Pergamon

0031-9422(95)00016-X

Phytochemistry, Vol. 39, No. 4, pp. 875–881, 1995
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0031-9422/95 $9.50 + 0.00

MEDICAGENIC ACID SAPONINS FROM *ASTER BATANGENSIS*

YU SHAO, BINGNAN ZHOU, KAN MA,* HOUMING WU,* LONGZE LIN† and GEOFFREY A. CORDELL†

Shanghai Institute of Materia Medica, Academia Sinica, Shanghai 200031, P.R. China; *Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai 200032, P.R. China; †Program for Collaborative Research in the Pharmaceutical Sciences, Department of Medicinal Chemistry and Pharmacognosy, College of Pharmacy, University of Illinois at Chicago, Chicago, U.S.A.

(*Received in revised form* 29 *November* 1994)

Key Word Index—*Aster batangensis*; Compositae; triterpene saponins; asterbatanoside J and K; medicagenic acid.

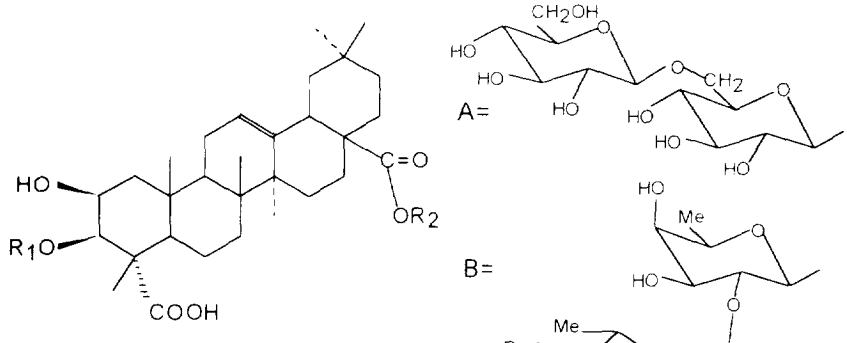
Abstract—Two new medicagenic acid saponins, named asterbatanoside J and K, were isolated from the roots of *Aster batangensis*. On the basis of chemical and spectral studies especially 2D NMR including COSY, HETCOR, HMQC, HOHAHA, TOCSY, ROESY and HMBC techniques, their structures were established as 3-O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl-2β,3β-dihydroxy-olean-12-en-23α,28-dioic acid-28-*O*-α-L-arabinopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-β-D-fucopyranoside and 3-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl- medicagenic acid-28-*O*-β-D-xylopyranosyl-(→ 4)-[α-L-arabinopyranosyl-(1 → 3)-]-α-L-rhamnopyranosyl-(1 → 2)-β-D-fucopyranside, respectively.

INTRODUCTION

The genus *Aster* is widely distributed in China, especially in the west district of China. Members of this genus such as *Aster tataricus* [1] and *Aster scaber* [2] contain rich triterpenoid saponins. Recently, we reported the structural elucidation of four triterpenoid saponins, asterbatanoside F–I, from the *n*-butanol soluble fraction of a 70% aqueous ethanol extract of the roots of *A. batangensis* [3]. Continuing the search for new bioactive saponins of this plant, two new triterpenoid saponins named asterbatanoside J (**1**) and K (**2**) were isolated from the more polar fraction. The present paper mainly describes their isolation and structural elucidation.

RESULTS AND DISCUSSION

The 70% ethanol extract of the dried roots of *A. batangensis* was extracted with petrol, ethyl acetate and

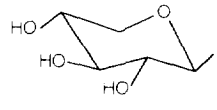


1 R_1 = A R_2 = B R_3 = H

1a R_1 = H R_2 = H

1b R_1 = A R_2 = H

2 R_1 = A R_2 = B R_3 =



n-butanol, successively. The *n*-butanol soluble fraction was chromatographed on SIP-1300, and silica gel columns and fractions further purified by MPLC to afford two saponins, asterbatanoside J (**1**) and K (**2**).

