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A New Furostanol Saponin from *Dioscorea futshauensis*

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Abstract: A new furostanol saponin presenting moderate bioactivity of inducing morphological deformation of *Pyricularia oryzae* mycelia was isolated from *Dioscorea futshauensis* R.Kunth by bioactivity-guided fractionation. The structure was established as 26-O-β-D-glucopyranosyl-3β, 26-diol-23(S)-methoxyl-(25R)-furost-5,20 (22)-diene-3-O-[α-L-rhamnopyranosyl (1→2)-β-D-glucopyranosyl (1→3)]-β-D-glucopyranoside on the basis of chemical evidencesand spectral analysis, especially by 2D-NMR techniques.

Keywords: Furostanol glycoside, *Dioscorea futshauensis*, *Pyricularia oryzae*.

In the previous paper we have reported the isolation and structure identification of a new spirostanol saponin from the ethanol extract of *Dioscorea futshauensis* R. Kunth (Dioscoreaceae) which showed a strong activity against the growth of *Pyricularia oryzae* P-2b[1]. In this paper, we describe the isolation and structure elucidation of a new furostanol saponin from *Dioscorea futshauensis*. The furostanol saponin fraction obtained by repeated silica gel column chromatography was subjected to reversed phase HPLC to afford a novel bioactive furostanol saponin (**1)** along with 3 known bioactive furostanol saponins, protodioscin, protogracillin and dioscoreside C. They induced morphological deformation of *Pyricularia oryzae* at the concentration of 100 μmol/L, 110 μmol/L, 120 μmol/L and 100 μmol/L, repectively.

Compound **1** was obtained as white amorphous powder, mp 256 - 258°C (dec.), $[\alpha]_D^{24}$ - 50.3 (*c* 0.005 pyridine), positive to the Libermann-Burchard reaction and Molish reagents. The negative HR-FAB-MS revealed the composition of $C_{52}H_{84}O_{23}$ by quasimolecular ion peak $[M-H]^+$ at *m/z* 1075.5347, calcd. 1076.5325. The IR spectrum (KBr) showed absorption bands at 3420, 2950, 1380, 1040 cm^{-1}. The ^{1}H-NMR spectrum of **1** showed the presence of four methyl groups at δ 0.69 (s, Me-18), 1.06 (s, Me-19), 1.10 (d, 3H, *J* = 6.0Hz, Me-27), 1.75 (s, Me-21) and one olefinic proton at δ 5.30 (br. s, H-6), which reminded us that compond **1** has steroidal skeleton. The four anomeric protons at δ 6.38 (br.s, Rha-1"), 4.93 (d, 1H, *J* = 6.8 Hz, Glc-1'), 5.10 (d, 1H, *J* = 7.5 Hz, Glc-1'"), 4.83 (d, 1H, *J* = 7.2 Hz, Glc-1"") and a methyl signal at δ 1.75 (br.s, 3H, Rha Me-6") suggested the presence of three glucose and one rhamnose units in the molecule. The ^{13}C-NMR assignments of the aglycone of **1** were based mainly on DEPT,

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^{1}H- ^{1}H COSY, HMQC and HMBC spectra. 28 carbon signals consisting four methyl, nine methylene, nine methine, five quaternary and one methoxyl carbons were exhibited in the ^{13}C-NMR spectra of **1** (**Table 1**). The NMR data of the aglycone of compound **1** were in good agreement with that of dioscoreside C[2]. In its ROESY spectrum, the methoxy-23 was correlated with Me-21 and the H-25. All the analysis tends to establish the aglycone of compound **1** as (25R) furost-5, 20 (22)-diene-23 (S)-methoxyl -3β, 26-diol (**Figure 1**).

