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Two New Steroidal Saponins from *Tacca plantaginea*

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Abstract: Two new C_{27} steroidal glycosides, named taccaoside A (**1**) and B (**2**), were isolated from the traditional Chinese herb *Tacca plantaginea*. The spectroscopic and chemical evidences revealed their structures to be 26-O- -D-glucopyranosyl-(25R)-3 ,26-dihydroxy furost-5,20-diene -3-O-[-L-rhamnopyranosyl(1→2)]-[-L-rhamnopyranosyl(1→3)]- -D-glucopyranoside **(1)** and 26-O- -D-glucopyranosyl-(25R)-3 ,26-dihydroxy furost-5,20-diene-3-O-[-L-rhamnopyranosyl-(1→2)]-[-D-glucopyranosyl(1→3)- -L-rhamnopyranosyl(1→3)]- -D-glucopyranoside (2), respectively.

Keywords: *Tacca plantaginea*, steroidal saponins, taccaoside **A** and **B**.

Tacca plantaginea (Hance) is a herbaceous plant, distributed in south China. Its rhizome has been used in folk medicine[1] as analgesic, antepyretic, anti-inflammatory agents and treated for incised wounds. As a part of our phytochemical studies on this plant, this paper deals with the structural elucidation of two new steroidal saponins taccoside A (**1**) and B (**2**) (**Figue 1**) by spectral means, especially 1D and 2D NMR spectroscopy.

Compound **1**, colorless needles, mp179~180°C, $[\alpha]_D^{26}$-58.5 (c 0.21, MeOH), its molecular form $C_{51}H_{82}O_{21}$ was determined from the quasi-molecular ion peak at *m/z* 1029 $[M-H]^-$ in its negative FAB mass spectrum and ^{13}C NMR (DEPT) spectrum. Compound **1** was positive to Ehrlich reagent, which suggested that it might be a furostanol glycoside. The aglycone of compound **1** could be proved to be 3β,26-d i-hydroxy-25 (R)-5-furostene by direct comparison of ^1H and ^{13}C NMR spectra (**Table 1**) with those of the literature[2]. Complete acid hydrolysis of compound **1** yielded an aglycone and sugar residues consisting of D-glucose and L-rhamnose. The ^1H NMR spectrum of compound **1** demonstrating the coupling constants of anomeric proton signals at 4.76(d,1H,6.2Hz), 4.84(d,1H,7.72Hz), 5.69(s,1H), 5.8(s,1H) suggested two -linkages and two -linkages in the sugar chain. The negative ion FAB mass spectrum displayed fragment ion peaks at *m/z* 883$[M-146-H]^-$, 867$[M-162-H]^-$, 721[M-

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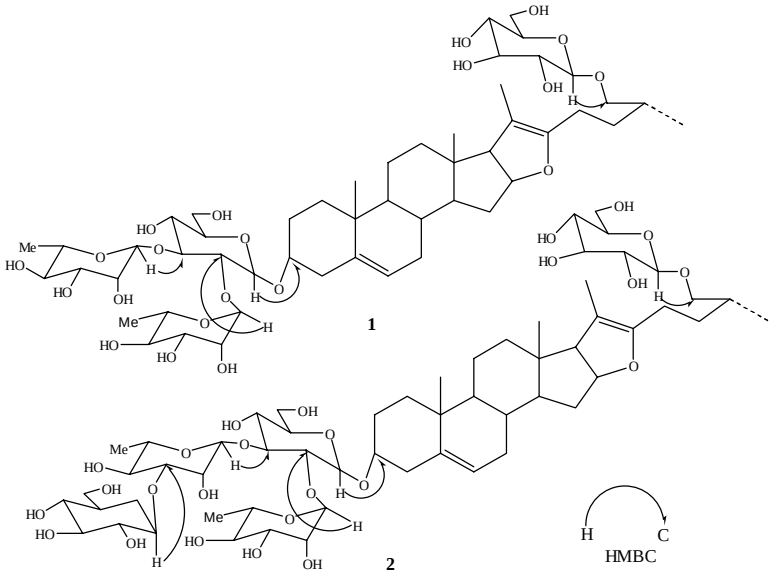
146-162-H]$^-$, 575[M-146-162-146-H]$^-$, which indicated that compound **1** contained two rhamnoses and one glucose as terminal sugars, and another glucose as inner sugar. This was further confirmed by 2D NMR. In HMBC spectrum, the long range correlations between C-3 (δ 78.5) of the aglycone and H-1 (δ 4.84) of glucose, C-2 (δ 78.1) of glucose and H-1 (δ 5.8) of terminal rhamnose, C-3 (δ 87.6) of glucose and H-1(δ 5.69) of another terminal rhamnose, C-26(δ 75.3) of aglycone and H-1(δ 4.76) of glucose were observed, which indicated that two glucosyl units were linked to C-26, C-3 of the aglycone, respectively and two rhanmosyl units were linked to C-2, C-3 of glucose. From the above evidence, the structure of compound **1** was assigned to be 26-O-β-D-glucopyranosyl- (25R)-3β,26-dihydroxyfurost-5,20-dien-3-O-[-L-rhamno-pyranosyl(1→2)]-[-L-rh-amnopyranosyl(1→3)]-β-D-glucopyranoside, named taccoside A.

