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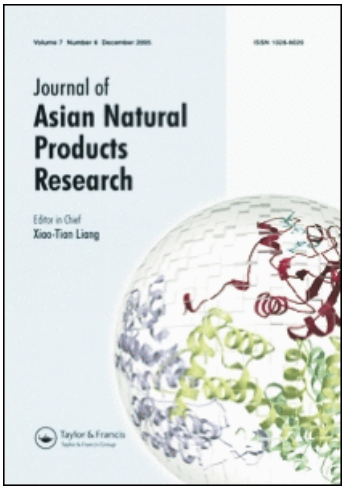

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FUROSTANOL OLIGOGLYCOSIDES FROM *ASPARAGUS COCHINCHINENSIS*

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

Three new furostanol oligoglycosides, named aspacochioside A (**1**), B (**2**) and C (**3**), together with the known compound 3-*O*-[{α-L-rhamnopyranosyl-(1→4)}{β-D-glucopyranosyl}]-26-*O*-[β-D-glucopyranosyl]-(25*S*)-5β-spirostane-3β-ol were isolated from the roots of *Asparagus cochinchinensis*. Their structures were elucidated by spectroscopic techniques (IR, HR-ESIMS, ESIMS/MS, 1D and 2D NMR) and chemical methods as 3-*O*-[{α-L-rhamnopyranosyl-(1→4)}{β-D-glucopyranosyl}]-26-*O*-[β-D-glucopyranosyl]-(25*S*)-5β-furostane-3β,22α,26-triol (**1**), 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**), and 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 (**3**).

Keywords: *Asparagus cochinchinensis*; Furostanol oligoglycosides; Aspacochiosides A–C

INTRODUCTION

"Tianmendong" is a well-known Chinese medicine used to treat fever, cough, hemoptysis, diabetes, constipation, swollen and throat pain [1,2]. Although the Chinese Pharmacopoeia [2] specified the roots of *Asparagus cochinchinensis* (Lour.) Merr. as the genuine "Tianmendong", the roots of several species of *Asparagus* plants are commercially used, such as *A. filicinus*, *A. meioclados* and *A. spinasissimus*. As a part of our studies on indicative compounds and fingerprinting of Chinese traditional medicines, we carried out a phytochemical study of the roots of *A. cochinchinensis* (the genuine "Tianmendong"). In a previous letter we have described the preliminary results [3]. Here we report in detail the isolation and structural elucidation of three new furostanol oligoglycosides, named aspacochiosides A (**1**), B (**2**) and C (**3**) from the ethanolic extract of the roots of this plant. By reversed-phase HPLC with an evaporative light-scattering detector, the most abundant component, aspacochioside A (**1**), could only be detected in eight genuine Tianmendong samples but not in 13 samples of different species collected in 21 cities of China.

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Therefore, aspacochioside A (**1**) may be an indicative component for identification of this Chinese remedy.

RESULTS AND DISCUSSION

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 reversed-phase silica gels and Sephadex LH-20 successively to afford compounds **1**–**3**, and 3-*O*-[{α-L-rhamnopyranosyl-(1→4)}{β-D-glucopyranosyl}]-26-*O*-[β-D-glucopyranosyl]-(25*S*)-5β-spirostane-3β-ol [4].

