Chinese Chemical Letters Vol. 14, No. 4, pp 379 – 382, 2003
http://www.imm.ac.cn/journal/ccl.html

A new Furostanoside from *Asparagus filicinus*

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Abstract: A new furostanoside, aspafilioside D (**1**) has been isolated from the root of *Asparagus filicinus.* Its structure was determined by spectral and chemical methods.

Keyword: Aspafilioside D, *Asparagus filicinus*, Liliaceae.

Asparagus filicinus Bunch. -Ham (Liliaceae) has been reported for its medicinal utility. The root is considered to be a tonic astringent in India, and used for the treatment of bronchitis, pneumonitis and cough as a folk medicine of China[1,2,3]. A new oligofurostanoside, named aspafilioside D, was obtained from the root of this plant. This paper deal with the structure elucidation of this compound.

Aspafilioside D (1) was isolated as amorphous powder; mp193-195°C; $[\alpha]_D^{20}$ -13 (*c* 0.27, MeOH); UV (MeOH) λ_{max} (log ε): 223 (4.06), 227 (3.61) nm; gave a red Ehrlich reaction characteristic of furostanolglycoside and shows no absorption of IR spectrum (3415, 2927, 1635, 1452, 1378, 1152, 1041cm^{-1}) corresponding to spirokatanol saponin. The ESI-MS (–) showed a peak at *m/z* 1021.9, corresponding to [M ($C_{49}H_{82}O_{22}$)-H]$^-$. On the basis of its ^{1}H- and ^{13}C-NMR data, the aglycone of **1** was determined as sarsasapogenin. The NMR and ESI-MS data indicated that **1** contained two pentose and two hexose unit. Hydrolysis of **1** yielded glucose and xylose. The β-configuration at the anomeric center of the glucopyranosyl moiety was suggested by the large coupling ($J_{H1\text{-}H2}$=7.5, 7.6Hz) of the anomeric proton in the ^{1}H-NMR spectrum. The xylosyl group was concluded to be in the β-configurations （$J_{H1\text{-}H2}$=6.6, 7.7Hz）, ^{1}H- and ^{13}C-NMR chemical shifts were assigned （**Table 1** and **2**） from a combination of 2D homonuclear ^{1}H-^{1}H (COSY, TOCSY) and heteronuclear ^{13}C-^{1}H (HMQC, HMBC) correlations that allowed unambiguous identifications of the aglycone and the various sugar moieties. The observation of cross-peaks 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.

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Figure 1 Structure of Compound **1**

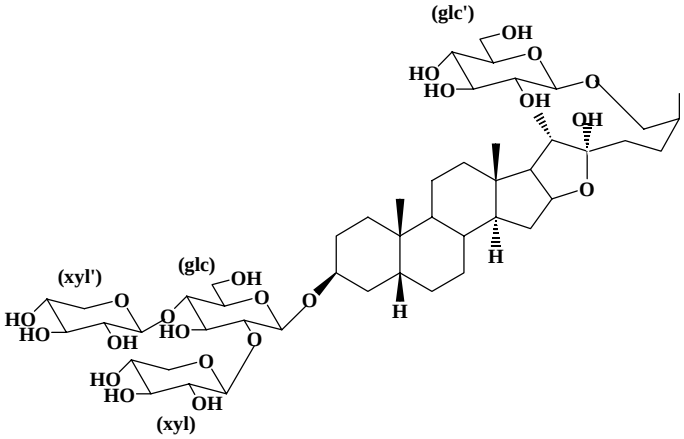

Table 1 NMR data for compound **1** (δ in C_5D_5N ppm, *J* Hz)

Position	^{1}H	^{13}C	Position	^{1}H	^{13}C
1	1.85 m	30.5	3-O-Glc		
2	1.95 m	27.1	G_1	4.95 d (7.5)	101.0
3	β 4.40 m	74.9	G_2	4.23 m	82.3
4	1.95 m	31.0	G_3	4.35 m	76.8
	1.60 m		G_4	4.37 m	80.7
5	2.20 m	37.4	G_5	3.90 m	76.7
6	1.35 m	27.3	G_{6a}	a 4.55 m	61.8
	1.25 m		G_{6b}	b 4.62 m	
7	1.25 m	27.3	2′ Xyl		
8	1.58 m	35.9	X_1	5.38 d (6.6)	106.5
9	1.85 m	40.6	X_2	4.13 m	75.5
10		35.6	X_3	4.32 m	77.9
11	1.22 m	21.5	X_4	4.35 m	71.4
12	1.38 m	40.7	X_{5a}	a 4.55 m	67.6
13		41.6	X_{5b}	b 3.85 m	
14	1.15 m	56.7	4′Xyl		
15	2.15 m	32.7	X_1'	5.15 d (7.7)	105.7
	1.54 m		X_2'	4.08 m	75.2
16	5.10 d (7.3)	81.6	X_3'	4.25 m	71.1
17	2.10 m	64.2	X_4'	4.35 m	76.8
18	0.99 s	17.0	X_{5a}'	a 3.75 m	67.5
19	1.10 s	24.2	X_{5b}'	b 3.82 m	
20	2.35 m	41.0	26-O-Glc		
21	1.42 d (6.5)	17.1	G_1'	4.88 d (7.6)	105.3
22		111.1	G_2'	4.12 m	75.5
23	2.38 m	36.5	G_3'	4.27 m	78.5
24	2.18 m	28.6	G_4'	4.32 m	72.0
	1.80 m		G_5'	4.05 m	78.7
25	2.05 m	34.7	G_{6a}'	a 4.45 m	63.1
26	3.60 t (8)	75.7	G_{6b}'	b 4.65 m	
27	1.14 d (6.5)	17.8			

