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A Novel Cardiac Glycoside from *Parepigynum funingesis*

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Abstract: From the dried aerial part of *Parepigynum funingesis* Tsiang et P. T. Li (Apocynaceae), a new cardiac glucoside, named parefuningoside (**1**) had been isolated. Its structure was determined by means of hydrolysis and spectral analysis.

Keywords: *Parepigynum funingesis*, Apocynaceae, cardiac glucoside, parefuningoside.

Parepigynum funingesis is an endemic species belonging to the family Apocynaceae. Its unique taxonomic position attracted us to investigate the chemical constituent of *P. funingesis*. This paper describes the hydrolysis and structural elucidation of the new cardiac glucoside from this plant.

Compound **1** was obtained as white powder; mp 143-145° (MeOH); $[\alpha]_D^{20.9}$-54.32 (*c* 2.20, MeOH); IR (KBr) ν: 3443，2934, 1780, 1740, 1701, 1628, 1457, 1371, 1244 cm^{-1}. The molecular formula of compound **1** was deduced as $C_{38}H_{56}O_{14}$ from negative-ion TOF MS and NMR spectrum (**Table 1**).

Mild acidic hydrolysis of **1** revealed the presence of cymarose and glucose by TLC. The ^{13}C NMR and HMQC-TOCSY spectra of **1** displayed the presence of one unsubstituted β-glucopyranosyl unit and one substituted α-cymaropyranosyl unit[1-3], and 25 carbon signals for the aglycone. The downfield shift of C-4' of the cymaropyranosyl unit proved that the substitution was at C-4'. This was supported by the HMBC spectral analysis (**Table 2**), in which significant correlation peaks displayed between H-1" of the glucopyranosyl residue and C-4' of the cymaropyranosyl unit. The linkage of saccharide chain to the aglycone was decided by correlation peak between H-1' of the cymaropyranosyl unit and C-3 of the aglycone in HMBC. In the ^1H NMR spectrum of **1**, the doublet signals at δ_H 5.01 (H-1") with coupling constant 7.9 Hz indicated the β linkage of glucopyranosyl residue. Moreover, the broad singlet at δ_H 5.14 (H-1') for the anomeric proton of the cymaropyranosyl unit indicated the α linkage.

When the carbons of the saccharide chain were completely assigned, the ^{13}C and DEPT spectra of **1** showed the presence of one olefinic bond, five methines, nine methylenes, three methyl groups, three quaternary carbons and three carbonyl groups.

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The chemical shifts of the aglycone carbons were similar to those of 3-O substituted oleangenin except for ring-A and C-9[4,5]. The form of ring-A was deduced by the correlation between δ_C 38.6 (C-1) , 25.3 (C-2) , 75.5 (C-3), 46.5 (C–5) and δ_H 5.38 (H-4) in HMQC-TOCSY spectrum. This was also supported by the correlations between δ_H 5.38 (H-4) and δ_C 75.5 (C-3), δ_C 46.5 (C–5) in HMBC spectrum and the strong cross peak of δ_H 5.38 (H-4) with δ_H 0.97 (H-5) and δ_H 3.75 (H–3) in ^{1}H-^{1}H COSY spectrum. The cross peak of H-4 with δ_C 170.8 (-OAc) in the HMBC (See **Table 2**) showed that the acetoxyl was attached to C-4. According to coupling constants, the broad singlet of H-4 and the broad doublet of H-3 indicated the α-configurations of H-4 and H-3 respectively. Furthermore, the cross peaks of δ_C 16.1

Table 1 ^{13}C NMR(125MHz) and ^{1}H NMR(500MHz) data of **1** and **1a** in C_5D_5N(δ in ppm; J in Hz)

