that the rhamnose had the α-configuration [11]. Consequently, asteryunnanoside A (**1**) was formulated as 2α,3β,23-trihydroxyolean-12-en-28-oic acid-28-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranoside.

Asteryunnanoside B (**2**), mp 221–223°, $[\alpha]_D$ + 17.12° (MeOH; *c* 0.92), had the molecular formula, $C_{42}H_{68}O_{15}\cdot 3H_2O$, deduced from the FAB-mass spectrum (*m/z* 835 $[M + Na]^+$ and 819 $[M + Li]^+$) as well as the elemental analysis (Anal. Calcd: C, 58.20; H, 8.55. Found: C, 58.10; H, 8.73%). The ^{1}H and ^{13}C NMR data correponding to the aglycone portion of **2** were essentially identical with those of compound **1**, indicating that **2** could be assigned as a glycoside of arjunolic acid with a sugar moiety at the C-28 position.

On acid hydrolysis, **2** afforded D-glucose as the sugar component. The two anomeric proton signals at δ6.20 (*d*, J = 8.2 Hz) and 5.74 (*d*, J = 7.6 Hz) indicated the presence of two β-D-glucose units. The ^{13}C NMR spectrum showed two glucosyl anomeric carbon signals at δ93.6 and 104.6. Assignment of the NMR spectral data of two glucose units was made possible by performing a series of 2D NMR experiments including COSY, HETCOR, HOHAHA and ROESY.

Examination of ^{13}C NMR data in the sugar region of **2** showed a significant downfield chemical shift of the inner glucose C-2′ by + 3.43 ppm by comparison with that of methyl β-D-glucopyranoside, demonstrating that the other glucose unit was attributed to the C-2′ position of the inner glucose moiety. Furthermore, a significant NOE contour observed between the outer glucose H-1″ and inner glucose H-2′ in the ROESY spectrum confirmed the connection of two glucose units. In addition, the inner glucose H-1′, showing a NOE correlation with its H-3′, H-5′, further confirmed the β-configuration. Similarly, the outer glucose H-1″, showing a NOE contour with H-3″ and H-5″, led to the confirmation of the β-configuration. Therefore, asteryunnanoside B (**2**) was determined to be 2α,3β,23-trihydroxyolean-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside.

Asteryunnanoside C (**3**) was obtained as needles, mp 216–218° (from MeOH), $[\alpha]_D$ − 19.69° (pyridine; *c* 0.32). The IR spectrum presented characteristic absorption for hydroxy (3400 cm^{-1}), ester group (1750 cm^{-1}) and glycosidic linkage (1000–1100 cm^{-1}). The FAB-mass spectrum exhibited two quasimolecular ion peaks at *m/z* 803 $[M + Na]^+$ and 787 $[M + Li]^+$, which together with elemental analysis (Anal. Calcd : C, 61.77; H, 8.82. Found: C, 62.01; H, 8.85%.) provided the molecular formula $C_{42}H_{68}O_{13}\cdot 2H_2O$ for **3**. The ^{1}H NMR spectrum showed the signals of seven singlet methyl groups (δ0.76, 0.85,

0.99, 1.03, 1.09, 1.21 and 1.22), one trisubstituted olefinic proton (δ5.44) and two anomeric protons δ6.21 (*d*, J = 7.9 Hz) and 6.67 (*br s*). The ^{13}C NMR spectrum revealed the presence of six quaternary carbons (δ30.7, 38.9, 39.8, 40.0, 42.4 and 47.1), a pair of olefinic carbons (δ122.5 and 144.3), one esteric carbon (δ176.4) and two anomeric carbons (δ94.9 and 101.4). These results suggested **3** was also an oleane-type triterpene carboxylic acid glycoside.

On mineral acid hydrolysis, followed by treatment with diazomethane, **3** provided an aglycone methyl ester (**3a**), glucose and rhamnose as sugar components which were determined by PC and TLC in direct comparison with authentic samples. The EI-mass spectrum of **3a** gave the molecular ion peak at *m/z* 486 together with the fragment ion peaks at *m/z* 262 and 203 deriving from the D/E ring and *m/z* 223 from the A/B ring, all of which were formed through the characteristic retro-Diels–Alder fragmentation at the C ring in the olean-12-en-28-oic acid methyl ester skeleton without any substitutions on the C, D and E rings and with two hydroxyl groups on the A and B rings. The ^{1}H NMR spectrum of **3a** showed two signals corresponding to two hydroxy-bearing axial methine protons at δ3.12 (*d*, J = 9.5 Hz, H-3α) and δ3.67 (*m*, H-2β), together with signals owing to seven tertiary methyl and one methoxy-carbonyl group. From these spectral features, the structure of aglycone methyl ester has been clarified as 2α,3β-dihydroxyolean-12-en-28-oic acid methyl ester. Its ^{13}C NMR spectral data were identical with the methyl ester of maslinic acid [12].