Table 2 Summary of the two-dimensional NMR correlations of **1** (δ in C_5D_5N ppm, *J* Hz)

Proton	H-H COSY	HMQC (^{13}C)	TOCSY	HMBC (^{13}C)
3-O-Glc				
G_1	G_2	G_1	G_2, G_3, G_4, G_5, G_{6a}, G_{6b}	C-3
G_2	G_1, G_3	G_2	G_1, G_3, G_4, G_5	G_1
G_3	G_2	G_3	G_1, G_2, G_4, G_5, G_{6a}, G_{6b}	
G_4	G_5	G_4	G_1, G_2, G_3, G_5, G_{6a}, G_{6b}	G_3, G_5
G_5	G_4, G_{6a}	G_5	G_1, G_2, G_3, G_4, G_{6a}, G_{6b}	G_6
G_{6a}	G_5	G_6	G_1, G_3, G_4, G_5	
G_{6b}		G_6	G_1, G_2, G_3, G_4	
2′-Xyl				
X_1	X_2	X_1	X_2, X_3, X_4, X_{5a}, X_{5b}	G_2
X_2	X_1, X_3'	X_2	X_1, X_3, X_4, X_{5a}, X_{5b}	X_1
X_3	X_2	X_3	X_1, X_2, X_4, X_{5a}, X_{5b}	X_2
X_4	X_{5b}	X_4	X_1, X_2, X_4, X_{5a}, X_{5b}	X_5
X_{5a}	X_{5b}	X_5	X_1, X_2, X_3, X_4, X_{5b}	X_4
X_{5b}	X_{5a}, X_4	X_5	X_1, X_2, X_3, X_4, X_{5a}	
4′-Xyl				
X_1'	X_2'	X_1'	X_2', X_3', X_4', X_{5a}',	G_4
X_2'	X_1', X_3'	X_2'	X_1', X_3', X_4', X_{5a}'	
X_3'	X_2', X_4'	X_3'	X_1', X_2', X_4', X_{5a}', X_{5b}'	X_2',
X_4'	X_3', X_{5a}', X_{5b}'	X_4'	X_1', X_2', X_3', X_{5a}', X_{5b}'	X_3', X_2'
X_{5a}'	X_4'	X_5'	X_1', X_2', X_3', X_4'	
X_{5b}'	X_4'	X_5'	X_1', X_3', X_4'	
26-O-Glc				
G_1'	G_2'	G_1'	G_2', G_3', G_4', G_5', G_{6a}', G_{6b}'	C-26
G_2'	G_1', G_3'	G_2'	G_1', G_3', G_4', G_5', G_{6a}', G_{6b}'	G_1'
G_3'	G_4'	G_3'	G_1', G_4', G_5', G_{6a}', G_{6b}'	
G_4'	G_5', G_3'	G_4'	G_1', G_2', G_3', G_5', G_{6a}', G_{6b}'	G_3', G_5'
G_5'	G_{6a}', G_4'	G_5'	G_1', G_2', G_3', G_4', G_{6a}', G_{6b}'	G_6'
G_{6a}'	G_5'	G_6'	G_1', G_2', G_5', G_{6b}'	
G_{6b}'		G_6'	G_1', G_2', G_3', G_4', G_5', G_{6a}'	

Hence, cross-peaks between H-1 (δ4.95) and C-1 (δ101.0) of glucose and C-3 (δ74.9) and H-3 (δ4.40) of the aglycone, respectively, indicated that the glucose moiety was attached at C-3 of the aglycone. Cross-peak between H-1 (δ4.88) and C-1 (δ105.3) of glucose and C-26 (δ75.7) and H-26 (δ3.60) of the aglycone, indicated that another glucose moiety was attached at C-26 of the aglycone. Cross-peaks between H-1 (δ5.38) of xylose and C-2 (δ82.3) of glucose, H-1 (δ5.15) of another xylose and C-4 (δ80.7) of glucose indicated that **1** consisted of a glucose unit bearing one xylose at C-2 and another xylose at C-4. Consequently, The structure of **1** was elucidated as (25s) -5β-furost-3β, 22, 26-triol-3-O-β-D-xylopyranosyl (1→2) [β-D-xylopyranosyl (1→4)]-D- glucopyranoside -26-O-β-D-glycopyranoside.

Acknowledgment

This work was supported by the National Natural Science Fundation of China (30100229) and Science and Technology Development Fundation of Shanghai, China (01QB14051), and these supports are gratefully acknowledged.

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Received 22 February, 2002
Revised 1 January, 2003