Asterbatanoside J (**1**) was obtained as an amorphous powder, mp 237–239°, $[\alpha]_D$ − 3.47° (MeOH, *c* 072). Its molecular formula, $C_{59}H_{94}O_{28}$, was established by positive ion FAB-MS (*m/z*: 1273 $[M + Na]^+$ and 1257 $[M + Li]^+$) and ^{13}C NMR data (Tables 1 and 2). The IR spectrum contained a hydroxyl band at 3400 cm^{-1}, a carboxylic band at 1709 cm^{-1}, an ester band at 1735 cm^{-1} and a double bond band at 1640 cm^{-1}. The ^1H NMR spectrum showed the signals of six tertiary methyl groups at δ0.79, 0.81, 1.11, 1.18, 1.54 and 1.91, one trisubstituted olefinic proton at δ5.43 (*br s*) and five anomeric protons at δ4.87 (*d*, *J* = 8 Hz), 4.97 (*d*, *J* = 8.5 Hz), 5.18 (*d*, *J* = 7.5 Hz), 5.95 (*d*, *J* = 8.5 Hz) and 6.64 (*br s*). The ^{13}C NMR spectrum revealed the presence of six sp^3 quaternary carbon atoms at δ52.3, 36.5, 40.0, 41.9, 46.7 and 30.3, a pair of olefinic carbon atoms at δ122.2 and 143.6, an ester carbonyl at δ176.1, a carboxylic group at δ180.1 and five anomeric carbon atoms at δ94.4, 101.4, 104.6, 104.6 and 107.2. The NMR spectral data and the molecular formula suggested that **1** was an oleanane-type dicarboxylic acid saponin having five sugar residues with an ester glycosidic-linkage.

Table 1. ^{13}C NMR data of aglycone parts of **1**, **2**, **1a** and **1b**

C	1	2	1b	1a	DEPT
1	43.7	44.1	43.9	44.9	CH_2
2	69.3	69.6	69.6	71.5	CH
3	86.2	86.5	86.5	75.7	CH
4	52.3	52.7	52.6	53.8	C
5	51.9	52.2	52.1	52.1	CH
6	21.1	21.3	21.0	21.4	CH_2
7	32.7	33.1	33.1	33.0	CH_2
8	34.0	40.5	39.9	40.1	C
9	48.2	48.7	48.5	48.7	CH
10	36.5	36.9	36.7	36.8	C
11	23.6	23.5	23.8	23.8	CH_2
12	122.2	122.7	122.4	122.4	CH
13	143.6	143.9	144.6	144.7	C
14	41.9	42.0	42.1	42.0	C
15	28.2	28.1	28.0	28.0	CH_2
16	23.3	23.5	23.5	23.5	CH_2
17	46.7	47.0	46.4	46.4	C
18	41.6	42.0	41.8	41.8	CH
19	46.0	46.4	46.3	46.3	CH_2
20	30.3	30.7	30.8	30.8	C
21	33.6	34.0	34.0	34.0	CH_2
22	31.9	32.4	32.8	33.0	CH_2
23	180.1	180.1	180.1	180.7	C
24	14.1	14.3	14.2	13.5	Me
25	17.1	17.5	17.1	17.2	Me
26	16.7	17.0	16.7	16.8	Me
27	25.5	26.1	26.1	26.0	Me
28	176.1	176.5	180.0	179.9	C
29	32.7	33.0	33.0	33.0	Me
30	23.5	23.9	23.6	23.6	Me

(Pyridine-d_5, 125 MHz for δ_C of **1**, 150 MHz for δ_C of **2**, 75 MHz for δ_C of **1a** and **1b**, ppm).

Acid hydrolysis of **1** yielded a sapogenin (**1a**) and glucose, fucose, rhamnose and arabinose as sugar components. The EIMS of **1a** showed a molecular ion peak at *m/z* 502. Together with the elemental analysis, the molecular formula, $C_{30}H_{46}O_6$ could be deduced. The EIMS of **1** revealed fragment ions at *m/z* 248 and 203 deriving from the D/E ring, *m/z* 253 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 skeleton without any substitutions on the C, D and E rings and with two hydroxyl and a carboxyl groups on the A and B rings. The ^1H NMR spectrum of **1a** showed two signals assignable to two hydroxy-bearing *ax–eq* methine protons at δ4.57 (*d*, *J* = 3.0 Hz, H-3α) and δ4.73 (*m*, H-2α), together with signals due to six tertiary methyl groups. These spectral features and comparison of ^{13}C NMR data of **1a** with literature data [4] suggested that **1a** was 2β, 3β-dihydroxyolean-12-en-23α, 28-dioic acid (medicagenic acid).

Comparison of ^{13}C NMR data of **1** with those of **1a** showed a glycosylation shift for the C-3 signal (+ 10.48 ppm, from δ75.7 to 86.2), demonstrating the C-3 position to be glycosylated. However, the esterified position was more challenging because the glycosylation might take place either at the C-23 or C-28 positions. In order to solve this problem, HMBC experiment was performed. A correlation contour, showing the 24-methyl signal at δ1.92 and a carboxyl carbon at δ180.1 in the HMBC spectrum, revealed the free carboxyl at the C-23 position. Thus, the esterified glycosylation took place at the C-28 position.

