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PHENOLIC AND TRITERPENOID GLYCOSIDES FROM *ASTER BATANGENSIS*

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Key Word Index—*Aster batangensis*; Compositae; phenolic glycoside; triterpenoid saponins; arjunolic acid; bayogenin; asterbatanosides A, B and C.

Abstract—A new phenolic glycoside, asterbatanoside A [*p*-hydroxyacetophenone-4-*O*-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside], and two new triterpenoid saponins, asterbatanoside B [2α,3β,23-trihydroxyolean-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside] and asterbatanoside C [3-*O*-β-D-glucopyranosyl-2β,3β,23-trihydroxyolean-12-en-28-oic acid-28-*O*-β-D-glucopyranoside] were isolated from the roots of *Aster batangensis*. Their structures were determined by spectroscopic methods and chemical evidence. The total synthesis of asterbatanoside A is also reported.

INTRODUCTION

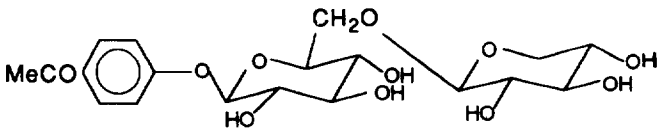
The genus *Aster* contains more than 100 species in China. Among them, 15 species have been used as drugs for the treatment of fevers, colds, tonsillitis, snake bites and bee stings in Chinese folk medicine [1]. However, only a few species have been chemically studied in China [2, 3]. During a search for bioactive extracts from the plants of this genus, pharmacological experiments showed that the *n*-butanol-soluble fraction of *Aster batangensis* had potent sedative activity. This encouraged us to further study the glycoside constituents of this plant. A new phenolic diglycoside named asterbatanoside A (**1**) and two triterpenoid saponins named asterbatanoside B (**2**) and C (**3**) have been isolated. The present paper mainly describes their structural elucidation. In addition, we also report the total synthesis of asterbatanoside A (**1**).

RESULTS AND DISCUSSION

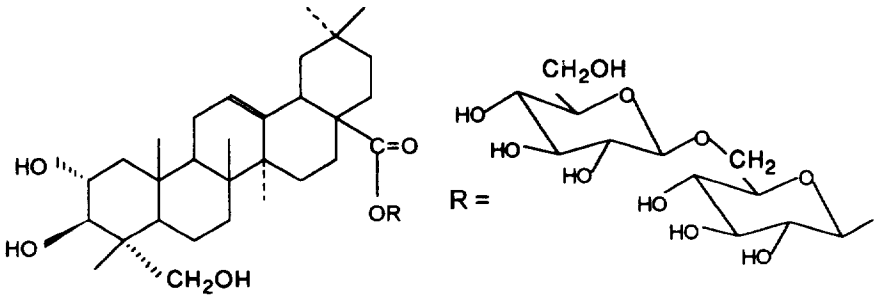
The *n*-butanol-soluble fraction of the 70% ethanol extract from the roots of *A. batangensis* was subjected to CC on highly porous resin (SIP-1300) and rechromatographed over silica gel, Sephadex LH-20 and reverse-phase C-8 columns to afford asterbatanosides A (**1**), B (**2**) and C (**3**).