Figue 1 The long range ^{1}H-^{13}C correlations for compounds **1** and **2**



Compound **2**, colorless needles, mp193~194ºC, [ ]$_D^{26}$ –54.8 (c 0.17, MeOH) gave a quasi-molecular ion peak [M] at *m/z* 1192, which corresponded to $C_{57}H_{92}O_{26}$ in the negative FAB mass spectrum and ^{13}C NMR(DEPT). Compound **2** was also positive to Ehrlich reagent reaction. Comparising the ^{13}C NMR spectral data of compound **2** with those of compound **1** indicated that the aglycone moieties of the two compounds were the same, but the sugar moieties were different. Compound **2** had one more sugar than compound **1**. Complete acid hydrolysis of compound **2** gave D-glucose and L-rhamnose. The ^{1}H, ^{13}C NMR spectrum of compound **2** indicated the presence of five anomeric signals, three of β-glucopyranosyl [H-1: 4.79(d, 7.52Hz), C-1: 106.4; H-1: 4.86(d, 7.64Hz), C-1: 100.1; H-1: 5.26(d, 7.52Hz), C-1: 105.2], and two of -rhamnopyranosyl [H-1: 5.69(s), C-1: 103.3; H-1: 5.74(s), C-1: 102.6]. The negative

ion FAB mass spectrum displayed the fragment ion peaks at *m/z* 1046[M-146], 1030[M-162], 884[M-162-146], which suggested that compound **2** contained two glucoses and one rhamnose as terminal sugars and another glucose and rhamnose as inner sugars in the sugar chain. This was further confirmed by 2D NMR. The HMBC spectrum showed five characteristic cross-peaks between C-3 (δ 78.4) of the aglycone and the anomeric proton (δ 4.86) of inner glucose, between the C-2 (δ 78.0) of inner glucose and anomeric proton(δ 5.69) of terminal rhamnose, between the C-3 (δ 87.6) of inner glucose and the anomeric proton (δ 5.74) of inner rhamnose, between the C-3 (δ 84.2) of inner rhamnose and the anomeric proton (δ 4.79) of terminal glucose and between C-26 (δ 75.3) of aglycone and the anomeric proton (δ 5.26) of glucose. Thus, compound **2** was identified as 26-O-β-D-glucopyranosyl-(25R)-3β,26-dihyxyfurost-5, 20-dien-3-O-[-L-rhamnopyranosyl(1→2)-[β-D-glucopyranosyl(1→3)- -L-rhamnopyr anosyl (1→3)]- β-D-glucopyranoside, named taccaoside B.

Table 1 Chemical shifts of ^{13}C NMR singals of compound **1** and **2** in pyridine-d_6 at 125.77MHz(δ in ppm)

The aglycone moieties			The sugar moieties			
C	**1**	**2**	C		**1**	**2**
1	37.7	37.7	3-O-Glc	1	99.9	100.1
2	30.6	30.3		2	78.0	78.0
3	78.5	78.4		3	87.6	87.0
4	39.8	39.9		4	70.7	70.0
5	140.9	141.1		5	77.9	78.4
6	121.9	121.9		6	62.4	62.5
7	32.6	32.6	2-Rha	1	102.6	102.6
8	31.6	31.6		2	72.6	72.8
9	50.4	50.6		3	72.5	72.7
10	37.2	37.3		4	73.6	72.5
11	21.4	21.5		5	69.9	68.9
12	38.8	38.9		6	18.5	18.4
13	43.6	43.6	3-Rha	1	103.9	103.3
14	55.1	55.2		2	72.8	71.7
15	34.6	34.7		3	72.5	84.2
16	84.6	84.7		4	73.9	72.5
17	64.6	64.8		5	70.7	70.0
18	14.3	14.3		6	18.7	18.7
19	19.5	19.6	Terminal-Glc	1		106.4
20	103.6	103.7		2		73.9
21	11.9	11.9		3		78.1
22	152.5	152.7		4		71.7
23	33.8	33.9		5		78.0
24	23.8	23.8		6		62.8
25	31.6	31.6	26-O-Glc	1	105.2	105.2
26	75.3	75.3		2	75.3	75.4
27	17.3	17.3		3	78.6	78.4
				4	71.8	71.7
				5	78.0	78.0
				6	62.9	62.8

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