Upon alkaline hydrolysis of **1**, the ester-linked sugar chain was selectively cleaved and a prosapogenin (**1b**) was obtained. Upon acid hydrolysis, **1b** afforded glucose and the aglycone **1a**. A molecular formula of $C_{42}H_{66}O_{16}$ was established for **1b** from its FAB-MS (*m/z*: 849 $[M + Na]^+$ and 833 $[M + Li]^+$) and it suggested **1b** contained 2 mol glucose units. This inference was also supported by the two anomeric proton signals at δ4.91 (*d*, *J* = 7.8 Hz) and 5.02 (*d*, *J* = 7.8 Hz) in the ^1H NMR spectrum and two overlapped anomeric carbon signals at δ104.9. Examination of ^{13}C NMR data in the sugar region of **1b** showed that one glucose C-6 resonated at δ70.0, which was more downfield than that of methyl β-D-glucopyranoside [5]. This allowed the (1 + 6) linkage between two glucose units to be made. A significant contour observed between the outer glucose H-1 and the inner glucose H-6 in the ROESY spectrum of **1** further confirmed the above conclusion. The configurations of two glucose units were confirmed as β, based on the anomeric coupling constants as mentioned before. The structure of **1b**, thus, was deduced to be 3-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl-2β,3β-dihydroxyolean-12-en-23α, 28-dioic acid. Therefore, the remaining fucose, arabinose and rhamnose in **1** must be contained in the 28-*O*-sugar moieties.

Elucidation of the structure of the 28-*O*-trisaccharide was performed by the following procedures. In the first

Table 2. NMR data of sugar moieties of **1**, **2** and **1b**

Position	1		2		1b	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
glc-1′	104.6	4.97 (*d*, 8.5)	104.8	4.99 (*d*, 7.7)	104.9	5.02 (*d*, 7.8)
2′	74.5	3.88	74.7	3.88	74.8	
3′	78.0	4.09	79.5	4.15	78.3	
4′	71.8	3.96	71.5	4.04	71.4	
5′	76.3	3.98	76.5	4.00	76.6	
6′a	69.8	4.08	69.9	4.24	70.1	
6′b		4.76		4.78		
glc-1″	104.6	4.87 (*d*, 8.0)	104.8	4.86 (*d*, 7.7)	104.9	4.91 (*d*, 7.8)
2″	75.0	4.00	75.2	3.99	75.2	
3″	77.8	4.21	78.3	4.16	78.2	
4″	71.1	4.18	71.3	4.21	71.5	
5″	78.0	3.87	78.7	3.88	78.1	
6″a	62.2	4.29	62.4	4.32	62.5	
6″b		4.47		4.48		
fuc-1	94.4	5.95 (*d*, 8.5)	94.5	6.00 (*d*, 7.5)		
2	73.3	4.66	74.04	4.61		
3	76.3	4.17	76.3	4.14		
4	72.8	3.84	72.7	3.87		
5	71.9	3.82	72.2	3.83		
6	16.6	1.40	16.8	1.43 (*d*, 5.8)		
rham-1	101.4	6.44 (*br s*)	101.2	6.31 (*br s*)		
2	71.3	4.96	71.3	5.04		
3	83.3	4.48	82.2	4.67		
4	72.6	4.44	78.1	4.48		
5	69.0	4.47	68.3	4.48		
6	18.2	1.54	18.7	1.64 (*d*, 5.0)		
ara-1	107.2	5.18 (*d*, 7.5)	106.1	5.19 (*d*, 7.2)		
2	72.9	4.48	73.0	4.45		
3	74.2	4.25	74.4	4.16		
4	69.2	4.37	69.7	4.28		
5	67.0	3.80, 4.28	67.5	3.71, 4.22		
xyl-1			105.0	5.30 (*d*, 8.0)		
2			75.7	3.85		
3			78.1	3.99		
4			71.0	4.13		
5			66.9	3.23, 4.13		

(Pyridine-d_5 500 MHz for δ_H of **1**, 600 MHz for δ_H of **2**, 300 MHz for δ_H of **1b**).

step, we proceeded to assign unambiguously the proton and carbon resonances of every monosaccharide unit by a series of 2D NMR experiments including COSY, HOHAHA and HETCOR spectra. ^1H subspectra of various carbohydrate moieties were obtained from the rows corrresponding to their anomeric proton resonances and to their other well resolved resonances (i.e. Me-6 for rhamnose and fucose methylene-5 for arabinose) in the COSY and HOHAHA spectra. The assignment of ^{13}C NMR data was then obtained from the HETCOR spectrum. The complete assignments of NMR data due to sugar units were given in Table 2.

