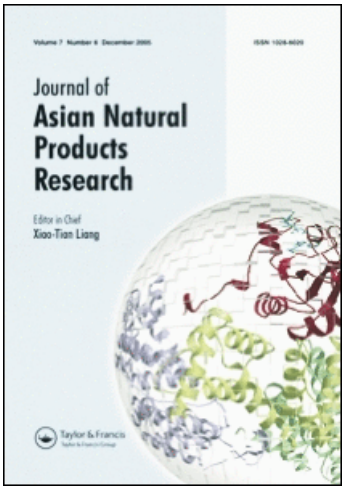

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Furostanoside from *Asparagus filicinus*

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A new furostanoside, named aspafilioside D (**1**), together with the five known compounds officinalisnin-II (**2**), Asp-IV′ (**3**), (+)-4′-*O*-methyl-nyasol (**4**), (+)-nyasol (**5**) and tormentic acid (**6**), have been isolated from the roots of *Asparagus filicinus*. The structure of **1** has been elucidated on the basis of spectral data.

Keywords: *Asparagus filicinus*; Liliaceae; Furostanosides; Aspafilioside D

1. Introduction

Asparagus filicinus Ham. ex D. Don (Liliaceae) has been reported for its medicinal utility. The root is considered to be a tonic astringent in India and has been used to treat bronchitis, cough and pneumonia as a folk medicine of China [1–3]. Some furostanol saponins have been obtained from the root of this plant in previous work [4,5]. In our present study on *Asparagus filicinus,* one new compound aspafilioside D (**1**) was isolated, together with the five known compounds officinalisnin-II (**2**), Asp-IV′ (**3**), (+)-4′-*O*-methyl-nyasol (**4**), (+)-nyasol (**5**), and tormentic acid (**6**).

2. Results and discussion

Aspafilioside D (**1**) was obtained as a white amorphous powder that gave a red Ehrlich reaction characteristic of furostanol glycoside. Its IR spectrum (3415, 2927, 1635, 1452, 1378, 1152, 1041 cm^{-1}) shows no absorption corresponding to a spiroketanol saponin (which show absorption bands near 860, 900, 920, and 980 cm^{-1}) [6]. The negative ESI-MS peak at *m*/*z* 1021.9 corresponds to $[(C_{49}H_{82}O_{22})-H]^-$. The NMR and ESI-MS data indicated that **1** contains two pentose and two hexose units. Enzymatic hydrolysis of **1** with amygdalase gives spirostanol saponin **1a**. Acid hydrolysis of **1** afforded sarsasapogenin as aglycone and glucose and xylose as the sugar components, which were identified by TLC by comparison with authentic samples [7]. Its ^1H NMR spectrum showed two singlet signals at δ 0.98 and 1.09 (each 3H), indicating

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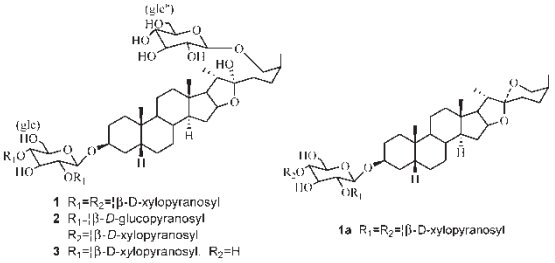
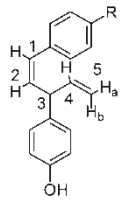
the presence of two angular methyl groups, as well as two doublet signals at δ 1.41 (3H, $J = 6.8$ Hz) and δ 1.12 (3H, $J = 6.5$ Hz) assignable to secondary methyl groups. The structure of **1** based upon a (25*S*)-spirostanol derivative was suggested by the above ^{1}H NMR data and a quaternary carbon signal at 111.1 in the ^{13}C NMR spectrum [8]. This was confirmed by the characteristic IR absorptions at ν_{max} 980, 915, 890, 840 cm^{-1} of **1a** with the absorption at 915 cm^{-1} being of greater intensity than that at 890 cm^{-1} [9–11].