The EI-mass spectrum of a peracetate of **3** exhibited the characteristic fragment ions of terminal $[Rham(OAc)_3]^+$ (*m/z* 273) and $[Rham(OAc)_3\text{-}Glc(OAc)_3]^+$ (*m/z* 561), which indicated that the sequence of sugar moieties was rhamnosyl-glucosyl at the C-28 carboxyl group. The ^{1}H and ^{13}C NMR spectral data of the sugar part in **3** were ambiguously assigned by ^{1}H–^{1}H COSY and HETCOR spectra (Table 2). The location of the rhamnosyl unit was elucidated by the fact that the C-2′ signal of the glycosyl unit appeared at lower field (+ 0.67 ppm) than that of methyl β-D-glucopyranoside [11] and the glucose H-2′ resonated at deshielded δ4.52 owing to the glycosidation effect. This demonstrated that the rhamnosyl unit was attached to the C-2′ position of the glucosyl unit. It was confirmed by the ROESY spectrum of **3**, which showed the NOE correlation contour between the H-1″ of the rhamnosyl moiety and H-2′ of the glucosyl unit. The anomeric configuration of the glucosyl unit was determined as β from the value of $J_{1,2}$(7.9 Hz) and the chemical shift (δ94.9) of the anomeric carbon. The C-5″ signal of the rhamnosyl unit in **3** was at δ69.8 and, therefore, the rhamnosyl unit had the α-configuration. Based on the above evidence, the structure of asteryunnanoside C (**3**) was confirmed as 2α,3β-dihydroxyolean-12-en-28-oic acid-28-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranoside.

Asteryunnanoside D (**4**) was obtained as needles of mp 217–219°C. The IR spectrum showed strong absorption bands owing to an ester group (1735 cm^{-1}) and a group of broad absorption bands (3400, 1100 cm^{-1}) corresponding to the glycosidic structure of **4**. The proton and carbon signals of its aglycone moiety were found to be identical with those of **3**. Thus, **4** could be assigned as a glycoside of maslinic acid with a sugar moiety at C-28.

Acid hydrolysis of **4** provided maslinic acid and glucose. In the ^{1}H NMR spectrum of **4**, the two anomeric protons at δ5.76 (*d*, J = 7.7 Hz) and 6.22 (*d*, J = 8.3 Hz) led to the assignments of the anomeric configurations of the two glucosyl moieties as β. Because of the obvious lower field shift of C-2′ by + 4.19 ppm in the inner glucosyl moiety than the signal of methyl β-D-glucopyranoside [11], the outer glucosyl unit was linked to the C-2′ of the inner glucosyl unit. Its structure was also confirmed by the identical NMR data corresponding to the sugar portion of **4** with those of **2**. Therefore, asteryunnanoside D (**4**) was determined to be 2α,3β-dihydroxyolean-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranoside.

EXPERIMENTAL

Mps: uncorr.; $[\alpha]_D$: at 28°; FAB-MS: glycerin matrix. ^{1}H and ^{13}C NMR, ^{1}H–^{1}H COSY, HETCOR spectra were obtained on a Bruker AM-400 spectrometer operating at 400 MHz for δ_H and 100 MHz for δ_C. HOHAHA and ROESY spectra were obtained on a GE OMEGA-500 spectrometer operating at 500 MHz for δ_H. PC of sugars were run on Whatman No. 1 using the solvent systems *n*-BuOH–pyridine–H_2O (6:4:3) and *n*-BuOH–HOAc–H_2O (4:1:5, high layer).

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

Extraction and separation. The dried roots (15 kg) of *A. yunnanensis* were extracted with 70% EtOH (5 ×) at room temp. After concn *in vacuo*, the residue (3.8 kg) was suspended in H_2O and then extracted with petrol, EtOAc and *n*-BuOH, successively. The *n*-BuOH layer was evapd. under red. pres. to give a residue (698 g). This residue was chromatographed on a column of highly porous resin (SIP-1300) eluting initially with H_2O and followed by EtOH. The EtOH eluate (350 g) was subjected to CC on silica gel (1.5 kg) eluting with $CHCl_3$–MeOH–H_2O (80:10:1–10:10:1) gradient to separate into 8 crude frs (frs 1–8). Fr. 3 was sepd by repeated CC over silica gel with $CHCl_3$–MeOH–H_2O (40:10:1) as eluent and finally purified by Lichroprep RP-8 column with MeOH–H_2O (1:1) to yield 125 mg asteryunnanoside C (**3**). Fr. 4 was initially subjected to CC on Sephadex LH-20 eluting with MeOH and the fr. showed the presence of saponins. This was followed by silica gel chromatography with $CHCl_3$–MeOH–H_2O (30:10:1) as eluent and 2 frs were obtained. Each fr. was finally purified by Lichroprep RP-8 CC with MeOH–H_2O (3:2) to give 458 mg of asteryunnanoside A (**1**) and 95 mg of asteryunnanoside D (**4**). Fr. 5 was repeatedly chromatographed on a silica gel column