Asterbatanoside A (**1**) was obtained as a white amorphous powder, mp 226–228°, $[\alpha]_D$ − 68.47° (pyridine; *c* 0.66). The FAB-mass spectrum ($[M + Na]^+$ at *m/z* 453 and $[M + Li]^+$ at *m/z* 437) in combination with its ^1H and ^{13}C NMR spectra suggested a molecular formula of $C_{19}H_{26}O_{11}$. The IR spectrum showed absorptions at 3400 (OH), 1665 (C=O of acetyl), 1600 and 1510 (aromatic ring), and 1000–1100 (glycosidic linkage). The ^1H NMR spectrum of **1** indicated four aromatic proton resonances at δ7.43 (2H, *d*, *J* = 8.8 Hz) and δ8.05 (2H, *d*, *J* = 8.8 Hz), one acetyl singlet at δ2.39 and 13 sugar proton resonances in the region δ3.36–5.63, including two anomeric proton resonances at δ5.63 (*d*, *J* = 7.4 Hz) and 4.91 (*d*, *J* = 7.2 Hz). These data suggested that **1** was a phenyl diglycoside and the two sugars were a pentose and a hexose. Acid hydrolysis of **1** afforded an aglycone (**1a**) identified as *p*-hydroxyacetophenone by means of its ^1H NMR and mass spectra and in direct comparison of co-TLC, co-mp with an authentic sample. The sugars obtained from the hydrolysates were identified as glucose and xylose by PC and TLC. In the El-mass spectrum of the peracetate of **1**, the observation of two prominent fragment ion peaks at *m/z* 259 ($[xyl(OAc)_3]^+$) and 547 ($[xyl(OAc)_3\text{-}glc(OAc)_3]^+$) supported this result and provided the sequence as xylosyl–glucosyl–aglycone. The $J_{1,2}$ values of two anomeric proton signals as mentioned above indicated β-glucosidic linkages of β-glucopyranose and β-D-xylopyranose, which were supported by the chemical shifts of the anomeric carbons. Examination of the ^{13}C NMR spectrum in the sugar carbon region showed that the glucose C-6 resonated at δ69.4, which was more downfield than the corresponding original sugar moiety. Thus, the xylosyl unit was attached to the C-6 position of the glucosyl unit. Therefore, asterbatanoside A (**1**) was proved to be *p*-hydroxyacetophenone-4-*O*-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside. The structure of **1** was unambiguously confirmed by the synthesis described here.

p-Hydroxyacetophenone (**1a**) was used a starting material, from which the target molecule **1** was prepared through a reaction sequence of seven steps in an overall



1



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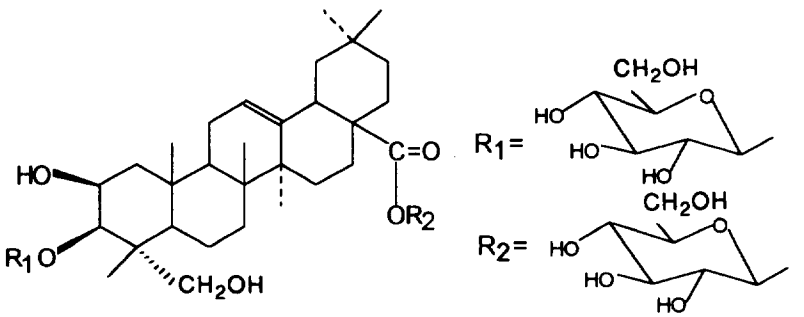