The β-configuration at the anomeric centers of the glucopyranosyl moieties was suggested by the coupling constants ($J_{H1-H2} = 7.5$, 7.6 Hz) of the anomeric proton in the ^{1}H NMR spectrum. The xylosyl group was concluded to be in the β-configuration ($J_{H1-H2} = 6.6$, 7.7 Hz). Both ^{1}H and ^{13}C NMR chemical shifts were assigned (table 1) from a combination of 2D homonuclear ^{1}H–^{1}H (COSY, TOCSY) and heteronuclear ^{13}C–^{1}H (HMQC, HMBC) correlations and allowed unambiguous identification of the aglycone and various sugar moieties. The cross-peaks seen in the HMBC spectrum, arising from through-bond couplings over three bonds between the anomeric protons and carbons in adjacent systems, allowed the determination of the sugar sequence and the aglycone linkage positions. Hence, cross-peaks between H-1 (δ 4.95) of glucose and C-3 (δ 74.9) of the aglycone and between H-3 (δ 4.40) of the aglycone and C-1 (δ 101.0) of the glucose indicated that the glucose moiety was attached at C-3 of the aglycone. Cross-peaks between H-1 (δ 4.88) of the glucose and C-26 (δ 75.7) of the aglycone, and H-26 (δ 3.60) of the aglycone and C-1 (δ 105.3) of glucose showed the linkage of another glucose moiety with C-26 of the aglycone. Cross-peaks between H-1 (δ 5.38) of xylose and C-2 (δ 82.3) of glucose, H-1 (δ 5.15) of another xylose and C-4 (δ 80.7) of glucose proved that **1** consisted of a glucose unit bearing one xylose at C-2 and another xylose at C-4. The ^{1}H–^{1}H COSY, TOCSY, and HMQC experiments permitted the full assignment of the glucose protons and carbons, H-2 (δ 4.23) and H-4 (δ 4.37) of this glucose showed cross-peaks with its anomeric proton (δ 4.95) in the TOCSY spectrum, which correlated with C-3 of aglycone in the HMBC spectrum, These evidences confirmed the linkage of two xyloses and the 3-*O*-glucose. Consequently, the structure of **1** was elucidated as (25*S*)-5β-furost-3β,22,26-triol-3-*O*-β-D-xylopyranosyl(1⟶2)[β-D-xylopyranosyl(1⟶4)]β-D-glucopyranoside-26-*O*-β-D-glucopyranoside.

On the basis of spectroscopic data, compound **2** was identified as officinalisnin-II, its NMR data are reported for the first time. Compounds **3**–**6** were identified by comparing their physical and spectral data with literature values.





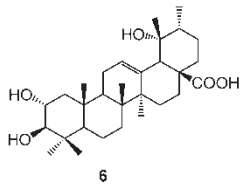


Table 1. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data for **1** and **2** (C_5D_5N, δ in ppm, J in Hz).

	1		***2***			***1***			***2***	
Position	δ_H	δ_C	δ_H	δ_C	*Position*	δ_H	δ_C		δ_H	δ_C
1	1.85 m	30.5	1.85 m	30.8	3-O-Glc					
2	1.95 m	27.1	1.92 m	27.0	G_1	4.95 d (7.5)	101.0		4.95 d (6.9)	101.8
3	α4.40 m	74.9	α4.35 m	75.1	G_2	4.23 m	82.3		4.35	81.5
4	1.95 m	31.0	1.92 m	31.0	G_3	4.35 m	76.8		4.35	76.4
	1.60 m		1.57 m		G_4	4.37 m	80.7		4.30	80.8
5	2.20 m	37.4	2.10 m	37.3	G_5	3.90 m	76.7		3.87	76.5
6	1.35 m	27.3	1.58 m	27.2	G_{6a}	a 4.55 m	61.8		a 4.50 m	61.9
	1.25 m		1.28 m		G_{6b}	b 4.62 m			b 4.60 m	
7	1.25 m	27.3	1.25 m	27.0	2′-O-Xyl			2′-O-Glc		
8	1.58 m	35.9	1.58 m	35.7	X_1	5.38 d (6.6)	106.5	G_1'	5.53 d (7.6)	105.5
9	1.85 m	40.6	1.83 m	40.5	X_2	4.13 m	75.5	G_2'	4.13m	77.1
10		35.6		35.4	X_3	4.32 m	77.9	G_3'	4.35 m	78.1
11	1.22 m	21.5	1.40 m	21.3	X_4	4.35 m	71.4	G_4'	4.35 m	72.1
12	1.38 m	40.7	1.37 m	40.5	X_{5a}	a 4.55 m	67.6	G_5'	4.08 m	78.6
13		41.6		41.3	X_{5b}	b 3.85 m		G_{6a}'	a 4.55 m	63.3
14	1.15 m	56.7	1.18 m	56.6				G_{6b}'	b 4.60 m	
15	2.15 m	32.7	2.11 m	32.5	4′-O-Xyl					
	1.54 m		1.50 m		X_1'	5.15 d (7.7)	105.7		5.15 d (7.7)	105.6
16	5.10 d (7.3)	81.6	5.05	81.4	X_2'	4.08 m	75.2		4.05 m	75.0
17	2.10 m	64.2	2.05 m	64.2	X_3'	4.25 m	71.1		4.17 m	78.5
18	0.99 s	17.0	0.98 s	16.6	X_4'	4.35 m	76.8		4.32 m	70.9
19	1.10 s	24.2	1.09 s	24.2	X_{5a}'	a 3.75 m	67.5		a 3.75 m	67.5
20	2.35 m	41.0	2.32 m	40.8	X_{5b}'	b 3.82 m			b 4.35 m	
21	1.42 d (6.5)	17.1	1.41 d (6.8)	16.8	26-O-Glc					
22		111.1		110.8	G_1'	4.88 d (7.6)	105.3	G_1''	4.88 d (7.7)	105.3
23	2.38 m	36.5	2.28 m	36.8	G_2'	4.12 m	75.5	G_2''	4.10 m	75.3
24	2.18 m	28.6	2.17 m	28.5	G_3'	4.27 m	78.5	G_3''	4.32 m	78.8
	1.80 m		1.78 m		G_4'	4.32 m	72.0	G_4''	4.28 m	71.8
25	2.05 m	34.7	2.02 m	34.5	G_5'	4.05 m	78.7	G_5''	4.02 m	78.6
26	3.60 t (8)	75.7	3.65 m	76.5	G_{6a}'	a 4.45 m	63.1	G_{6a}''	a 4.45 m	63.0
27	1.14 d (6.5)	17.8	1.12 d (6.5)	17.6	G_{6b}'	b 4.65 m		G_{6b}''	b 4.60 m	