Position	**1**		**1a**	
	δ_C	δ_H	δ_C	δ_H
1	38.6 (t)	0.87 (m), 1.77 (m)	38.6 (t)	0.87 (m), 1.77 (m)
2	25.3 (t)	1.76 (m), 1.88 (m)	27.0 (t)	1.72 (m), 1.86 (m)
3	75.5 (d)	3.75 (br, d)	70.5 (d)	3.90 (m)
4	72.3 (d)	5.38 (br, s)	76.2 (d)	5.55 (br, s)
5	46.5 (d)	0.97 (m)	47.0 (d)	1.14 (m)
6	23.4 (t)	1.25 (m), 1.83 (m)	23.5 (t)	1.36 (m), 1.80 (m)
7	35.1 (t)	0.89 (m), 2.18 (m)	35.2 (t)	0.88 (m), 2.18 (m)
8	49.6 (s)		49.5 (s)	
9	60.6 (d)	1.65 (m)	60.6 (d)	1.65 (m)
10	38.5 (s)		38.5 (s)	
11	21.2 (t)	1.63 (m)	21.4 (t)	1.63 (m)
12	42.3 (t)	1.98 (m)	42.3 (t)	1.98 (m)
13	47.7 (s)		47.6 (s)	
14	221.0 (s)		221.0 (s)	
15	43.5 (t)	1.64(m), 1.82 (m)	43.5 (t)	1.65 (m), 1.82 (m)
16	26.3 (t)	1.32 (m)	26.3 (t)	1.32 (m)
17	52.8 (d)	2.95 (br, d)	52.8 (d)	2.95 (br, d)
18	23.3 (q)	0.92 (s)	23.3 (q)	0.96 (s)
19	16.1 (q)	0.91 (s)	16.1 (q)	0.93 (s)
20	171.8 (s)		171.7 (s)	
21	73.6 (t)	4.81 (m)	73.5 (t)	4.81 (m)
22	116.4 (d)	5.88 (s)	116.4 (d)	5.89 (s)
23	174.0 (s)		173.9 (s)	
-O<u>C</u>OCH$_3$	170.8 (s)		170.7 (s)	
-OCO<u>CH$_3$</u>	21.1 (q)	2.00 (s)	21.1 (q)	1.96 (s)
1'	94.9 (d)	5.14 (br, s)		
2'	31.7 (t)	1.73 (m), 2.27 (m)		
3'	73.2 (d)	3.95 (m)		
4'	78.6 (d)	4.20 (m)		
5'	64.9 (d)	4.55 (m)		
6'	18.5 (q)	1.44 (d, J = 6.3)		
3'-OMe	56.4 (q)	3.41 (s)		
1"	101.9 (d)	5.01 (d, J = 7.7)		
2"	75.2 (d)	3.98 (m)		
3"	78.4 (d)	4.00 (m)		
4"	71.8 (d)	4.15 (m)		
5"	78.7 (d)	4.20 (m)		
6"	63.0 (t)	4.22 (m), 4.40 (m)		

Figure 1 The structure of compound **1**

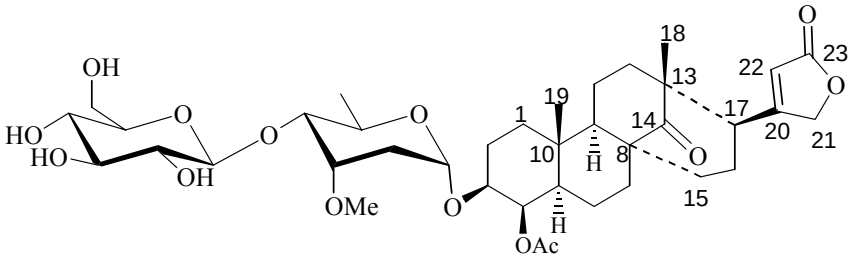

Table 2 HMBC and ROESY data for compound **1**

H	HMBC	ROESY	H	HMBC	ROESY
1α	C-2, C-3, C-5	H-3	12	C-9, C-11, C-14, C-18	H-17
1β	C-19	H-19	15α	C-9, C-14	
2α	C-1, C-3, C-4	H-3	15β	C-16	
2β		H-19	16	C-8, C-15, C-17, C-20	H-17
3	C-1, C-2, C-4, C-1'	H-1α, H-2, H-4, H-5, H-1'	17	C-12, C-14, C-16, C-18, C-20, C-22	H-12, H-16, H-18, H-21, H-22
4	C-2, C-3, C-5. OAc	H-3, H-5	18	C-12, C-13, C-14, C-17	H-12, H-17, H-22
5	C-6, C-7, C-10, C-19	H-3, H-4, H-9.	19	C-5, C-9, C-10	
7α	C-14	H-6	21	C-20, C-22, C-23	H-17
7β	C-14	H-6	22	C-17, C-20, C-21, C-23	H-17, H-18
9	C-5, C-8, C-10, C-11, C-12, C-14, C-19	H-5.	1'	C-3, C-5', C-3'	H-3
			1"	C-4', C-5'	
11	C-9, C-12		OAc	C-4	

with δ_H 0.87 (H-1), δ_H 0.97 (H-5) and δ_H1.65 (H-9) in the HMBC showed that the chemical shift of C-19 was δ_C 16.1. This value was very downfield compared with that of literature[4,5], and the shifts of C-1, C-5 and C-9 were also downfield. Combined the analysis of the data of uzarigenin and digitoxigenin[6], **1** was deduced to be A/B *trans*-configuration. This result was supported by the correlations from H-5 to H-3 and H-9 in the ROESY (See **Table 2**). Finally, the obvious correlation between H-17 and H-12 in the ROESY showed the β-configuration of the α,β-unsaturated five-membered lactone.

According to the above spectral data, the structure of 1 was elucidated as 4-β-acetoxyl-5-α H-odeangenin-3β-O-(1 → 4)-β-D-glucopyranosyl-α-D-cymaropyranoside (**Figure 1**).

Acid hydrolysis of **1** gave an aglycone **1a**. Its NMR data was similar to those of **1** except for the δ_C of C-2, C-3 and C-4 and the corresponding δ_H. This was explained by glycosylation shifts.

Compound **1a**: white powder; mp 168-170˚C (MeOH); $[\alpha]_D^{18.2}$-12.0 (*c* 0.75, C_5H_5N); ^{13}C NMR and ^1H NMR data were listed in **Table 1**.

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