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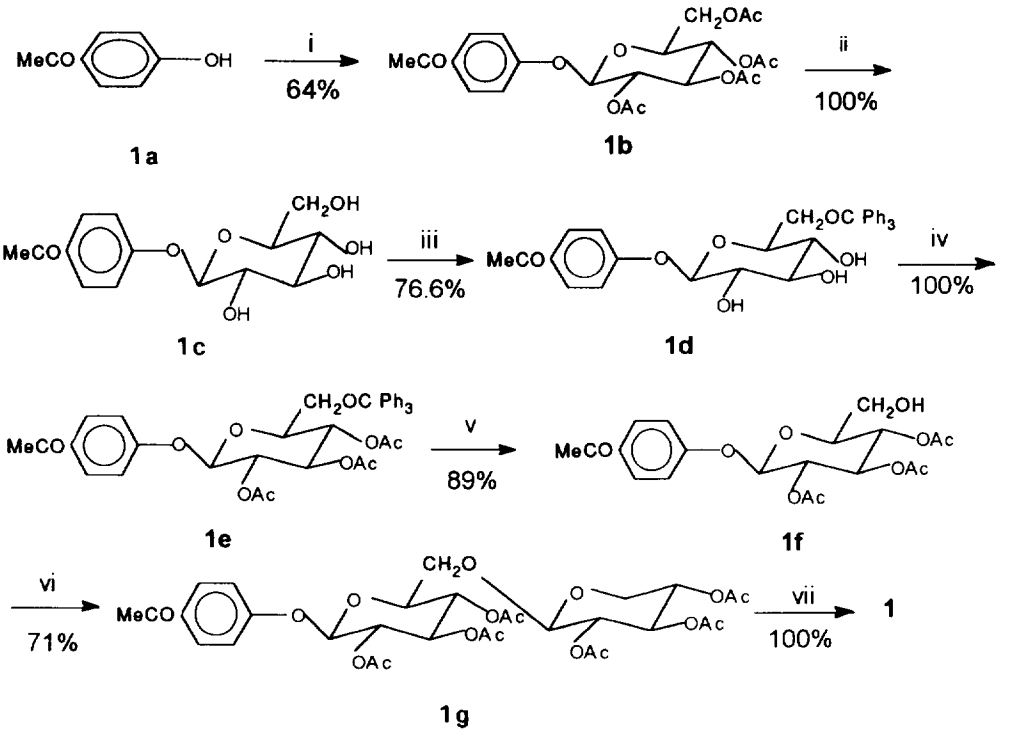
yield of 31% (Scheme 1). Glycosylation of **1a** with α-D-glucopyranosyl bromide tetraacetate in acetone–water (1:1) in the presence of NaOH afforded the desired compound **1b** in 64% yield. This reaction was stereoselective, affording only the β-D-anomer [4]. Deacetylation of **1b** in a MeOH–NEt_3–H_2O (8:1:1) mixture gave **1c** in essentially quantitative yield [5]. The configuration of the glucopyranosyl was β based on the coupling constant of the anomeric proton ($J_{1,2}$ = 7.6 Hz) in the ^{1}H NMR spectrum of **1c**. Selective protection of **1c** as the trityl ether (Ph_3CCl–pyridine–DMAP, reflux) followed by usual acetylation provided **1e** [6]. Selective cleavage of the trityl ether with HOAc–H_2O (4:1) yielded compound **1f** (89%). Treatment of **1f** with α-D-xylopyranosyl bromide tetraacetate in the presence of silver oxide and molecular sieves (4Å) furnished the desired β-D-xyloside (71%) and a small amount of the α-anomer (< 10%) [7]. The β-D-configuration of the xylosyl unit was confirmed by the coupling constant ($J_{1,2}$ = 7.2 Hz) of the anomeric proton. Deacetylation of **1g** with MeOH–Et_3N–H_2O (8:1:1) led to **1**. The IR, MS, ^{1}H NMR and ^{13}C NMR data of synthetic **1** were identical with those of asterbatanoside A.

Asterbatanoside B (**2**) was obtained as an amorphous powder from MeOH mp 206–208°, $[\alpha]_D$ + 16.32° (MeOH; *c* 0.34). The molecular formula, $C_{42}H_{68}O_{15}H_2O$ was deduced from its FAB-mass spectrum (*m/z*: 835 $[M + Na]^+$ and 819 $[M + Li]^+$) and elemental analysis (Found: C, 60.69; H, 8.45. Anal. calcd: C, 60.72; H, 8.43%). Acid hydrolysis of compound **2** afforded an aglycone and a sugar constituent. The aglycone was identified as arjunolic acid by comparison of co-TLC and ^{1}H NMR data with an authentic sample in our laboratory. The sugar constituent was identified as glucose by PC and TLC (direct comparison with a standard sugar). It was suggested that **2** was an ester glycoside as its IR spectrum showed an absorption at 1730 cm^{-1}. The ^{1}H NMR spectrum of compound **2** showed the signals of two anomeric protons at δ5.03 (*d*, *J* = 7.9 Hz) and 6.26 (*d*, *J* = 8.0 Hz). The ^{13}C NMR spectrum revealed the presence of two anomeric carbon signals at δ95.4 and 104.9. The number of anomeric signals suggested that **2** contained 2 mol of glucose units. The two glycosidic linkages could be regarded as having β-configurations from the coupling constants of the anomeric protons. Comparison of the ^{13}C NMR data (Table 1) of **2** with those of methyl β-D-glucopyranoside indicated that the C-6 resonance of the inner glucose unit was significantly shifted downfield by + 6.8 ppm to δ69.3, and the C-5 signal was shifted slightly upfield. This suggested that the



Reagents and Conditions:
(i) α-D-glucopyranosyl bromide tetraacetate-acetone, NaOH–H_2O, 14°, 6 hrs; (ii) MeOH–NEt_3–H_2O (8:1:1) r.t., overnight; (iii) Ph_3CCl–Pyridine–DMAP, 100°, 12 hrs; (iv) Ac_2O–Pyridine, r.t., overnight; (v) AcOH–H_2O (8:2), 100°, 1 hr; (vi) α-D-xylopyranosyl bromide triacetate–$CHCL_3$, Ag_2O, 4Å molecular sieve, N_2, r.t., 25 hrs; (vii) MeOH–NEt_3–H_2O (8:1:1), r.t., overnight.