3. Experimental

3.1 General experimental procedures

Melting points were determined using a XT-4 point apparatus and are uncorrected. Optical rotations were determined on a Perkin-Elmer Model 341 polarimeter. UV spectra were obtained on an Ultrospec 4000 UV/visible spectrophotometer using MeOH as solvent, and IR spectra were measured with a Perkin-Elmer 559B apparatus. NMR spectra were recorded with Varian Mercury-300 and Bruker AMX-400 NMR spectrometers in pyridine-d_5 and acetone-d_6 using TMS as internal standard. MS were determined on a MAT 711 mass spectrometer. D-101 macroporous resin (Nankai University, China), MCI gel CHP-20P (Mistubishi Kasei Industry Co. Ltd, Japan) and Sephadex LH-20 (Merck, German) were employed in the separations.

3.2 Plant material

Roots of *Asparagus filicinus* Ham. ex D. Don were collected at feina, Xizang province, China in August 2000. A voucher specimen (NPLE00139) has been deposited at the herbarium of the Chinese National Center for Drug Screening, Shanghai Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences, Shanghai, China.

3.3 Extraction and isolation

The roots of *Asparagus filicinus* (1.0 kg) were powdered and extracted three times at room temperature with 95% EtOH (each time for 3 days). After concentration *in vacuo*, the extract was diluted with H_2O and extracted with $CHCl_3$, and evaporated to dryness *in vacuo* to provide a $CHCl_3$ part (0.5 g), The remaining aqueous solutions were chromatographed over D-101 macroporous resin and eluted gradiently with H_2O–EtOH to afford a 15% EtOH part (11 g) and a 30% EtOH part (0.3 g).

The $CHCl_3$ extract (0.5 g) was chromatographed over silica gel (200–300 mesh) using light petroleum–acetone mixtures of increasing polarity. Elution by light petroleum–acetone (4:1) afforded compounds **4** (10 mg), **5** (8 mg) and **6** (10 mg); elution by light petroleum–acetone (3:1) afforded **5** (7 mg). The 30% EtOH part (11 g) was repeatedly chromatographed over MCI gel and Sephadex LH-20 to afford **1** (35 mg), **2** (54 mg) and **3** (38 mg).

Aspafilioside D (**1**): a white amorphous powder (MeOH), mp 190–191°C; $[\alpha]_D^{20}$ –18 (*c* 0.27, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3415, 2927, 1635, 1452, 1378, 1152, 1041; ESI-MS *m/z*1021.9 $[M - H]^-$, ^1H and ^{13}C NMR data see table 1.

Enzymatic hydrolysis of **1**. Compound **1** (10 mg) was treated with β-glucosidase (30 mg) in HOAc–NaOAc buffer (pH 4.5, 5 ml) at room temperature for 24 h. The reaction mixture was then chromatographed on MCI gel to give the corresponding spirostanol saponin **1a**.

Officinalisnin-II (**2**): a white amorphous powder (MeOH), mp 193–195°C; $[\alpha]_D^{20}$ –13 (*c* 0.27, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3386, 2927, 1637, 1452, 1378, 1162, 1078, 1043; ^1H and ^{13}C NMR data (table 1) are consistent with literature values [12].

Asp -IV′ (**3**): a white amorphous powder (MeOH), mp 165–167°C; ^1H and ^{13}C NMR data are consistent with literature values [2,13].

(+)-4′-O-Methyl-nyasol (**4**): a brown oil; $[\alpha]_D^{20}$ + 162 (*c* 0.102, MeOH); UV (MeOH) λ_{max} (nm) (log ε): 241.2 (4.57), 285.9 (4.12); ^{1}H and ^{13}C NMR data are consistent with literature values [14].

(+)-Nyasol (**5**): a brown oil; $[\alpha]_D^{20}$ + 169 (*c* 0.074, MeOH); UV (MeOH) λ_{max} (nm) (log ε): 236 (4.31), 277.9 (4.08); ^{1}H and ^{13}C NMR data are consistent with literature values [15].

Tomentic Acid (**6**): a white amorphous powder; HREI-MS (*m*/*z*): 488.3492; ^{13}C NMR data are consistent with literature values [16].

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