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Two New Furostanol Glycosides from *Asparagus cochinchinensis*

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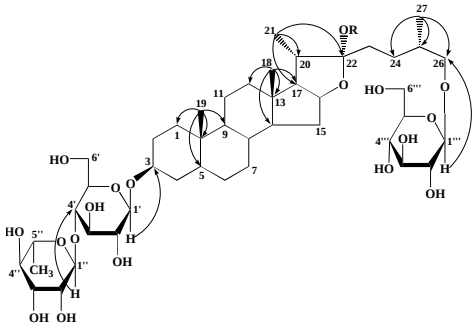
Abstract: Two new furostanol oligoglycosides named as aspacochioside A (**1**) and B (**2**) were isolated from the roots of *Asparagus cochinchinensis* (Lour.) Merr.. Their structures were elucidated to be 3-O-[{α-L-rhamnopyranosyl-(1→4)}{β-D-glucopyranosyl}]-26-O-[β-D-glucopyranosyl]-(25*S*)-5β-furostane-3β,22α,26-triol **1** and 3-O-[{α-L-rhamnopyranosyl-(1→4)}{β-D-glucopyranosyl}]-26-O-[β-D-glucopyranosyl]-22α-methoxy-(25*S*)-5β-furostane-3β,26-diol **2** on the basis of spectroscopic techniques and chemical methods.

Keywords: *Asparagus cochinchinensis* (Lour.) Merr., Liliaceae, furostanol glycoside, aspacochiosides A, B.

Asparagus cochinchinensis (Lour.) Merr. is a perennial climbing herb of the Liliaceae family. The dried roots of this plant called "Tianmendong" are well-known chinese medicine used for treatments of fever, cough, hemoptysis, diabetes, constipation, swollen and throat pain[1]. There have been some reports of the chemical constituents of this chinese medicine[2-6]. We report here the isolation and structural elucidation of two new furostanol glycosides, named as aspacochiosides A **1** and B **2** from the ethanolic extract of the roots of this plant.

Figure 1 The Structures and key HMBC correlations of **1** and **2**



1 R = H **2** R=CH_3

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The ethanolic extract of the air-dried and ground roots of *Asparagus cochinchinensis* (Lour.) Merr. was subjected to column chromatography on macroporous adsorbent resin, normal phase and reverse phase silica gels and Sephadex LH-20 successively to afford compounds **1** and **2**.

Aspacochioside A **1** was obtained as colorless crystals, mp 212-213°C, $[\alpha]_D^{25}$ -48.5 (*c* 0.10, acetone-H_2O 1:1). Its IR spectrum showed a strong broadened absorption band at 3386 cm^{-1} for hydroxy groups. The positive ESIMS spectrum of **1** exhibited a quasi-molecular ion peak at *m/z* 927 $[M+Na]^+$, and the molecular formula **1** was established as $C_{45}H_{76}O_{18}$ by positive high resolution ESIMS at 927.4919 $[M+Na]^+$ (calcd. for $C_{45}H_{76}O_{18}Na$ 927.4929). The ^1H, ^{13}C and DEPT NMR spectral data at δ_H 5.92 (brs, 1H, H-1″), 4.85 (d, 1H, *J*=7.0 Hz, H-1′) and 4.81 (d, 1H, *J*=7.0 Hz, H-1‴), and at δ_C 105.2 (C-1‴), 103.0 (C-1′), and 102.7 (C-1″), which were assignable to anomeric protons and carbons respectively, indicated that **1** possessed a triglycosidic structure with an α sugar and two β sugar units. A 5β-furostanol aglycon moiety was characterized by two methyl singlets at δ_H 0.82 (s, 3H) and 0.86 (s, 3H) and two methyl doublets at δ_H 1.31 (d, 1H, *J*=7.0 Hz, H-21) and 1.02 (d, 1H, *J*=7.0 Hz, H-27) in the ^1H NMR spectrum[7]. All of signals in the ^1H and ^{13}C NMR spectra (see **Table 1**) were unambiguously assigned by ^1H-^1H DQF-COSY, TOCSY, HMQC and HMBC experiments. The signals assigned to the aglycon moiety were in good agreement with those of (25*S*)-5β-furostane-3β,22α, 26-triol glycosylated at C-3 and C-26[8]. Signals assigned to sugar units revealed the presences of one terminal α-L-rhamnopyranosyl unit, one terminal β-D-glucopyranosyl and one 4-substituted β-D-glucopyranosyl unit[4]. After acidic hydrolysis of **1** the TLC and PC confirmed the releasing of rhamnose and glucose from **1**. In the HMBC spectrum (see **Figure 1**), long range correlations from H-1′ to C-3, H-1″ to C-4′ and H-1‴ to C-26 unequivocally revealed that a disaccharide α-L-rhamnopyranosyl(1→4)-β-D-glucopyra-nosyl moiety and the remained β-D-glucopyranosyl unit were located at C-3 and C-26 of the aglycon, respectively. Accordingly, the structure of **1** was determined as 3-O-[{α-L-rhamnopyranosyl(1→4)}{β-D-glucopyranosyl}]-26-O-[β-D-glucopyrano-syl]-(25*S*)-5β-furostane-3β,22α,26-triol.

