

A Novel Pregnane Glycoside from *Biondia chinensis*

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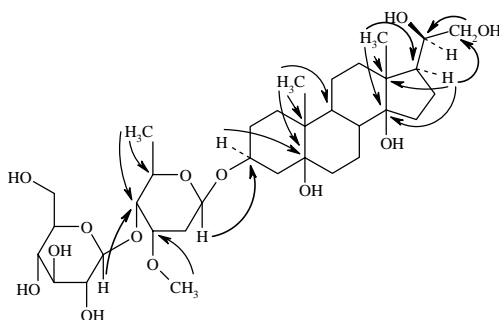
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Abstract: A novel pregnane glycoside, biondianoside E, was isolated from the roots of *Biondia chinensis*. By the spectroscopic and chemical methods, this structure was elucidated as $3\beta, 5\beta, 14\beta, 20S, 21$ -pentahydroxypregnane 3- O - β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-cymaropyranoside.

Keywords: *Biondia chinensis*, pregnane glycoside, biondianoside E.

Biondia chinensis Schltr. (Asclepiadaceae), an endemic plant mainly distributed in southwestern China, is used as a folk medicine for the treatment of traumatic injury^{1,2}. Four new pregnane glycosides, biondianosides A~D, have been isolated from a closely related species, *B. hemsleyana*^{3,4}. From the ethanolic extract of the roots of *B. chinensis*, a novel pregnane glycoside, named biondianoside E, was isolated by repeated column chromatography on normal and reversed phase silica gel.

Figure 1 The key HMBC correlations for biondianoside E



Biondianoside E was obtained as white powder (18 mg). Its molecular formula was assigned as $C_{34}H_{58}O_{13}$ by HR-ESI-MS ($[M+H]^+$ m/z 675.3953, calcd. 675.3956). The ESI-MS (-) signals at m/z 673 $[M-H]^-$, 511 $[M-163]^-$ and 367 $[M-163-144]^-$ showed it had a hexose and a dideoxy- O -methylhexose. Glucose and cymarose were detected by acid hydrolysis on thin-layer chromatography and the coupling constant of each anomeric proton (Table 1) revealed that both sugar units have β -configuration. The ^{13}C

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NMR spectra showed twenty-one carbon signals except the signals of two sugar units, indicating that it has a pregnane type aglycone. The NMR data showed the signals of two tertiary methyl groups (δ_{H} 1.26, s, 3H, H-18; 1.11, s, 3H, H-19) and five carbons attached to oxygen atoms (δ_{C} 83.8, s; 76.1, s; 73.8, s; 71.1, d; 65.8, t). The signals at δ_{C} 76.1 and 83.8 indicated the presence of two β -linked hydroxyl groups at C-5 and C-14. The secondary carbon signal (δ_{C} 65.8, t) showed the existence of a hydroxyl group at C-21. The ^1H NMR signal of H-21 (δ_{H} 4.06, dd, 1H, $J=10.5, 7.1$ Hz; 3.87, dd, 1H, $J=10.5, 6.1$ Hz) and H-20 (δ_{H} 4.33, m, 1H) manifested the occurrence of a hydroxyl group at C-20. These substitutions were confirmed by HMBC correlations (**Figure 1**). By comparison of the NMR spectra with those of similar compounds, its aglycone was suggested to be $3\beta, 5\beta, 14\beta, 20S, 21$ -pentahydroxypregnane^{3,5}. The HMBC correlations showed that cymarose was connected to the C-3 of aglycone and glucose to the C-4 of cymarose (**Figure 1**). Therefore, this compound was identified as $3\beta, 5\beta, 14\beta, 20S, 21$ -pentahydroxypregnane 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 4)- β -D-cymaropyranoside.

Table 1 The ^1H and ^{13}C NMR spectral data of biondianoside E ($\text{C}_5\text{D}_5\text{N}$)(δ ppm)

No.	^{13}C	^1H	No.	^{13}C	^1H
1	26.0(t)	1.39(1H, m); 1.5(1H, m)	19	17.3(q)	1.11(3H, s)
2	26.4(t)	2.05(1H, m); 1.88(1H, m)	20	71.1(d)	4.33(1H, m)
3	76.1(d)	4.29(1H, br. s)	21	65.8(t)	4.06(1H, dd, $J=10.5, 7.1$ Hz)
4	35.5(t)	2.17(1H, m); 1.52(1H, m)			3.87(1H, dd, $J=10.5, 6.1$ Hz)
5	73.8(s)		1'	97.3(d)	5.13(1H, br. d, $J=8.8$ Hz)
6	35.5(t)	1.96(1H, m); 1.70(1H, m)	2'	36.5(t)	2.11(1H, br. d, $J=8.8$ Hz)
7	24.4(t)	2.35(1H, m); 1.32(1H, m)			1.66(1H, br. s)
8	39.9(d)	1.97(1H, m)	3'	77.9(d)	4.03(1H, br. s)
9	39.0(d)	1.63(1H, m)	4'	82.9(d)	3.62(1H, dd, $J=9.6, 2.4$ Hz)
10	41.2(s)		5'	69.5(d)	4.24(1H, m)
11	21.9(t)	1.56(1H, m); 1.30(1H, m)	6'	18.6(q)	1.60(3H, d, $J=6.4$ Hz)
12	40.2(t)	1.42(1H, m); 1.30(1H, m)	OMe	58.8(q)	3.42(3H, s)
13	47.8(s)		1''	106.5(d)	4.93(1H, d, $J=7.8$ Hz)
14	83.8(s)		2''	75.3(d)	4.00(1H, m)
15	33.1(t)	2.03(1H, dd, $J=8.8, 3.6$ Hz)	3''	78.3(d)	4.06(1H, m)
		1.80(1H, br. s)	4''	71.7(d)	4.19(1H, m)
16	19.0(t)	2.23(1H, m); 1.82(1H, m)	5''	78.4(d)	4.26(1H, m)
17	51.5(d)	2.20(1H, m)	6''	63.0(t)	4.57(1H, dd, $J=11.6, 2.0$ Hz)
18	15.5(q)	1.26(3H, s)			4.39(1H, dd, $J=11.6, 5.2$ Hz)

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