The next step was the determination of the linkages among the sugar residues. The NOE contours between the rhamnose H-1 and the fucose H-2, the arabinose H-1 and the rhamnose H-3, were observed in the ROESY spectrum. Moreover, the strong correlations between the rhamnose H-1 and the fucose C-2, the arabinose H-1 and the rhamnose C-3, the fucose H-1 and the aglycone C-28 appeared in the HMBC spectrum. These findings allowed the establishment of the linkages (1 → 2) between the rhamnose and the fucose units; (1 → 3) between the arabinose and the fucose units; (1 → 28) between the fucose and the aglycone, the downfield shifted fucose C-3 signal at δ73.3 and the rhamnose C-3 signal at δ83.3 favoured the interlinkages of these sugars. In addition, in the EIMS of peracetated **1**, the presence of the characteristic ion peaks at *m/z* 259, 331, 489, 619 and 719 which were in accord with $[ara(OAc)_3]^+$, $[glc(OAc)_4]^+$, $[ara(OAc)_3\text{-}rham(OAc)_2]^+$, $[glc(OAc)_4\text{-}glc(OAc)_3]^+$ and $[ara(OAc)_3\text{-}rham(OAc)_2\text{-}fuc(OAc)_2]^+$, respectively, also supported the sugar sequence above.

The large $J_{1,2}$ values of fucose and arabinose units (8.5 and 7.5 Hz, respectively) indicated their anomeric centres

as β and α-configurations. The C-5 signal of the rhamnose unit appeared at δ69.0, thus, the rhamnosyl group had the α-configuration [5].

All above data suggested the structure of asterbatanoside J (**1**) as 3-*O*-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl-2β,3β-dihydroxy-olean-12-en-23α,28-dioic acid-28-*O*-α-L-arabinopyranosyl-(1 → 3)-α-L-rhamnopyranosyl-(1 → 2)-β-D-fucopyranoside.

Asterbatanoside K (**2**) was obtained as needles, mp 242–243°, $[\alpha]_D$ + 8.41° (pyridine, *c* 0.35). The FAB-MS spectrum of **2** exhibited a pseudomolecular ion peak at *m/z* 1405 $[M + Na]^+$. In conjunction with the ^{13}C NMR data this allowed us to deduce its molecular formula as $C_{64}H_{102}O_{32}$. Its IR, ^1H and ^{13}C NMR spectra due to aglycone part were almost superimposable on those of **1**, which suggested that **2** was also a medicagenic acid 3,28-bisdesmoside.

Acidic hydrolysis of **2** provided medicagenic acid and glucose, arabinose, xylose, rhamnose and fucose as the sugar components. Alkaline hydrolysis of **2** with 5% KOH yielded a prosapogenin which was elucidated as the same structure as the prosapogenin (**1b**) of asterbatanoside J by comparison of their ^{13}C NMR data. Thus, the structure of the 3-*O*-sugar chain of **2** was established as β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl.

The ^1H NMR spectrum of **2** showed the presence of six anomeric proton signals at δ4.92 (*d*, *J* = 7.7 Hz), 5.02 (*d*, *J* = 7.7 Hz), 5.21 (*d*, *J* = 7.2 Hz), 5.35 (*d*, *J* = 8.0 Hz), 6.02 (*d*, *J* = 7.5 Hz) and 6.31 (*br s*). Its ^{13}C NMR parameter showed six anomeric carbon signals at δ105.9, 104.9, 104.7 (2C), 101.2 and 94.7. These data indicated that 28-*O*-sugar units consisted of each one of β-D-fucose, α-L-rhamnose, α-L-arabinose and β-D-xylose units. The unambiguous assignment of ^1H and ^{13}C resonances of each monosaccharide was made possible by COSY, TOCSY and HMQC spectra. The 2D NMR data are summarized in Table 4.