Aspacochioside B (**2**), white crystals (MeOH), mp199-200°C, $[\alpha]_D^{25}$ –64.7 (*c* 0.10, MeOH), showed a strong broadened absorption band at 3404 cm^{-1} for hydroxy groups in the IR spectrum. The ^1H, ^{13}C NMR and DEPT spectra of **2** were very similar to those of **1**, except for the appearance of signals at δ_H 3.24 (s, 3H) and δ_C 47.4 (q) attributed to a methoxy group. By comparison of the ^{13}C NMR and DEPT spectral data of **2** with those of **1**, the signals assigned to C-22 and C-23 were shifted from δ 37.2 and 110.6 of **1** to δ 31.1 and 112.5 of **2**, respectively, indicating that the hydroxy group at C-22 of **1** was replaced by the methoxy group in **2**. Consequently, the structure of **2** was determined as 3-O- [{α-L-rhamnopyranosyl-(1→4)} {β-D-glucopyranosyl}] -26-O- [β-D-glucopy-ranosyl]-22α-methoxy-(25*S*)-5β-furostane-3β,26-diol. Refluxing in aqueous acetone, **2** was converted into **1**, and refluxing in methanol **1** converted into **2**. These results proposed that **1** or **2** might be an artificial product formed in the isolation procedure although several pairs of 22-hydroxy and 22-methoxy oligofurostanosides were reported from *Asparagus* plants[3,4,9].

Table 1 NMR data for compounds **1** and **2**[a]

