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A New Furost-20(22)-ene Oligoglycoside from *Asparagus cochinchinensis*

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Abstract: A new furost-20(22)-ene oligoglycoside named as aspacochioside C was isolated from the roots of *Asparagus cochinchinensis* (Lour.) Merr.. Its structure was elucidated to be 26-O-β-D-glucopyranosyl-(25*S*)-5β-furost-20(22)-en-3β,26-diol-3-O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranoside on the basis of spectroscopic techniques including 1D and 2D NMR experiments.

Keywords: *Asparagus cochinchinensis* (Lour.) Merr., Liliaceae, furost-20(22)-ene oligoglycoside, aspacochioside C.

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]. Although the Chinese Pharmacopoeia[2] specified the roots of *A. cochinchinensis* as the genuine "Tianmendong", roots of several species of *Asparagus* plants are commercially used such as *A. filicinus*, *A. meioclados*, *A. spinasissimus*. As part of our studies on indicative compounds and fingerprinting of Chinese traditional medicines, we carried out a systematic study of chemical constituents of roots of *A. cochinchinensis*. In the previous paper we reported two new furostanol glycosides named as aspacochiosides A and B[3]. This paper deals with the isolation and structural elucidation of a new furost-20(22)-ene oligoglycoside, named as aspacochioside C **1** from the same material.

The ethanolic extract of the air-dried and ground roots of *A. cochinchinensis* was subjected to column chromatography on macroporous adsorbent resin, normal phase and reverse phase silica gels and Sephadex LH-20 successively to afford compound **1** which was obtained as colorless crystals (MeOH-H_2O, 1:1), mp 140-141°C, $[\alpha]_D^{22}$ –26.3 (*c* 0.09, MeOH). The IR (KBr) spectrum of **1** showed a strong broadened absorption bands for hydroxy groups (3396 cm^{-1}) and characteristic absorption bands for glycosyl moiety (1076, 1038, 1026 and 910 cm^{-1}). The positive ESIMS spectrum of **1** exhibited a quasi-molecular ion peak at *m/z* 887$[M+H]^+$, and the molecular formula of **1** was established as $C_{45}H_{74}O_{17}$ by the positive high resolution ESIMS at *m/z* 887.5012 $[M+H]^+$

†This paper is dedicated to Professor Xiao-Tian Liang on the occasion of his 80th birthday.

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Figure 1 The Structure and key HMBC correlations of **1**

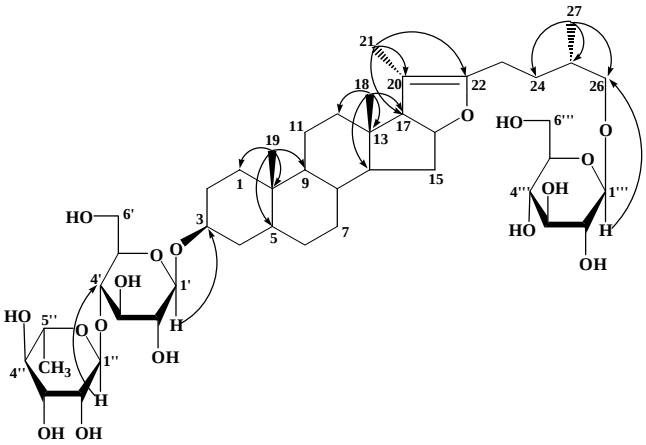

Table 1 NMR data for compounds **1** and **2**[a]