Aspacochioside A (**1**) showed a strong broadened absorption band at 3386 cm^{-1} for hydroxy groups in its IR spectrum. The positive HR-ESIMS of **1** exhibited a quasi-molecular ion peak at *m/z* 927.4919 $[M + Na]^+$, and the molecular formula of **1** was established as $C_{45}H_{76}O_{18}$. The ^1H, ^{13}C and DEPT NMR data at δ_H 5.92 (1H, br s, H-1″), 4.85 (1H, d, $J = 7.5$ Hz, H-1′) and 4.81 (1H, d, $J = 7.5$ Hz, H-1″), and at δ_C 105.2 (d, C-1″), 103.0 (d, C-1′), and 102.7 (d, C-1″), which were assignable to anomeric protons and carbons respectively, indicate that **1** has a triglycosidic structure with an α and two β sugar units. A 5β-furostanol aglycon moiety was characterized by two methyl singlets at δ_H 0.82 (3H, s, H-18) and 0.86 (3H, s, H-19) and two methyl doublets at δ_H 1.31 (1H, d, $J = 7.0$ Hz, H-21) and 1.02 (1H, d, $J = 7.0$ Hz, H-27) in the ^1H NMR spectrum of **1** [5]. All signals in the ^1H and ^{13}C NMR spectra (see Table I) were unambiguously assigned by ^1H–^1H DQF-COSY, TOCSY, HMQC and HMBC experiments. The signals assigned to the aglycon moiety are in good agreement with those of (25*S*)-5β-furostane-3β,22α,26-triol glycosylated at C-3 and C-26 [6]. Meanwhile, the signals assigned to three sugar units are consistent with those reported for a terminal α-L-rhamnopyranosyl, a terminal β-D-glucopyranosyl and a 4-subustituted β-D-glucopyranosyl [7]. After acidic hydrolysis of **1**, the TLC and paper chromatography with authentic sugar samples indicated the release of rhamnose and glucose from **1**. In the HMBC spectrum (see Fig. 2 below) the long-range correlations from H-1′ to C-3, H-1″ to C-4′, and H-1″ to C-26 unequivocally revealed that an α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl moiety and the remaining β-D-glucopyranosyl unit were located at C-3 and C-26 of the aglycon, respectively. In the ROESY spectra the correlations from H-20 to H-18 and H-23 confirmed the α orientation of the hydroxy group at C-22. Accordingly, 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-furostane-3β,22α,26-triol (Fig. 1).

Aspacochioside B (**2**) gave quasi-molecular ion peaks at *m/z* 941 $[M + Na]^+$, and 919.5219 $[M + H]^+$ in its HR-ESIMS. Compound **2** showed IR and NMR spectral features very similar to those of **1**, except for the appearance of signals at δ_H 3.24 (3H, s) and δ_C 47.4 (q), attributed to a methoxy group in the ^1H and ^{13}C NMR and DEPT spectra of **2**. Comparison of the ^{13}C NMR data of **2** (see Table I) with those of **1** revealed that the signals assigned to C-22 and C-23 were, respectively, shifted from δ 37.1 and 110.6 of **1** to δ 31.1 and 112.7 of **2**. This evidence indicated that the hydroxy group at C-22 of **1** was replaced by a methoxy group in **2**. In the phase-sensitive NOESY spectra the correlation of the methoxy protons to H-16 confirmed the α orientation of the methoxy group. Consequently, the structure of **2** was determined as 3-*O*-[{α-L-rhamnopyranosyl-(1→4)}{β-D-glucopyranosyl}]-26-*O*-[β-D-glucopyranosyl]-22α-methoxy-(25*S*)-5β-furostane-3β,26-diol.

Compound **2** was converted into **1** by refluxing in acetone-water (1:1), and **1** was converted into **2** by keeping it in MeOH at room temperature. These results confirmed the structural assignment of **2**, and also indicated that either **1** or **2** might be an artificial product

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TABLE I NMR data (δ in ppm) for compounds **1–3**