Scheme 1. Reaction sequence for preparation of **1**.

other glucose unit was attached through the glycoside linkage to the C-6 hydroxyl group of the inner glucose unit. The EI-mass spectrum of peracetylated **2** gave the prominent fragment ion peaks at *m/z* 331 and 619 corresponding to $[glc(OAc)_4]^+$ and $[glc(OAc)_4glc(OAc)_3]^+$, respectively, which provided additional evidence for the proposed sequence of the sugar units. Therefore, asterbatanoside B (**2**) was identified as 2α,3β,23-trihydroxyolean-12-en-28-oic acid-28-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranoside.

Asterbatanoside C (**3**) was obtained as an amorphous powder, mp 231–233°, $[\alpha]_D$ + 29.18° (MeOH; *c* 0.49). Its molecular formula, $C_{42}H_{68}O_{15}$, was established by FAB-MS (*m/z* 835 $[M + Na]^+$ and 819 $[M + Li]^+$) and ^{13}C NMR data (Table 1). The ^1H and ^{13}C NMR data of the aglycone part of compound **3** were identical with those of asteryunnanoside E isolated from *Aster yunnanensis* [8]. Thus, compound **3** was determined as a 3,28-bisdesmoside of bayogenin. The structure of the aglycone was further confirmed by the acidic hydrolysis of **3**, which afforded bayogenin and glucose. The ^{13}C NMR spectrum of **3** showed signals at δ95.8 and 105.6 due to anomeric carbons of two glucose units. The former was considered to be an ester-linkage glucose unit and the latter was linked to the C-3 position of the aglycone. In the ^1H NMR spectrum, two anomeric protons at δ5.18 and 6.33 appeared as doublets (J = 8.0 Hz) indicating their β-configurations. When **3** was subjected to alkaline hydrolysis, a prosapogenin was obtained. The methyl ester of the prosapogenin was proved to be 3-*O*-β-D-glucopyranosyl-bayogenin methyl ester identified by comparison of co-TLC and ^{13}C NMR data with an authentic sample, which was obtained from asteryunnanoside E [8]. Therefore, asterbatanoside C (**3**) was deduced to be 3-*O*-β-D-glucopyranosyl-2β,3β,23-trihydroxyolean-12-en--28-oic acid-28-*O*-β-D-glucopyranoside.

EXPERIMENTAL

Mps: uncorr.; $[\alpha]_D$: at 28°. FAB-MS: glycerin as matrix. EIMS were obtained on a MAT-95 mass spectrometer. ^1H and ^{13}C NMR spectra were obtained on Burker AM-400 spectrometer operating at 400 MHz for δ_H, and 100.6 MHz for δ_C. 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, upper layer), respectively, and detected with aniline hydrogen phthalate.

Plant materials. The roots of *Aster batangensis* were collected in August 1992 from Li-Jiang County, Yunnan

Table 1. ^{13}C NMR data of compounds **2** and **3** (pyridine-d_5, 100.6 MHz)

Position	2	3	Position	2	3
Aglycone			Sugar moieties		
1	47.5	44.2	28-*O*-inner glc		
2	68.6	70.5	1	95.4	95.8
3	78.1	83.3	2	73.6	74.2
4	43.3	42.4	3	78.4[a]	79.2[a]
5	48.0	48.9	4	71.4	71.4[b]
6	18.3	18.2	5	77.6	78.6[a]
7	32.6	32.7	6	69.3	62.5
8	39.8	40.2	28-*O*-outer glc		
9	47.5	47.9	1	104.9	
10	38.2	37.1	2	74.8	
11	23.7	24.1	3	78.3[a]	
12	122.5	123.3	4	70.9	
13	143.9	144.2	5	78.0[a]	
14	42.0	42.4	6	62.5	
15	28.0	28.3	3-*O*-glc		
16	23.2	23.6	1		105.6
17	46.8	47.1	2		75.5
18	41.5	41.9	3		78.9[a]
19	46.0	46.3	4		71.7[b]
20	30.4	30.8	5		78.2[a]
21	33.8	34.2	6		62.8
22	32.3	32.7			
23	66.7	65.9			
24	13.9	14.9			
25	17.4	17.2			
26	17.2	17.4			
27	25.7	26.0			
28	176.1	176.4			
29	32.8	33.1			
30	23.4	23.8			

glc = β-D-glucopyranosyl.
[a,b]Interchangeable values.