No.	^{1}H	^{13}C (DEPT)	No.	^{1}H	^{13}C
1	1.43 (m) 1.69 (m)	30.5 (CH_2)	22	-	151.9 (C)
2	1.52 (m) 1.70 (m)	26.6 (CH_2)	23	2.21 (m) 2.11 (m)	23.3 (CH_2)
3	4.28 (m)	74.8 (CH)	24	1.34 (m) 1.78 (m)	30.1 (CH_2)
4	1.77 (m) 1.86 (m)	31.0 (CH_2)	25	1.94 (m)	33.3 (CH)
5	1.95 (m)	36.6 (CH)	26	3.47(dd, *J*=10.0, 7.2) 4.10 (dd, *J*=10.0, 7.2)	74.8 (CH_2)
6	1.66 (m) 1.84 (m)	26.6 (CH_2)	27	1.03 (d, *J*=7.0 Hz)	16.8 (CH_3)
7	1.25 (m) 1.51 (m)	26.6 (CH_2)	1′	4.85 (d, *J*=7.5)	102.6 (CH)
8	1.50 (m)	34.8 (CH)	2′	3.98 (dd, *J*=7.5, 8.0)	75.2 (CH)
9	1.15 (m)	39.7 (CH)	3′	4.22 (dd, *J*=8.0, 9.0)	76.4 (CH)
10	-	34.8 (C)	4′	4.49 (dd, *J*=9.0, 9.0)	78.2 (CH)
11	0.95 (m) 1.32 (m)	21.0 (CH_2)	5′	3.71 (brd, *J*=9.0)	76.8 (CH)
12	1.74 (m) 1.76 (m)	39.7 (CH_2)	6′	4.13 (brd, *J*=10.5) 4.27 (brd, *J*=10.5)	61.1 (CH_2)
13	-	43.4 (C)	1″	5.92 (brs)	102.2 (CH)
14	0.88 (m)	54.3 (CH)	2″	4.70 (brs)	72.2 (CH)
15	1.42 (m) 2.04 (m)	34.0 (CH_2)	3″	4.56 (brd, *J*=9.5)	72.4 (CH)
16	4.83 (m)	84.2 (CH)	4″	4.34 (dd, *J*=9.0, 9.5)	73.6 (CH)
17	2.48 (d, 9.6)	64.2 (CH)	5″	5.03 (dq, J=9.0, 7.0)	69.9 (CH)
18	0.69 (s)	14.1 (CH_3)	6″	1.73 (d, J=7.0)	18.2 (CH_3)
19	0.84 (s)	23.5 (CH_3)	1‴	4.83 (d, *J*=8.0)	104.8 (CH)
20	-	103.2 (C)	2‴	4.00 (dd, *J*=8.0, 8.0)	74.8 (CH)
21	1.62 (s)	11.5 (CH_3)	3‴	4.23 (dd, *J*=8.0, 9.0)	78.2 (CH)
			4‴	4.25 (dd, *J*=9.0, 9.0)	71.3 (CH)
			5‴	3.96 (m)	78.2 (CH)
			6‴	4.44 (brd, *J*=12.5) 4.58 (brd, *J*=12.5)	62.4 (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.

(calcd. for $C_{45}H_{75}O_{17}$ 887.5004). The ESIMS/MS on the peak *m/z* 887 showed fragment peaks successively losing three glycosyl units at *m/z* 725, 581, 579, 435 and 415, and the ESIMS/MS on the peak *m/z* 725 gave fragment peaks successively losing two glycosyl units at *m/z* 581, 435 and 417. These fragmentations clearly demonstrated that there are three glycosyl units in the structure of **1**.

The ^{1}H, ^{13}C and DEPT NMR spectral data at δ_H 5.92 (brs, 1H, H-1″), 4.85 (d, 1H, *J*=7.5 Hz, H-1′) and 4.83 (d, 1H, *J*=8.0 Hz, H-1‴), and at δ_C 104.8 (d, C-1‴), 102.6 (d, C-1′), and 102.2 (d, C-1″), which were assignable to anomeric protons and carbons respectively, confirmed that **1** possessed a triglycosidic structure with one α sugar and two β sugar units. In the ^{1}H NMR spectrum, the diagnostic signals attributed to three methyl singlets at δ_H 1.62 (s, 3H, H-21), 0.84 (s, 3H, H-19) and 0.69 (s, 3H, H-18) and a methyl doublet at δ_H 1.03 (d, 3H, *J*=7.0 Hz, H-27) suggested that there is a 5β-furostenol aglycone moiety in the structure[4]. All of signals in the ^{1}H and ^{13}C NMR spectra (see **Table 1**) were unambiguously assigned by ^{1}H-^{1}H DQF-COSY, TOCSY, HMQC and HMBC experiments. The signals assigned to the aglycone moiety were in good agreement with those of (25*S*)-5β-furost-20(22)-en-3β,26-diol glycosylated at C-3 and C-26[5,6]. Signals assigned to three sugar units were consistent with those reported for a terminal α-L-rhamnopyranosyl, a terminal β-D-glucopyranosyl and a 4-substituted β-D-glucopyranosyl in literature[7]. After acidic hydrolysis of **1** the Co-TLC and Co-PC, using $CHCl_3$-MeOH (2.5:1) and the upper layer of *n*-BuOH-AcOH- H_2O (4:1:5) as developing solvents respectively, confirmed the releasing of rhamnose and glucose from **1**. The locations of the glycosyl units were established by long range correlations from H-1′ to C-3, H-1″ to C-4′ and H-1‴ to C-26 in the HMBC spectrum (see **Figure 1**). Therefore, the structure of **1** was determined as 3-O-[{α-L-rhamnopyranosyl(1→4)}{β-D-glucopyranosyl}]-26-O-[β-D-glucopyranosyl]-(25*S*)-5β-furost-20(22)-en-3β,26-diol.

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