with $CHCl_3$–MeOH–H_2O (30:10:1) as solvent, and purified by Sephadex LH-20 (MeOH) and Lichroprep RP-8 to obtain 7.2 g of asteryunnanoside B (**2**).

Asteryunnanoside A (**1**). Obtained as needles, mp 238–239°, $[\alpha]_D$ − 3.16° (pyridine; *c* 0.12). Anal: Calcd for $C_{42}H_{68}O_{14}\cdot 3H_2O$: C, 59.29; H, 8.71. Found: C, 59.51: H, 8.36%. IR ν_{KBr} cm^{-1}: 3400, 1750, 1640, 1000–1100. ^1H NMR (pyridine-d_5): aglycone moieties: δ0.75, 0.82, 1.03, 1.08, 1.12 1.14 (each *s*, 6 × tert-Me), 3.08 (1H, *dd*, *J* = 13.5, 3.5 Hz, H-18), 3.63 (1H, *d*, *J* = 10.5 Hz, H-23a), 4.18 (1H, *d*, *J* = 10.5 Hz, H-23b), 5.43 (1H, *br s*, H-12), 4.20 (1H, *m*, H-3), 4.23 (1H, *m*, H-2); sugar moieties: see Table 2. ^{13}C NMR: see Tables 1 and 2. FAB-MS *m/z*: 819 $[M + Na]^+$ and 803 $[M + Li]^+$.

Acid hydrolysis of compound **1**. A soln of **1** (80 mg) in 2 M HCl–MeOH (8 ml) was heated at 100° for 4 hr. After cooling to room temp., the reaction mixt. was neutralized with Ag_2CO_3 and filtrated. 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 in direct comparison with authentic samples. The Et_2O soln was washed with H_2O and evapd to dryness. The residue was recrystallized with MeOH to afford the aglycone, arjunolic acid (**1a**) (35 mg), needles, mp 251–253° (from MeOH), $[\alpha]_D$ + 64° (MeOH; *c* 0.23). IR ν_{KBr} cm^{-1}: 3400, 1700, 1640; EIMS *m/z*: 488 $[M]^+$ ($C_{30}H_{48}O_5$), 470, 452, 248, 240, 230, 215, 203 and 147. ^1H NMR (pyridine-d_5): δ0.89, 0.97, 1.02, 1.04, 1.05, 1.17 (each 3H, each *s*, tert-Me × 6), 3.26 (1H, *dd*, *J* = 10.5, 4.0 Hz, H-18), 3.71 and 4.19 (each 1H, each *d*, *J* = 10.4 Hz, H-23), 4.20 (1H, overlap, H-3), 4.21 (1H, overlap, H-2) 4.23 (1H, overlap, H-12). ^{13}C NMR: see Table 1. Acetylation of **1a** with Ac_2O–pyridine (1:1) at room temp. overnight gave arjunolic acid triacetate (**1b**), mp 133–135°, ^1H NMR (pyridine-d_5): δ0.85, 0.91, 0.95, 0.97, 0.98, 1.28 (each 3H, each *s*, tert-Me × 6), 2.05, 2.07 and 2.11 (each 3H, each *s*, OAc × 3), 3.28 (1H, *dd*, *J* = 10.4, 4.0 Hz, H-18), 3.88 and 3.99 (2H, AB*q*, *J* = 11.8 Hz, H-23), 5.41 (1H, *d*, *J* = 10.0 Hz, H-3α), 5.45 (1H, *m*, H-2β), 5.46 (1H, *br s*, H-12).