Table 3. Summary of NMR data of **1**

Proton	COSY(H)	HETCOR(C)	HOHAHA(H)	ROESY(H)
3-*O*-sugar				
inner glc				
1′	2′	1′	2′, 3′	3, 3′, 5′
2′	1′, 3′	2′	1′, 3′, 4′	
3′	2′, 4′	3′	1′, 2′, 4′, 5′	1′, 5′
4′	3′, 5′	4′	2′, 3′, 5′, 6′a	
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″	
3″	2″, 4″	3″	1″, 2″, 4″, 5″	1″, 5″
4″	3″, 5″	4″	2″, 3″, 5″, 6″a	
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
6″b	5″, 6″a	6″	5″, 6″a	6″a
28-*O*-sugar				
F-1	F-2	F-1	F-2, F-3	F-3, F-5
2	F-1, F-3	F-2	F-1, F-3, F-4	R-1
3	F-2, F-4	F-3	F-1, F-2, F-4, F-5	F-1, F-5
4	F-3, F-5	F-4	F-2, F-3, F-5, F-6	
5	F-4, F-6	F-5	F-3, F-4, F-6	F-1, F-3, F-6
6	F-5	F-6	F-4, F-5	F-5
R-1	R-2	R-1	R-2	R-2, R-4, F-2
2	R-1, R-3	R-2	R-1, R-3, R-4	R-1, R-1
3	R-2, R-4	R-3	R-2, R-4, R-5	R-5, A-1
4	R-3, R-5	R-4	R-3, R-5, R-6	R-1, R-2
5	R-4, R-6	R-5	R-3, R-4, R-6	R-6, R-3
6	R-5	R-6	R-4, R-5	R-5
A-1	A-2	A-1	A-2, A-3	A-3, R-3
2	A-1, A-3	A-2	A-1, A-3, A-4	
3	A-2, A-4	A-3	A-1, A-2, A-4, A-5a	A-1
4	A-3, A-5a, 5b	A-4	A-2, A-3, A-5a, A-5b	
5a	A-4, A-5b	A-5	A-3, A-4, A-5b	A-5b
5b	A-4, A-5a	A-5	A-4, A-5a	A-5a

glc = β-D-Glucopyranosyl; F = β-D-fucopyranosyl; R = α-L-rhamnopyranosyl; A = α-L-arabinopyranosyl.

Table 4. Summary of 2D NMR data of **2**

Proton	COSY(H)	HMQC(C)	TOCSY(H)	ROESY(H)
inner glc				
1′	2′	1′	2′, 3′, 4′, 5′	3, 3′, 5′
2′	1′, 3′	2′	1′, 3′, 4′, 5′, 6′a	
3′	2′, 4′	3′	1′, 2′, 4′, 5′, 6′a, 6′b	1′, 5′
4′	3′, 5′	4′	1′, 2′, 3′, 5′, 6′a, 6′b	
5′	4′, 6′a, 6′b	5′	1′, 2′, 3′, 4′, 6′a, 6′b	1′, 3′, 6′a
6′a	5′, 6′b	6′	2′, 3′, 4′, 5′, 6′b	5′, 6′b, 1″
6′b	5′, 6′a	6′	3′, 4′, 5′, 6′a	6′a, 1″
outer glc				
1″	2″	1″	2″, 3″, 4″, 5″	3″, 5″, 6′a, 6′b
2″	1″, 3″	2″	1″, 3″, 4″, 5″, 6″a	
3″	2″, 4″	3″	1″, 2″, 4″, 5″, 6″a, 6″b	1″, 5″
4″	3″, 5″	4″	1″, 2″, 3″, 5″, 6″a, 6″b	
5″	4″, 6″a, 6″b	5″	1″, 2″, 3″, 4″, 6″a, 6″b	1″, 3″, 6″a
6″a	5″, 6″b	6″	2″, 3″, 4″, 5″, 6″b	5″, 6″b
6″b	5″, 6″a	6″	3″, 4″, 5″, 6″a	6″a
F-1	F-2	F-1	F-2, F-3, F-4	F-3
2	F-1, F-3	F-2	F-1, F-3, F-4	R-1
3	F-2, F-4	F-3	F-1, F-2, F-4, F-5	F-1
4	F-3, F-5	F-4	F-1, F-2, F-3, F-5, F-6	
5	F-4, F-6	F-5	F-3, F-4, F-6	F-6
6	F-5	F-6	F-4, F-5	F-5
R-1	R-2	R-1	R-2	R-2, F-2
2	R-1, R-3	R-2	R-1, R-3, R-4, R-5	R-1
3	R-2, R-4	R-3	R-2, R-4, R-5, R-6	A-1
4	R-3, R-5	R-4	R-1, R-2, R-3, R-5, R-6	X-1
5	R-4, R-6	R-5	R-2, R-3, R-4, R-6	R-6
6	R-5	R-6	R-3, R-4, R-5	R-5
A-1	A-2	A-1	A-2, A-3, A-4, A-5	R-3
2	A-1, A-3	A-2	A-1, A-3, A-4, A-5	
3	A-2, A-4	A-3	A-1, A-2, A-4, A-5	A-1
4	A-3, A-5	A-4	A-1, A-2, A-3, A-5	
5	A-4, A-5	A-5	A-1, A-2, A-3, A-4	
X-1	X-2	X-1	X-2, X-3, X-4, X-5	R-4, X-3
2	X-1, X-3	X-2	X-1, X-3, X-4, X-5	
3	X-2, X-4	X-3	X-1, X-2, X-4, X-5	X-1
4	X-3, X-5	X-4	X-1, X-2, X-3, X-5	X-5
5	X-4	X-5	X-1, X-2, X-3, X-4	X-4