Province, 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 (14 kg) of *A. batangensis* were extracted with 70% EtOH (5×) at room temp. After concn *in vacuo*, the residue (2469 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 eluate (368.9 g) was chromatographed on a column of silica gel (1.8 kg, 200–300 u) eluted with $CHCl_3$–MeOH–H_2O (80:10:1–10:1) 10: gradient to separate into five crude frs (frs 1–5). Fr. 1 was further sepd by CC over Sephadex LH-20 with MeOH as the mobile phase to give 65 mg of asterbatanoside A (**1**). Fr. 2 was rechromatographed with Sephadex LH-20 using MeOH as solvent and further sepd by Lichroprep RP-8 CC with MeOH–H_2O (3:2) to afford 182 mg of asterbatanoside B (**2**) and 70 mg of asterbatanoside C (**3**).

Asterbatanoside A (**1**). Obtained as an amorphous powder. Mp 226–228°. $[\alpha]_D$ − 68.47° (pyridine; *c* 0.66). $C_{19}H_{26}O_{11}$. FAB-MS *m/z*: 453 $[M + Na]^+$ and 437 $[M + Li]^+$. IR ν_{max}^{KBr} cm^{-1}: 3400, 1665, 1600, 1510, 1000–1100. ^{1}H NMR (pyridine-d_5, 400 MHz): δ4.91 (1H, *d*, *J* = 7.2 Hz, H-1 of xylopyranosyl unit), 5.63 (1H, *d*, *J* = 7.4 Hz, H-1 of glucopyranosyl unit), 2.39 (3H, *s*, Me of acetyl), 7.43 (2H, *d*, *J* = 8.8 Hz, H-2, 6) and 8.05 (2H, *d*, *J* = 8.8 Hz, H-3, 5). ^{13}C NMR (pyridine-d_5, 100 MHz): aglycone moiety: δ28.1 (Me of acetyl), 196.1 (C=O of acetyl), 116.6 (C-2, 6), 130.6 (C-3, 5), 131.7 (C-4), 161.7 (C-1); sugar moiety: glucopyranosyl: 101.7, (C-1), 74.5 (C-2), 77.8 (C-3), 71.1 (C.4), 77.5 (C-5) and 69.4 (C-6); xylopyranosyl: 105.3 (C-1), 74.7 (C-2), 78.1 (C-3), 70.8 (C-4), 66.7 (C-5).

Acid hydrolysis of **1**. A soln of **1** (20 mg) in 2 N HCl–MeOH (4 ml) was heated at 100° for 4 hr. After cooling to room temp., the reaction mixt. 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 xylose 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 Me_2CO to afford the aglycone (**1a**, 8 mg). **1a**: Needles.

Mp 109–111°, $C_8H_8O_2$. EIMS *m/z*: 136 $[M]^+$, 95, 123, 77, 65 IR ν_{max}^{KBr} cm^{-1}: 3350, 1660, 1600, 1580, 850. ^1H NMR (pyridine-d_5, 400 MHz) δ2.50 (Me of acetyl), 7.18 (2H, *d*, *J* = 8.8 Hz, H-2, 6) and 8.07 (2H, *d*, *J* = 8.8 Hz).

Asterbatanoside B (**2**). Mp 205–207° $[\alpha]_D$ + 16.32° (MeOH; *c* 0.34. IR ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1630 and 1000–1100 $C_{42}H_{68}O_{15}$. FAB-MS *m/z*: 835 $[M + Na]^+$ and 819 $[M + Li]^+$. ^1H NMR (pyridine-d_5): aglycone moiety: δ0.82, 0.84, 1.06, 1.11, 1.13, 1.14 (each 3H, each *s*, tert-Me × 6), 5.39 (1H, *br s*, 12-H); sugar moiety: 5.03 (1H, *d*, *J* = 7.9 Hz, H-1 of the outer glucopyranosyl unit), 6.26 (1H, *d*, *J* = 8.0 Hz, H-1 of the inner glucopyranosyl unit). ^{13}C NMR: Table 1.