	1		***2***		***3***	
Number	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1a	1.46 m	30.5 t	1.44 m	30.6 t	1.43 m	30.5 t
1b	1.70 m		1.71 m		1.69 m	
2a	1.54 m	27.0 t	1.55 m	27.0 t	1.52 m	26.6 t
2b	1.70 m		1.72 m		1.70 m	
3	4.25 m	74.6 d	4.25 m	74.6 d	4.28 m	74.8 d
4a	1.77 m	30.9 t	1.75 m	30.9 t	1.77 m	31.0 t
4b	1.88 m		1.88 m		1.86 m	
5	1.95 m	37.0 d	1.97 m	37.0 d	1.95 m	36.6 d
6a	1.67 m	27.0 t	1.65 m	26.9 t	1.66 m	26.6 t
6b	1.89 m		1.82 m		1.84 m	
7a	1.28 m	26.8 t	1.25 m	26.8 t	1.25 m	26.6 t
7b	1.53 m		1.50 m		1.51 m	
8	1.48 m	35.5 d	1.52 m	35.6 d	1.50 m	34.8 d
9	1.07 m	40.3 d	1.09 m	39.5 d	1.15 m	39.7 d
10	–	35.2 s	–	35.3 s	–	34.8 s
11a	1.09 m	21.2 t	1.05 m	21.1 t	0.95 m	21.0 t
11b	1.36 m		1.30 m		1.32 m	
12a	1.74 m	40.4 t	1.73 m	40.2 t	1.74 m	39.7 t
12b	1.76 m		1.76 m		1.76 m	
13	–	41.2 s	–	41.3 s	–	43.4 s
14	0.95 m	56.4 d	1.01 m	56.4 d	0.88 m	54.3 d
15a	1.77 m	32.4 t	1.67 m	32.2 t	1.42 m	34.0 t
15b	2.03 m		1.92 m		2.04 m	
16	4.98 m	81.2 d	4.50 m	81.5 d	4.83 m	84.2 d
17	1.95 m	64.2 d	1.75 m	64.5 d	2.48 d (9.6)	64.2 d
18	0.82 s	16.7 q	0.78 s	16.5 q	0.69 s	14.1 q
19	0.86 s	23.9 q	0.80 s	23.9 q	0.84 s	23.5 q
20	2.22 m	40.7 d	2.20 m	40.6 d	–	103.2 s
21	1.31 d (7.0)	16.5 q	1.15 d (7.0)	16.4 q	1.62 s	11.5 q
22	–	110.6 s	–	112.7 s	–	151.9 s
23a	1.94 m	37.1 t	1.35 m	31.1 t	2.21 m	23.3 t
23b	2.08 m		1.85 m		2.21 m	
24a	1.92 m	28.3 t	1.34 m	28.3 t	1.34 m	30.1 t
24b	1.92 m		1.78 m		1.78 m	
25	1.90 m	34.4 d	1.86 m	34.5 d	1.94 m	33.3 d
26a	3.46 dd (10.0, 7.2)	75.4 t	3.50 dd (10.0, 7.2)	75.0 t	3.47 dd (10.0, 7.2)	74.8 t
26b	4.07 dd (10.0, 7.2)		4.30 dd (10.0, 7.2)		4.10 dd (10.0, 7.2)	
27	1.02 d (7.0)	17.5 q	1.02 d (7.0 Hz)	17.6 q	1.03 d (7.0)	16.8 q
OMe	–	–	3.25 s	47.4 q	–	–
1′	4.85 d (7.5)	103.0 d	4.85 d (7.0)	103.0 d	4.85 d (7.5)	102.6 d
2′	4.02 dd (7.5, 6.5)	75.6 d	3.98 dd (8.0, 7.0)	75.6 d	3.98 dd (7.5, 8.0)	75.2 d
3′	4.21 dd (6.5, 9.0)	76.8 d	4.21 dd (8.0, 9.0)	76.8 d	4.22 dd (8.0, 9.0)	76.4 d
4′	4.48 dd (9.0, 9.5)	78.2 d	4.47 dd (9.0, 9.5)	78.4 d	4.49 dd (9.0, 9.0)	78.2 d
5′	3.70 br d (9.5)	77.2 d	3.69 br d (9.5)	77.4 d	3.71 br d (9.0)	76.8 d
6′a	4.13 br d, (10.5)	61.5 t	4.10 br d (10.5)	61.6 t	4.13 br d (10.5)	61.1 t
6′b	4.25 br d (10.5)		4.27 br d (10.5)		4.27 br d (10.5)	
1″	5.92 br s	102.7 d	5.91 br s	102.7 d	5.92 br s	102.2 d
2″	4.70 br s	72.7 d	4.69 br s	72.9 d	4.70 br s	72.2 d
3″	4.58 br d (8.5)	72.8 d	4.57 br d (8.5)	72.7 d	4.56 br d, 9.5	72.4 d
4″	4.35dd (9.0, 8.5)	74.0 d	4.32 dd (9.0, 8.5)	74.1 d	4.34 dd (9.0, 9.5)	73.6 d
5″	5.03 dq (9.0, 7.0)	70.3 d	5.02 dq (9.0, 7.0)	70.4 d	5.03 dq (9.0, 7.0)	69.9 d
6″	1.69 d (7.0)	18.6 q	1.69 d (7.0)	18.6 q	1.73 d (7.0)	18.2 q
1″	4.81 d (7.5)	105.2 d	4.83 d (7.0)	105.1 d	4.83 d (8.0)	104.8 d
2″	3.99 dd (8.0, 7.5)	75.2 d	3.91 dd (7.0, 8.0)	75.3 d	4.00 dd (8.0, 8.0)	74.8 d
3″	4.20 dd (8.0, 9.0)	78.6 d	4.20 dd (8.0, 9.0)	78.7 d	4.23 dd (8.0, 9.0)	78.2 d
4″	4.25 dd (9.0, 9.0)	71.7 d	4.28 dd (9.0, 9.0)	71.8 d	4.25 dd (9.0, 9.0)	71.3 d
5″	3.93 m	78.5 d	3.95 m	78.5 d	3.96 m	78.2 d
6″a	4.39 br d (12.5)	62.8 t	4.42 br d (12.5)	62.9 t	4.44 br d (12.5)	62.4 t
6″b	4.54 br d (12.5)		4.57 br d (12.5)		4.58 br d (12.5)	