Asteryunnanoside B (**2**). Needles, mp 221–223°, $[\alpha]_D$ + 17.12° (MeOH; *c* 0.92), Anal. Calcd for $C_{42}H_{68}O_{15}\cdot 3H_2O$: C, 58.20; H, 8.55. Found: C, 58.10; H, 8.73%. IR ν_{KBr} cm^{-1}: 3400, 1730, 1640, 1000–1100. FAB-MS *m/z*: 835 $[M + Na]^+$ and 819 $[M + Li]^+$. ^1H NMR (pyridine-d_5): aglycone moiety: δ0.82, 0.82, 0.976, 0.99, 1.04 and 1.11 (each *s*, tert-Me × 6), 3.10 (1H, *dd*, *J* = 11, 2.5 Hz, H-18), 3.61 and 4.14 (each *d*, each 1H, *J* = 10.5 Hz, H-23), 5.39 (1H, *br s*, H-12); sugar moiety: see Table 2.

Acid hydrolysis of compound **2**. A soln of **2** (10 mg) in 2 M HCl–MeOH (2 ml) was heated at 100° for 4 hr and arjunolic acid was obtained and identified by comparison with an authentic sample. The sugar part was detected by PC and TLC as glucose in direct comparison with a standard sugar.

Asteryunnanoside C (**3**). Mp 216–217°, $[\alpha]_D$ − 19.69° (pyridine; *c* 0.32). IR ν_{KBr} cm^{-1}: 3400, 1750, 1630, 1000–1100. FAB-MS *m/z*: 803 $[M + Na]^+$ and 787 $[M + Li]^+$. Anal. Calcd for $C_{42}H_{68}O_{13}\cdot 2H_2O$: C, 61.77; H, 8.82. Found: C, 62.01; H, 8.85%. ^1H NMR: aglycone moiety: δ0.76, 0.85, 0.99 1.03, 1.09, 1.21, 1.22 (each *s*, each 3H, tert-Me × 6), 3.13 (1H, *dd*, *J* = 13.5, 4.0 Hz, H-18), 3.36 (1H, *d*, *J* = 9.1 Hz), 5.44 (1H, *br s*, H-12); sugar moiety: see Table 2. ^{13}C NMR: see Tables 1 and 2.

Acid hydrolysis of compound **3**. Compound **3** (50 mg) was hydrolysed in 2 M HCl–MeOH (5 ml) at 100° for 4 hr. The aglycone was isolated and after methylation with etheral CH_2N_2 the aglycone methyl ester (20 mg) (**3a**) was obtained. The sugar part was determined as glucose and rhamnose by PC and TLC in direct comparison with standard sugars. Compound **3a** (maslinic acid methyl ester): needles, mp 249–252°, $[\alpha]_D$ + 78° ($CHCl_3$; *c* 0.5). $C_{31}H_{50}O_4$. EIMS *m/z*: 486 $[M + Na]^+$, 468 $[M - H_2O]^+$, 426 $[M - HCO_2Me]^+$, 450 $[M - 2H_2O]^+$, 409 $[M - HCO_2Me - H_2O + 1]^+$, 391 $[M - HCO_2Me - 2H_2O + 1]^+$, 262 (95), 203 (100), 223, 189, 249, 190, 471, 233. ^1H NMR (pyridine-d_5): δ0.85, 0.94, 1.02, 1.05, 1.10, 1.15 and 1.25 (each 3H, each *s*, tert-Me × 7), 3.12 (1H, *d*, *J* = 9.5 Hz, H-3α), 3.59 (3H, *s*, OMe), 3.67 (1H, *m*, H-2β), 5.40 (1H, *dd*, *J* = 3.4, 3.0 Hz, H-12). ^{13}C NMR: see Table 1.

Asteryunnanoside D (**4**). Mp 217–219°, $[\alpha]_D$ + 6.93° (pyridine; *c* 0.44). IR ν_{KBr} cm^{-1}: 3400, 1735, 1635, 1050–1100. FAB-MS *m/z*: 819 $[M + Na]^+$ and 803 $[M + Li]^+$. ^1H NMR: aglycone moiety: δ0.85, 0.86, 0.91, 1.00, 1.02, 1.20, 1.20 (each 3H, each *s*, tert-Me × 7), 3.14 (1H, *dd*, *J* = 13.5, 4.0 Hz, H-18), 3.36 (1H, *d*, *J* = 9.3 Hz, H-3), 4.05 (1H, *m*, H-2), 5.43 (1H, *br s*, H-12); sugar moiety: see Table 2. ^{13}C NMR: see Tables 1 and 2.

Acid hydrolysis of compound **4**. Compound **4** (10 mg) was hydrolysed under the conditions and worked-up under the procedure described for **3** to give the aglycone methyl ester identified as maslinic acid methyl ester by comparison of physical and ^1H NMR data with an authentic sample. The sugar part was determined as glucose by PC and TLC in direct comparison with a standard sugar.

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