No.	**1**		**2**	
	^{1}H	^{13}C (DEPT)	^{1}H	^{13}C (DEPT)
1	1.46. m 1.70, m	30.5 (CH_2)	1.44. m 2.03, m	30.5 (CH_2)
2	1.54, m 1.70, m	27.0 (CH_2)	1.55, m 1.72, m	27.0 (CH_2)
3	4.25, m	74.6 (CH)	4.25, m	74.4 (CH)
4	1.77, m 1.88, m	30.9 (CH_2)	1.75, m 1.88, m	30.9 (CH_2)
5	1.45, m	37.0 (CH)	2.00, m	37.0 (CH)
6	1.67, m 1.89, m	27.0 (CH_2)	0.96, m 1.82, m	26.9 (CH_2)
7	1.28, m 1.53, m	26.8 (CH_2)	1.25, m 1.50, m	26.8 (CH_2)
8	1.48, m	35.5 (CH)	1.52, m	35.5 (CH)
9	0.95, m	40.3 (CH)	1.69, m	39.5 (CH)
10	-	35.2 (C)	-	35.2 (C)
11	1.26, m 1.75, m	21.2 (CH_2)	1.12, m 1.35, m	21.1 (CH_2)
12	1.12, m 1.24, m	40.4 (CH_2)	1.13, m 1.25, m	41.1 (C)
13	-	41.2 (C)	-	41.3 (CH)
14	1.07, m	56.4 (CH)	1.00, m	56.3 (CH)
15	1.38, m 2.03, m	32.4 (CH_2)	1.38, m 1.92, m	32.2 (CH_2)
16	4.98, m	81.2 (CH)	4.50, m	81.4 (CH)
17	1.95, m	64.2 (CH)	1.75, m	64.4 (CH)
18	0.82, s	16.7 (CH_3)	0.78, s	16.6 (CH_3)
19	0.86, s	23.9 (CH_3)	0.80, s	23.8 (CH_3)
20	2.22, m	40.7 (CH)	2.20, m	40.5 (CH)
21	1.31, d, (7.0)	16.5 (CH_3)	1.15, d, (7.0)	16.5 (CH_3)
22	-	10.6 (C)	-	112.5 (C)
23	1.94, m 2.08, m	37.1 (CH_2)	1.35, m 1.85, m	31.1 (CH_2)
24	1.92, m 1.92, m	28.3 (CH_2)	1.34, m 1.78, m	28.2 (CH_2)
25	1.90, m	34.4 (CH)	1.86, m	34.5 (CH)
26	3.46, dd, (10.0, 7.2) 4.07, dd, (10.0, 7.2)	75.4 (CH_2)	3.50, dd, (10.0, 7.2) 4.30, dd, (10.0, 7.2)	74.9 (CH_2)
27	1.02, d, (7.0)	17.5 (CH_3)	1.02, d, (7.0)	17.6 (CH_3)
OCH_3	-		3.24, s	47.4 (CH_3)
1′	4.85, d, (7.0)	103.0 (CH)	4.85, d, (7.0)	102.9 (CH)
2′	4.02, dd, (7.5, 7.0)	75.6 (CH)	3.98, dd, (8.0, 7.0)	75.5 (CH)
3′	4.21, dd, (7.5, 9.0)	76.8 (CH)	4.21, dd, (8.0, 9.0)	76.7 (CH)
4′	4.48, dd, (9.0, 9.5)	78.2 (CH)	4.47, dd, (9.0, 9.5)	78.1 (CH)
5′	3.70, br d, (9.5)	77.2 (CH)	3.69, br d, (9.5)	77.1 (CH)
6′	4.13, br d, (10.5) 4.25, br d, (10.5)	61.5 (CH_2)	4.10, br d, (10.5) 4.27, br d, (10.5)	61.5 (CH_2)
1″	5.92, br s	102.7 (CH)	5.91, br s	102.6 (CH)
2″	4.70, br s	72.7 (CH)	4.69, br s	72.8 (CH)
3″	4.58, br d, (8.5)	72.8 (CH)	4.57, br d, (8.5)	72.6 (CH)
4″	4.35, dd, (9.0, 8.5)	74.0 (CH)	4.32, dd, (9.0, 8.5)	74.0 (CH)
5″	5.03, d q, 9.0, 7.0)	70.3 (CH)	5.02, d q, (9.0, 7.0)	70.3 (CH)
6″	1.69, d, (7.0)	18.6 (CH_3)	1.69, d, (7.0)	18.6 (CH_3)
1‴	4.81, d, (7.0)	105.2 (CH)	4.83, d, (7.0)	105.0 (CH)
2‴	3.99, dd, (8.0, 7.0)	75.2 (CH)	3.91,dd, (7.0, 8.0)	75.2 (CH)
3‴	4.20, dd, (8.0, 9.0)	78.6 (CH)	4.20, dd, (8.0, 9.0)	78.6 (CH)
4‴	4.25, dd, (9.0, 9.0)	71.7 (CH)	4.28, dd, (9.0, 9.0)	71.7 (CH)
5‴	3.93, m	78.5 (CH)	3.95, m	78.5 (CH)
6‴	4.39, br d, (12.5) 4.54, br d, (12.5)	62.8 (CH_2)	4.42, br d, (12.5) 4.57, br d, (12.5)	62.8 (CH_2)

[a] NMR data were measured in pyridine-d_5 at 500 MHz for proton and at 125 MHz for carbon. Proton coupling constants (*J*) in Hz are given in parentheses. The assignments were based on ^{1}H-^{1}H DQF-COSY, TOCSY, HMQC, HMBC and DEPT experiments.

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