Acid hydrolysis of **2**. A soln of **2** (10 mg) in 2 N HCl (4 ml) was hydrolysed under the conditions and work-up procedure as described for **1** to give the aglycone arjunolic acid (**2a**, 4 mg), mp 251–253°, $[\alpha]_D$ + 64° (MeOH; *c* 0.23) ^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). The sugar part was determined as glucose by PC and TLC in direct comparison with an authentic sample.

Asterbatanoside C (**3**). Mp 231–233° $[\alpha]_D$ + 29.18° (MeOH; *c* 0.49). $C_{42}H_{68}O_{15}$. FAB-MS *m/z*: 835 $[M + Na]^+$ and 819 $[M + Li]^+$. ^1H NMR (pyridine-d_5): aglycone moiety: δ0.84, 0.86, 1.16, 1.19, 1.34 and 1.56 (each 3H, each *s*, *tert*-Me × 6), 3.19 (1H, *dd*, *J* = 14.0, 3.6 Hz, 18-H), 3.67 and 4.43 (each 1H, each *d*, *J* = 10.4 Hz, 23-H), 5.41 (1H, *br s*, 12-H); sugar moiety; 5.18 (1H, *d*, *J* = 8.0 Hz, H-1 of 3-*O*-glucopyranosyl unit), 6.33 (1H, *d*, *J* = 8.0 Hz, H-1 of 28-*O*-glucopyranosyl unit). ^{13}C NMR: Table 1.

Acid hydrolysis of **3**. A soln of **3** (15 mg) in 2 N HCl (4 ml) was hydrolysed under the conditions and work-up procedure as described for **1** to give the aglycone. It was methylated with ethereal CH_2N_2 to afford its methyl ester (**3a**, 5 mg), mp 198–200°, $[\alpha]_D$ + 85° ($CHCl_3$; *c* 0.51). ^1H NMR (pyridine-d_5): δ0.87, 0.90, 0.91, 1.18, 1.37, 1.62 (each 3H, each *s*, *tert*-Me × 6), 3.09 (1H, *dd*, *J* = 13.7, 4.0 Hz, 18-H), 3.69 (3H, *s*, OMe), 3.72 and 4.18 (each 1H, each *d*, *J* = 10.1 Hz, H-23), 4.27 (1H, *d*, *J* = 3.0 Hz, 3-H), 4.53 (1H, *m*, 2-H), 5.40 (1H, *br s*, 12-H).

Alkaline hydrolysis of **3**. A soln of **3** (15 mg) in 5% KOH–MeOH was heated at 100° for 4 hr. The reaction mixt. was cooled to room temp. and neutralized to PH 6 with dilute HCl. After removal of MeOH, the remaining mixt. 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 (**3c**).

Preparation of p-hydroxyacetophenone-4-O-2′,3′,4-*tri*-O-*acetyl*-β-D-*glucopyranoside* (**1b**). Under stirring and cooling to 14°, a soln of peracetyl-α-glucopyranosyl bromide (16 g, 39 mmol) in Me_2CO (136 ml) was added drop by drop to a soln of *p*-hydroxyacetophenone (5.576 g, 41 mmol) in 0.294 M NaOH (136 ml, 40 mmol). The reaction soln was stirred at room temp. for 6 hr in the dark, and then concd to dryness. The syrup was acetylated with Ac_2O (20 ml) in pyridine (2 ml) for 50 min at 90°. The soln was then concd to dryness in *vacuo* and purified by chromatography on a silica gel column eluted with $CHCl_3$–EtOAc (10:1) and compound **1b** was obtained as needles from MeOH, mp 170–171°, $[\alpha]_D$ − 35.29° (MeOH; *c* 0.23), FAB-MS *m/z*: 489 $[M + Na]^+$ and 473 $[M + Li]^+$ EIMS *m/z*: 331 $[glc(OAc)_4]^+$. IR ν_{max}^{KBr} cm^{-1}: 3350, 2880, 1650, 1600, 1580, 1508, 1425, 1390, 1365, 1285, 1245, 1000–1100, 835. ^1H NMR ($CDCl_3$): δ2.02, 2.04, 2.05, (12H, 1:2:1, 4 × OAc), 2.55 (3H, *s*, Ac), 3.89 (1H, *m*, 5′-H), 4.15 (1H, *dd*, *J* = 12.4, 2 Hz, 6′a-H), 4.27 (1H, *dd*, *J* = 12.4, 6.5 Hz, 6′b-H), 5.16 (2H, *m*, 1′, 4′-H), 5.29 (2H, *m*, 2′, 3′-*H*), 7.00 (2*H*, *d*, *J* = 8.8 Hz, 3, 5-H), 7.92 (2H, *d*, *J* = 8.8 Hz, 2, 6-H).

