A New Enolate Furostanoside from *Asparagus Filicinus*

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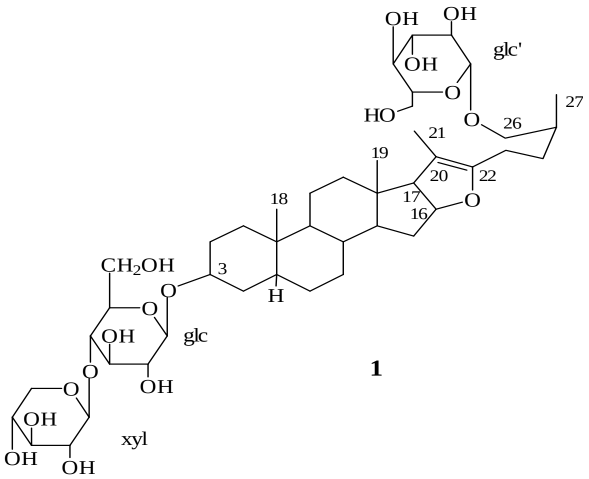
Abstract: A new enolate derivative of furostanol glycoside, named asparagusin A, was isolated from the roots of *Asparagus filicinus* and established as 3-*O*-β-D-xylopyranosyl(1→4)-β-D-glucopyranosyl (25S)-furost-20(22)-ene-3β, 26-diol 26-*O*-β-D-glucopyranoside (**1**) by spectroscopic and chemical methods. Asparagusin A (**1**) exhibited a cytotoxic activity effect on PC_{12} cells.

Keywords: *Asparagus filicinus*, Liliaceae, furostanol glycoside, asparagusin A, cytotoxic activity.

The roots of *Asparagus filicinus* Buch.-Ham are used to treat lung diseases such as bronchitis, pneumonities and cough in folk medicine[1]. Some steroidal glycosides have been isolated and characterized from the roots of this plant by several research groups[2-3]. In this paper, we report the isolation of a new unusual furostanol glycoside possessing an enolate moiety, whose structure was determined by 1D and 2D NMR methods, FABMS, and hydrolysis. Bioassay results showed that the compound exhibited a cytotoxic activity on PC_{12} cells with IC_{50} 9.2 μg/mL value.

Figure 1. Structure of asparagusin A



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Compound **1** was isolated as an amorphous powder from the EtOH extract of the roots of this plant. The FAB-MS of **1** displayed quasi-molecular ions $[M + H]^+$ and $[M + Na]^+$ at m/z 873 and 895, respectively, consistent with a molecular formula of $C_{44}H_{72}O_{17}$.

Complete acid hydrolysis of **1** afforded sarsasapogenin, which was identified by comparison of its NMR and IR data with those reported in the literature[4], and glucose and xylose identified by comparison with authentic samples by TLC. Acetolysis of **1** yielded a genuine aglycon (25S)-furost-20(22)-ene-3β, 26-diol which was confirmed by its NMR and MS data[5]. The ^{1}H and ^{13}C NMR spectra (**Table 1**) of **1** clearly showed the presence of a steroid skeleton possessing an 20(22)-en moiety (δc 103.6 and 152.4), which formed an enolate moiety with the oxygen atom of furan ring, the three sugar residues were clearly indicated by three anomeric carbon signals at δ103.0, 105.3 and 105.7, and the corresponding three anomeric proton signals at δ 4.90 (d, J = 7.6 Hz), 4.83 (d, J =7.2 Hz), and 5.15 (d, J =7.2 Hz). The above data together with 2D NMR results indicated that the saccharide part was composed of two β-glucose and one β-xylose residues, and their absolute configurations were assumed to be D.

Comparison of the ^{13}C NMR data of **1** with those of the aglycon[5] indicated main glycosylation shifts at C-3 (+ 8.8 ppm) and C-26 (+ 7.8 ppm) positions, respectively. Thus, both the hydroxyl at C-3 and that at C-26 were glycosylated. In the HMBC spectrum of **1**, correlation peaks were observed between H-1 (δ 4.90) of the glucose and C-3 (δ 74.8) of the aglycon, as well as H-1 (δ 5.15) of xylose and C-4 (δ 81.1) of the glucose. It was concluded that a disaccharide chain possessing one glucose and one xylose units was bonded to the hydroxyl at C-3 position of the aglycon. Moreover, the HMBC spectrum revealed a correlation peak between another glucose anomeric proton (δ 4.83, H-1′) and C-26 (δ 75.3) of the aglycon. Hence, asparagusin A (**1**) was established to be 3-*O*-β-D-xylopyranosyl(1→4)-β-D-glucopyranosyl (25S)-furost-20(22)-ene-3β, 26-diol 26-*O*-β-D-glucopyranoside.

Table 1. ^{13}C NMR Data of **1**

C	δ	C	δ	C	δ	C	δ
1	30.7	15	31.6	C-3		C-26	
2	27.2	16	84.7	Glc 1	103.0	Glc 1′	105.3
3	74.8	17	64.8	2	75.2	2′	75.1
4	31.1	18	14.6	3	76.7	3′	78.7
5	37.1	19	24.1	4	81.1	4′	71.8
6	27.2	20	103.6	5	76.6	5′	78.7
7	27.0	21	12.0	6	62.0	6′	63.0
8	35.4	22	152.4				
9	40.3	23	34.6	Xyl 1	105.7		
10	35.4	24	23.8	2	75.3		
11	21.5	25	33.9	3	78.5		
12	40.2	26	75.3	4	71.0		
13	44.0	27	17.4	5	67.5		
14	54.9						

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