glc = β-D-Glucopyranosyl; F = β-D-fucopyranosyl; R = α-L-rhamnopyranosyl; A = α-L-arabinopyranosyl; X = β-D-xylopyranosyl.

By comparison of the ^{13}C NMR data of 28-*O*-sugar moieties in **2** with those of the corresponding individual methyl glycopyranoside indicated that one xylose unit and one arabinose unit were located in terminal positions, because their ^{13}C NMR data were identical with those of methyl β-D-xylopyranoside and methyl α-L-arabinoside, respectively. In addition, glycosylation shifts were observed at the C-2 signal by + 2.04 ppm of fucose group, at the C-3 signal by + 9.65 ppm and the C-4 signal by + 4.45 ppm of rhamnose group, i.e. glycosylations took place at these positions. The anomeric proton and carbon signals of the fucose unit at δ6.00 and 94.5, respectively, suggested that the fucose unit was located at the inner position of the 28-*O*-sugar units.

The sequence and interglycosidic linkages of the 28-*O*-sugar units of **2** were determined by ROESY and HMBC experiments in the ROESY spectrum, three significant contours were observed between the H-1 signal of the rhamnose group and the H-2 signal of the fucose group, the H-1 signal of the arabinose group and the H-3 of the rhamnose unit, and the H-1 of the xylose unit and the H-4 of the rhamnose group. This allowed the establishments of a (1 → 2) linkage between the rhamnose unit and the fucose unit, a (1 → 3) linkage between the arabinose unit and the rhamnose unit and a (1 → 4) linkage between the xylose unit and the rhamnose group. The HMBC spectrum showed cross-peaks between the H-1 of the rhamnosyl unit and the C-2 of fucosyl group, the H-4 of the rhamnosyl group and between the C-1 of the xylosyl unit, the H-3 of the rhamnosyl unit and the C-1 of the arabinosyl unit. These results further confirmed the conclusions obtained from the ROESY spectrum.

Therefore, the structure of asterbatanoside K (**2**) was determined as 3-*O*-β-D-glucopyranosyl-(1→6)-β-D-glu- and filtered. The filtrate was evapd *in vacuo*. The residue was dissolved in H_2O and extracted with Et_2O. From the

acid identified by comparison of co-TLC, ^{1}H NMR data with an authentic sample.

Alkaline hydrolysis of **2.** A soln of **2** (30 mg) in 5% KOH (5 ml) was heated at 100° for 4 hr. The reaction mixt. was cooled at room temp. and neutralized 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 H_2O eluate was evapd and followed by acidic hydrolysis which showed the presence of fucose, arabinose, xylose and rhamnose identified by PC and TLC in direct comparison with standard sugars. The MeOH eluate was subjected to CC over silica gel using $CHCl_3$–MeOH (3:1) as the solvent to afford the prosapogenin which was identified as 3-*O*-*β*-D-glucopyranosyl-(1 → 6)-*β*-D-glucopyranosylmedicagenic acid by comparison of co-TLC and ^{13}C NMR data of an authentic sample.

Acknowledgements—The authors are greatly indebted to the Research Resources Center of the University of Illinois at Chicago, U.S.A., and the State Key Laboratory of Bioorganic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, China, for the provision of NMR spectroscopic facilities. The authors of Shanghai Institute of Organic Chemistry wish to thank the Chinese Committee of Science and Technology for financial support. This work was supported by the National Natural Science Foundation of China and the doctoral program, Chinese Academy of Sciences.

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