NMR data 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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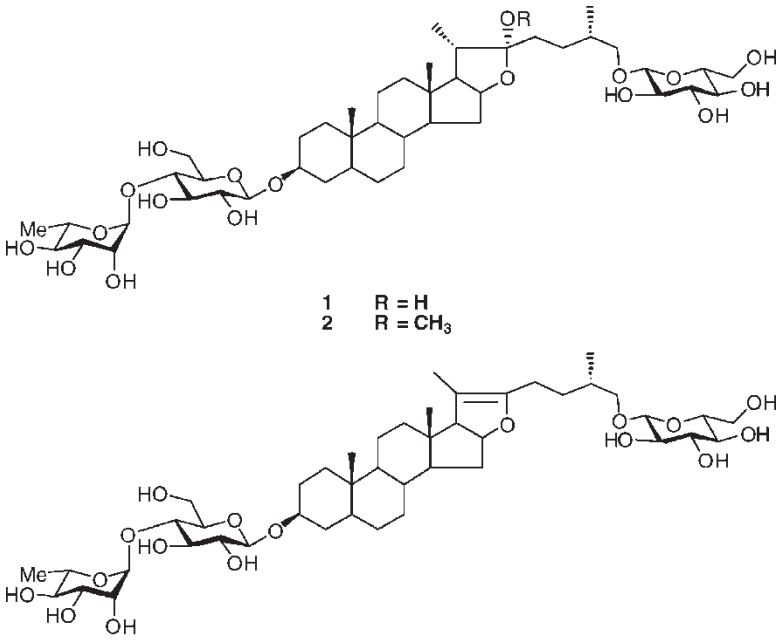

FIGURE 1 Structures of compounds **1**–**3**.

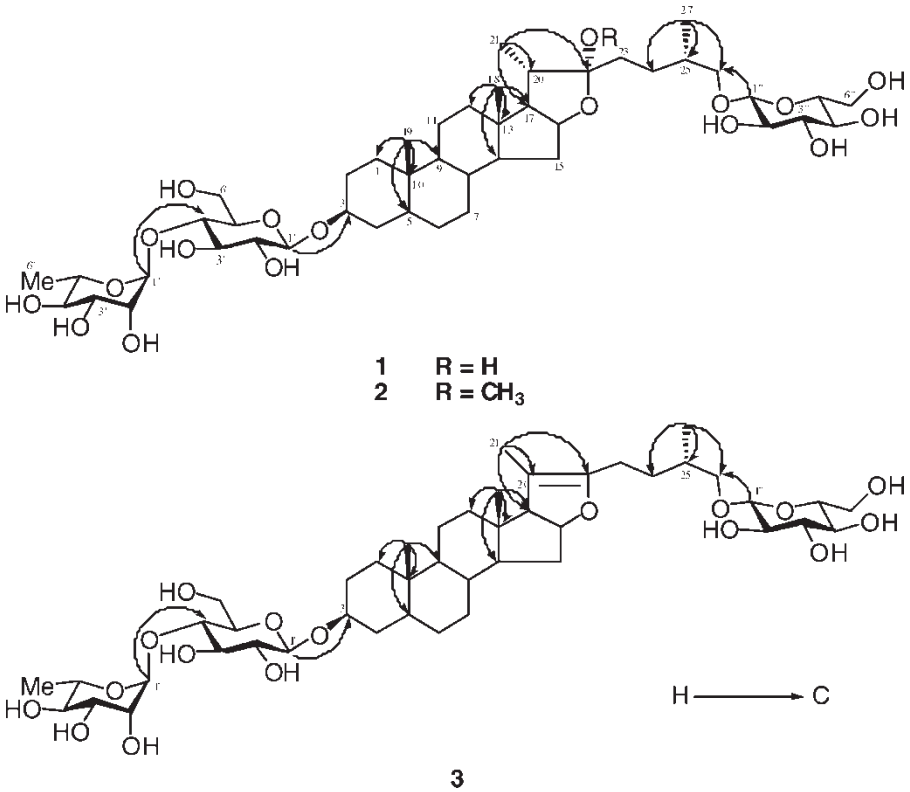

FIGURE 2 Key HMBC correlations of **1**–**3**.