On acid hydrolysis, the sugar moieties were detected as glucose, rhamnose by silica gel TLC in comparison with the authentic samples. The negative FAB-MS of **1** gave the quasimolecular ion peak $[M-H]^+$ at *m/z* 1075, and four fragments $[M-H-Glc]^+$ at *m/z* 913, $[M-H-Rha-Glc]^+$ at *m/z* 767, $[M-H-Glc\times2-Rha]^+$ at *m/z* 605 and $[M-H-Glc\times3-Rha]^+$ at *m/z* 443. By analyzing the DEPT, ^{1}H - ^{1}H COSY, HMQC, HMBC spectra and comparing with the report for dioscoreside C, ^{1}H and ^{13}C NMR signals (**Table 1**) of sugar moiety could be assigned. The linkage siteof sugar moiety on aglycone and internal linkages among sugars were determinedby HMBC spectra analysis and comparison with that of protogracillin[3]. β-configuration of the anomeric carbon in three glucopyranosyl units may be inferred from the values of the coupling constants (6.8, 7.2 and 7.5 Hz). The α-configuration of the anomeric carbon of the rhamnose was assured by comparison of the chemical shift values of carbons 3'' and 5'' with those of the corresponding carbons of methyl α- and β-rhamnopyronoside[4]. Therefore, the structure of compound **1** is proposed to be 26-O-β-D-glucopyranosyl-3β, 26-diol-23 (S)-methoxyl-(25R)-furost-5, 20 (22)-diene-3-O-[α-L-rhamnopyranosyl (1→2)-β-D-glucopyranosyl (1→3)]-β-D-glucopyranoside.

Figure 1 The structure of compound **1**

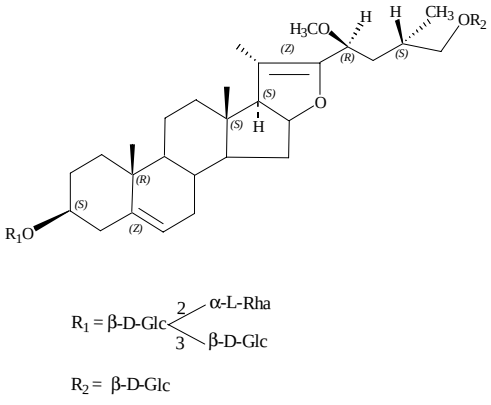

Table 1 ^{13}C NMR (75 MHz) data for **1** in C_5D_5N (δ in ppm)

Position	**1**	dioscoreside C	Position	**1**	dioscoreside C
1	37.5	37.6	3-O-Glc		
2	30.1	30.2	1'	100.0	100.3
3	77.9	78.1	2'	77.0	78.7
4	38.7	39.0	3'	89.5	77.0
5	140.8	140.9	4'	69.6	78.6
6	121.9	121.9	5'	77.9	77.9
7	32.4	32.4	6'	62.4	61.3
8	31.7	31.4	Rha (1→2)		
9	50.3	50.3	1"	102.2	102.1
10	37.1	37.2	2"	72.5	72.6
11	21.2	21.3	3"	72.8	72.8
12	40.8	39.6	4"	74.1	74.2
13	43.5	43.5	5"	69.6	69.6
14	55.0	54.9	6"	18.7	18.7
15	34.5	34.5	Rha (1→4)		
16	84.6	84.7	1'''		102.9
17	64.8	64.9	2'''		72.6
18	14.3	14.4	3'''		72.9
19	19.4	19.5	4'''		73.9
20	108.6	108.7	5'''		70.5
21	11.4	11.5	6'''		18.5
22	152.2	151.8	Glc (1→3)		
23	73.4	73.4	1''''	104.5	
24	37.7	37.7	2''''	75.0	
25	30.1	30.1	3''''	78.5	
26	75.3	75.2	4''''	71.7	
27	17.6	17.6	5''''	77.9	
23-OCH_3	56.1	56.2	6''''	62.4	
			26-O-Glc		
			1'''''	104.9	105.0
			2'''''	75.2	75.2
			3'''''	78.5	78.6
			4'''''	71.5	71.8
			5'''''	78.6	78.0
			6'''''	62.8	62.7

Table 2 ^{1}H NMR (300 MHz) data for **1** in C_5D_5N (δ in ppm, *J* Hz)

Position	**1**	Position	**1**
H-18	0.69 (s)	Rha (1→2)	
H-19	1.06 (s)	1"	6.38 (br.s)
H-21	1.75 (s)	2"	4.86 (m)
H-27	1.10 (d, 6.0)	3"	4.58 (m)
H-3	3.94 (m)	4"	4.25 (m)
H-6	5.31 (br.s)	5"	4.90 (m)
H-16	4.85 (m)	6"	1.75 (br.s)
H-17	2.49 (d, 6.9)	Glc (1→3)	
H-26	3.69, 4.00 (m)	1''''	5.10 (d, 7.5)
H-OMe	3.33 (s)	2''''	4.02 (m)
3-O-Glc		26-O-Glc	
H-1'	4.92 (d, 6.8)	1'''''	3.83 (d, 7.2)
H-2'	4.18 (m)	2'''''	4.02

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