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Two New Cardenolide Glycosides from *Biondia hemsleyana*

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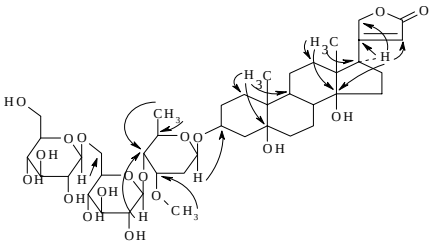
Abstract: Two new cardenolide glycosides, biondianosides A and B, were isolated from the roots of endemic plant of *Biondia hemsleyana* (Warb.) Tsiang. Their structures were elucidated as periplogenin-3-*O*- -D-glucopyranosyl-(1→6)- -D-glucopyranosyl-(1→4)- -D-cymaropyranosid e (**1**) and 17 H-periplogenin-3-*O*- -D-cymaropyranoside (**2**) by the spectroscopic and chemical methods.

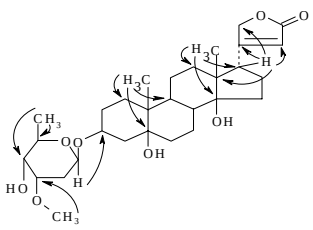
Keywords: *Biondia hemsleyana*, cardenolide glycoside, biondianosides A and B.

Biondia hemsleyana (Warb.) Tsiang (Asclepiadaceae), an endemic plant mainly in southwestern China, is used as a chinese medicine for treating stomachache[1]. The chemical constituents of the genus *Biondia* were not reported until now. From the ethanolic extract of the roots of *B. hemsleyana* , two new cardenolide glycosides, named biondianosides A and B, were isolated by repeated column chromatography on normal and reversed phase silica gel.

Figure 1 The key HMBC correlations for **1** and **2**



1



2

Biondianoside A (**1**), $[\alpha]_D^{20}$ –14.7 (MeOH; *c* 2.2), was obtained as white powder (55mg). Its molecular formula was assigned as $C_{42}H_{66}O_{18}$ by HR-ESI-MS($[M+Na]^+$ *m/z* 881.4167, calc. 881.4149). The positive Liebermann-Burchardt and Kedde tests indicated it to be a cardenolide confirmed by the ^{1}HNMR signals at δ 6.07 (brs, H-22), 5.25, 4.99 (brd, each 1H, J = 18.0 Hz, H_2-21), 4.22 (m, 1H, H-3), 2.75 (m, H-17), 0.96 and 0.94 (s, each 3H, 2×CH_3). By comparing the ^{13}CNMR data of **1** with those of periplocin[2], **1** had one more glucose attached to the C-6 of the inner glucose according to

the glycosylation shift. The glucose, cymarose and periplogenin (ESI-MS *m/z*: 391[M+H]$^+$) were detected by acid hydrolysis of **1**. The ESI-MS/MS signals at *m/z* 857 [M-H]$^-$, 695 [M-163]$^-$, 533 [M-163-162]$^-$ and 389 [M-163-162-144]$^-$ showed **1** has two hexose and a dideoxy-*O*-methylhexose. In the ^{1}H NMR spectrum of **1**, three anomeric proton signals at δ 5.07 (brd, 1H, *J* = 7.2 Hz), 4.95 (d, 1H, *J* = 7.6 Hz) and 4.75 (d, 1H, *J* = 7.7 Hz) indicated the three sugars were -configuration. Finally, by the HMBC correlations (**Figure 1**), **1** was confirmed as periplogenin-3-*O*- -D-glucopyranosyl-(1→6)- -D-glucopyranosyl-(1→4)- -D-cymaropyranoside.

Biondianoside B (**2**), $[\alpha]_D^{20}$ +34.3 (MeOH; *c* 2.1), was obtained as white powder (18mg). Its molecular formula was assigned as $C_{30}H_{46}O_8$ by HR-ESI-MS([M+Na]$^+$ *m/z* 557.3137, calc. 557.3092). The positive Liebermann-Burchardt and Kedde tests indicated the presence of a cardenolide supported by the ^{1}HNMR signals at δ 5.95 (brs, H-22), 4.88, 4.80 (brd, each 1H, *J* = 18.0 Hz, H_2-21), 4.01 (m, 1H, H-3), 3.07 (m, 1H, H-17), 0.90 and 0.81 (s, each 3H, 2×CH_3). By comparing the NMR data of **2** with those of **1**, the methine proton signal of H-17 was shifted downfield to 3.07 (m, 1H), and the C-12 signal was shifted upfield to δ 30.6 showing that H-17 has the β-configuration[3]. The ESI-MS signals at *m/z* 557 [M+Na]$^+$, 391 [M-143]$^+$ showed that **2** has a dideoxy-*O*-methylhexose. Cymarose was detected by TLC acid hydrolysis of **2**. In the ^{1}H NMR spectrum of **2,** the anomeric proton signal at δ 4.69 (brd, 1H, *J* = 8.8 Hz) showed that **2** was a β-linking cardenolide monoglycoside. The HMBC correlations (**Figure 1**) confirmed **2** as 17βH-periplogenin-3-*O*-β-D- cymaropyranoside.

Table 1 The ^{13}CNMR spectral data of **1** (C_5D_5N) and **2** (DMSO-d_6)

C	**1**	**2**	C	**1**	**2**	C	**1**
1	25.6(t)	25.2(t)	16	26.9(t)	23.9(t)	Glc-1″	105.1(d)
2	26.0(t)	25.4(t)	17	50.9(d)	48.0(d)	2″	74.7(d)
3	74.7(d)	74.6(d)	18	15.9(q)	18.1(q)	3″	77.9(d)
4	34.9(t)	34.4(t)	19	16.8(q)	16.8(q)	4″	71.3(d)
5	73.5(s)	73.0(s)	20	175.9(s)	173.6(s)	5″	76.5(d)
6	34.9(t)	34.5(t)	21	73.5(t)	73.6(t)	6″	70.3(t)
7	23.9(t)	22.9(t)	22	117.2(d)	115.3(d)	Glc-1‴	106.0(d)
8	40.6(d)	39.7(d)	23	174.5(s)	173.4(s)	2‴	75.4(d)
9	38.8(d)	38.1(d)	Cym-1′	97.0(d)	96.2(d)	3‴	78.0(d)
10	40.8(s)	40.1(s)	2′	36.1(t)	34.8(t)	4‴	71.4(d)
11	21.7(t)	20.3(t)	3′	77.8(d)	77.5(d)	5‴	78.0(d)
12	39.6(t)	30.6(t)	4′	82.8(d)	72.7(d)	6‴	62.3(t)
13	49.7(s)	48.2(s)	5′	69.2(d)	69.8(d)		
14	84.4(s)	84.3(s)	6′	18.3(q)	18.4(q)		
15	32.7(t)	30.2(t)	OCH_3	58.3(q)	57.7(q)		

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