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formed in the isolation procedure, although several pairs of 22α-hydroxy and 22α-methoxy oligofurostanosides have been reported from *Asparagus* plants [4,8–11].

Aspacochioside C (**3**) gave a quasi-molecular ion peak at *m/z* 887.5012 $[M + H]^+$. That its molecular formula ($C_{45}H_{74}O_{17}$) differed from **1** by an H_2O unit was established by positive high-resolution ESIMS. The ESIMS/MS of *m/z* 887 showed a fragment at *m/z* 725; in turn, the ESIMS/MS of *m/z* 725 gave fragments at *m/z* 581 and 417, which suggested that **3** possesses a triglycosidic structural feature similar to that of **1**, except for the loss of H_2O from the aglycon moiety of **3**. This was confirmed by the NMR data (see Table I) assigned through $^1H-^1H$ DQF-COSY, TOCSY, HMQC and HMBC experiments. Comparison of the ^1H, ^{13}C and DEPT NMR spectral data of **3** with those of **1** revealed significant differences in that signals at δ_H 1.62 (3H, s), and δ_C 103.2 (s) and 151.9 (s) of **3** replaced signals at δ_H 1.31 (3H, d, $J = 7.0$ Hz, H-21), and δ_C 40.7 (d, C-20) and 110.6 (s, C-22) of **1**, respectively, indicating the presence of a double bond between C-20 and C-22 in the aglycon moiety of **3** [12,13]. Thus, the structure of **3** 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.

In our recent investigation of the Chinese remedy "Tianmendong" in the Chinese markets of 21 cities, 21 samples were collected. The ethanolic extracts of these samples were analyzed by reversed-phase HPLC equipped with an evaporative light-scattering detector. The most abundant component, aspacochioside A (**1**), could only be detected in eight genuine "Tianmendong" samples, but not in other misused samples of *Asparagus* species. Therefore, aspacochioside A (**1**) may be an indicative component for identification of this Chinese remedy.

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EXPERIMENTAL

General Experimental Procedures

Melting points were determined on an XT-4 micro melting point apparatus and are uncorrected. Optical rotations were measured on a Rudolph Research Autopol III automatic polarimeter. IR spectra were recorded as KBr disks on a Nicolet Impact 400 FT-IR Spectrophotometer. 1D and 2D NMR spectra were obtained on a Varian Inova 500 MHz spectrometers in pyridine-d_5 with TMS as internal standard. ESIMS and HR-ESIMS data were measured with a Micromass Autospec-Ultima ETOF spectrometer. Column chromatography was performed with RA macro porous resin (Beijing Seventh Chemical Inc., China), silica gel (200–300 mesh, Qingdao Marine Chemical Inc., China), RP-18 reversed-phase silica gel (43–60 μm) and Sephadex LH-20 (Pharmacia Biotech AB, Uppsala, Sweden). TLC was carried out with glass precoated silica gel GF_{254} plates. Spots were visualized by spraying with 7% H_2SO_4 in 95% EtOH followed by heating. All solvents used were either spectral grade or were distilled prior to use.

Plant Material

Roots of *A. cochinchinensis* were collected in Fang County of Hubei province, China in September 2000. The plant identification was verified by Professor Wanzhi Song (Department of Medicinal Plants, Institute of Materia Medica, Beijing 100050, China). A voucher specimen (No. 200021) is deposited at the Herbarium of the Department of Medicinal Plants, Institute of Materia Medica.

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Extraction and Isolation

Air-dried and ground roots of *A. cochinchinensis* (18.6 kg) were extracted with EtOH at room temperature for 3 × 48 h, and the solvent was removed under reduced pressure at $<40°C$ to give a residue (1516 g). The residue was suspended in H_2O and then partitioned with EtOAc. After evaporation to remove the remaining EtOAc *in vacuo*, the H_2O phase was subjected to column chromatography over RA resin, eluting with H_2O and EtOH successively. The EtOH eluted solution was concentrated to give a residue (127 g) that was chromatographed over silica gel (500 g), eluting with an $CHCl_3$–MeOH (80:1-0:1) gradient, and separated into 12 fractions (I-XII) on the basis of TLC analyses. Fraction IV was purified by column chromatography over silica gel using $CHCl_3$–MeOH (8:1) as eluent to give the known compound 3-*O*-[{α-L-rhamnopyranosyl-(1→4)}{β-D-glucopyranosyl}]-26-*O*-[β-D-glucopyranosyl]-(25*S*)-5β-spirostane-3β-ol (78 mg). Fraction VI was separated into three sub-fractions by column chromatography over Sephadex LH-20, eluting with $CHCl_3$–MeOH (5:1). Subsequent purifications of the second fraction by repeated column chromatography over reversed-phase silica gel (RP-18), eluting with an increasing gradient of acetonitrile (0–100%) in H_2O, yielded compounds **1** (2.126 g), **2** (162 mg) and **3** (203 mg).