Preparation of p-*hydroxyacetophenone*-4-O-β-D-*glucopyranoside* (**1c**). A soln of **1b** (5 g 10.7 mmol) in a mixt. of MeOH–NEt_3–H_2O (8:1:1, 100 ml) was stirred overnight at room temp. The resultant clear soln was then evapd *in vacuo* several times with H_2O until the odourless solid residue (free from triethylammonium salts) reached a constant weight. The product was crystallized and compound **1c** (3.17g) was isolated as needles from MeOH, mp 195°, $[\alpha]_D$ −59.72° (pyridine; *c* 0.21) (Found C, 56.30; H, 6.10. $C_{14}H_{18}O_7$ requires: C, 56.37; H, 6.04%) FAB-MS *m/z*: 321 $[M + Na]^+$ and 305 $[M + Li]^+$. IR ν_{max}^{KBr} cm^{-1}: 3350, 2890, 1660, 1600, 1580, 1500, 1000–1100, 850, ^1H NMR (pyridine-d_5): δ2.43 (3H, *s*, Ac), 4.18 (1H, *m*, 5′-H), 4.30–4.41 (5H, *m*, 2′, 3′, 4′, 6′-H), 4.58 (1*H*, *dd*, *J* = 12.5, 2.0 Hz, 6′-H) 5.73 (1H, *d*, *J* = 7.6 Hz, 1′-H), 7.30 (2H, *d*, *J* = 8.8 Hz, 3, 5-H), 7.98 (2H, *d*, *J* = 8.8 Hz, 2, 6-H). ^{13}C NMR (pyridine-d_5): δ26.32 (Me), 62.5 (6′, CH_2), 71.4 (4′, CH), 74.8 (2′, CH), 79.0 (3′, CH), 78.5 (5′, CH), 101.7 (1′, C), 116.6 (3, 5, CH), 130.8 (2, 6, CH), 131.9 (1. C), 162.1 (4, C), 192.3 (C=O).

p-*Hydroxyacetophenone*-4-O-6′-O-*trityl*-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranoside* (**1e**). A soln of **1c** (2 g, 6.7 mmol) in pyridine (6 ml) was added to trityl chloride 2.8 g, 10.1 mmol) and DMAP (2 mg). The mixt. was stirred under nitrogen at 100° for 12 hr. After cooling to room temp, Ac_2O (5 ml) was added. The mixt. was kept at room temp. for 3hr, diluted with 1:1 ice–water (40 ml), stirred at room temp. for 5 min and extracted with ether (5 × 25 ml). The combined ethereal extracts were washed with 1% HCl soln, water, satd NaCl soln, successively, and dried with Na_2SO_4. After removal of the solvents, the residue was chromatographed using $CHCl_3$–EtOAc (4:1) as eluent to afford **1e** as yellow oil (3.42 g) **1e**: ^1H NMR ($CDCl_3$): δ1.76, 2.00, 2.05 (each 3H, each *s*, 3 × AcO), 2.53 (3H, *s*, Ac), 3.71 (1H, *m*, 5′-H), 4.09 (1H, *m*), 5.09–5.31 (6H, *m*), 7.15 (2H, *d*, *J* = 8.6 Hz, 3, 5-H), 7.91 (2H, *J* = 8.8 Hz, 2, 6-H). FAB-MS *m/z*: 689 $[M + Na]^+$ and 673 $[M + Li]^+$.