Aspacochioside A (1)

Colorless plates (acetone–H_2O, 1:1), mp 212–213°C; $[\alpha]_D^{22}$ −48.5 (*c* 0.11, Me_2CO–H_2O 1:1); IR (KBr) ν_{max} (cm^{-1}): 3366, 2927, 1641, 1452, 1379, 1169, 1075, 1038, 993, 910, 814; ^1H NMR (pyridine-d_5, 500 MHz) see Table I; ^{13}C NMR (pyridine-d_5, 125 MHz) see Table I; ESIMS *m/z* 927 $[M + Na]^+$, 905 $[M + H]^+$, 887 $[M + H - H_2O]^+$, 725; HR-ESIMS *m/z* 927.4919 (calcd for $C_{45}H_{76}O_{18}Na$, 927.4929).

Aspacochioside B (2)

White needles (MeOH), mp 199–200°C; $[\alpha]_D^{22}$ −64.7 (*c* 0.10, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3404, 2929, 2641, 1452, 1379, 1167, 1128, 1072, 1041, 1022, 910, 893, 814; ^1H NMR (pyridine-d_5, 500 MHz) see Table I; ^{13}C NMR (pyridine-d_5, 125 MHz) see Table I; ESIMS *m/z* 941 $[M + Na]^+$, 919 $[M + H]^+$, 887 $[M + H - MeOH]^+$; HR-ESIMS *m/z* 919.5219 (calcd for $C_{46}H_{79}O_{18}$, 919.5266).

Conversions between 1 and 2

A solution of **1** (50 mg) in MeOH (3 ml) was kept at room temperature for 48 h. After drying with nitrogen, the residue was subjected to column chromatography over reversed-phase silica gel (RP-18), eluting with a gradient of increasing MeCN (0–100%) in H_2O, to give **2** (17 mg). Compound **2** (50 mg) was refluxed with Me_2CO–H_2O (1:1, 5 ml) at 60°C for 8 h. After the solution was cooled, colorless plates were crystallized, and filtration of the solution then gave **1** (23 mg).

Aspacochioside C (3)

White needles (MeOH–H_2O, 1:1), mp 140–141°C; $[\alpha]_D^{22}$ −26.3 (*c* 0.09, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3396, 2927, 1691, 1635, 1448, 1379, 1304, 1221, 1076, 1038, 1026, 910, 812; ^1H NMR (pyridine-d_5, 500 MHz) see Table I; ^{13}C NMR (pyridine-d_5, 125 MHz) see Table I; ESIMS *m/z* 887 $[M + H]^+$, 741 $[M + H - rhamnosyl]^+$, 725 $[M + H - glucosyl]^+$, 579;

ESIMS/MS *m/z* 887, 725, 579, 581, 435, 415, 399, 285, 273, 255, 163, 147, 129, 85, 71; ESIMS/MS *m/z* 725, 581, 435, 417, 399, 273, 225, 161, 147, 129, 85, 71; HR-ESIMS *m/z* 887.5012 (calcd for $C_{45}H_{75}O_{17}$, 887.5004).

Acidic Hydrolysis of 1–3

A solution of each compound (20 mg) in 2 M HCl (3 ml) was refluxed for 8 h at 94°C. The reaction mixture was partitioned with EtOAc. The aqueous phase was neutralized with 1 M NaOH and blow-dried with nitrogen. The residue was then dissolved in EtOH (0.5 ml) and analysed by TLC and PC together with authentic sugar samples. The developing solvent systems were $CHCl_3$–MeOH (2.5:1) for TLC and the upper layer of *n*-BuOH–AcOH–H_2O (4:1:5) for PC; the spots were colored by spraying aniline hydrogen phthalate followed by heating at 105°C.

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