Preparation of p-*hydroxyacetophenone*-4-O-2′,3′,4-*tri*-O-*acetyl*-β-D-*glucopyranoside* (**1f**). Compound **1e** (1.5g) was dissolved in HOAc-H_2O 4:1 (10 ml). The soln was stirred at 100° for 1 hr and then cooled to room temp., and left overnight. The resulting crystals were filtered and

washed with 75% MeOH (5 ml). The filtrate and the washings were combined and the soln was concd to give a residue, which was dissolved in toluene (25 ml). Concn of the toluene soln gave material which was chromatographed on a silica gel column eluted with $CHCl_3$–EtOAc (10:1) as solvent to afford pure **1f** (849 mg) as needles from MeOH, mp 140–142°, $[\alpha]_D$ − 40.26° (MeOH; *c* 0.7). FAB-MS *m/z*: 447 $[M + Na]^+$ and 431 $[M + Li]^+$. ^1H NMR ($CDCl_3$): δ2.40 (3H, *s*, Ac), 1.85, 1.89, 1.90 (each 3H, each *s*, 3 × OAc), 3.51 (1H, *t*, *J* = 9.4 Hz, 3′-H), 3.71 (1H, *m*, 5′-H), 4.11, (1*H*, *dd*, *J* = 11.9, 6.1 Hz, 6′a-H), 4.27 (1H, *dd*, *J* = 11.9, 2.0 Hz, 6′b-H), 4.91 (1H, *dd*, *J* = 7.9, 9.4 Hz, 2′-H), 5.04 (1H, *t*, *J* = 9.4 Hz, 4′-H), 5.25 (1H, *d*, *J* = 7.9 Hz, 1′-H), 6.93 (2H, *d*, *J* = 8.6 Hz, 3, 5-H), 7.81 (2H, *d*, *J* = 8.6 Hz, 2, 6-H).

Preparation of p-*hydroxyacetophenone*-4-O-2″,3″,4″*tri*-O-*acetyl*-β-D-*xylopyranosyl*-(1 → 6)-2′,3′,4′-*tri*-O-*acetyl*-β-D-*glucopyranoside* (**1g**). A soln of 2, 3, 4-tri-*O*-acetyl-α-D-xylopyranosyl bromide (644 mg) in $CHCl_3$ (50 ml) was added dropwise in the darkness to a stirred soln of **1f** (424 mg), Ag_2O (500 mg), 4Å molecular sieve (1.5 g) in anhydrous $CHCl_3$ (50 ml), stirring was continued for 30 min at room temp. under nitrogen. The mixt. was filtered and after removal of $CHCl_3$ in *vacuo*, silica gel CC of the residue eluted with benzene–Et_2O (4:1) gave **1g** as needles (484 mg), mp 85–87° $[\alpha]_D$ − 56.84° ($CHCl_3$; *c* 1.43). FAB-MS *m/z*: 705 $[M + Na]^+$ and 689 $[M + Li]^+$. IR ν_{max}^{KBr} cm^{-1}: 3400, 1720, 1630, 10000–1100. ^1H NMR ($CDCl_3$): δ1.98, 2.00, 2.02 (18H, each *s*, 6 × OAc), 2.55 (3H, *s*, Ac), 3.21 (1H, *dd*, *J* = 8.9, 11.4 Hz, 5″a-H), 3.60 (1H, *dd*, *J* = 11.2, 7.4 Hz), 3.85 (2H, *m*, overlap), 4.05 (1H, *dd*, *J* = 12.1, 5.0 Hz), 4.47 (1H, *d*, *J* = 7.0 Hz), 4.88 (2H, *m*) 4.98 (1H, *dd*, *J* = 9.2, 9.5 Hz), 5.06 (1H, *d*, *J* = 8.5 Hz), 5.11 (1H, *d*, *J* = 7.6 Hz), 5.23 (2H, *m*), 6.98 (2H, *d*, *J* = 8.2 Hz, 3, 5-H), 7.95 (1H, *d*, *J* = 8.2 Hz, 2, 6-H).

Preparation of p-*hydroxyacetophenone*-4-O-β-D-*xylopyranosyl*-(1 → 6)-β-D-*glucopyranoside* (**1**). A soln of **1g** (300 mg) in a mixt. of MeOH–NEt_3–H_2O (8:1:1, 50 ml) was stirred overnight at room temp. The reaction soln was then evapd *in vacuo* several times with water until the odourless solid residue reached a constant weight. The product was crystallized to give compound **1** (180 mg) as a white powder, mp 223–224°. It was identical with the natural compound asterbatanoside A in mp, co-TLC, IR, FAB-MS, ^1H and ^{13}C NMR data.

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