

A New Sesquiterpene from the Roots of *Biondia hemsleyana*

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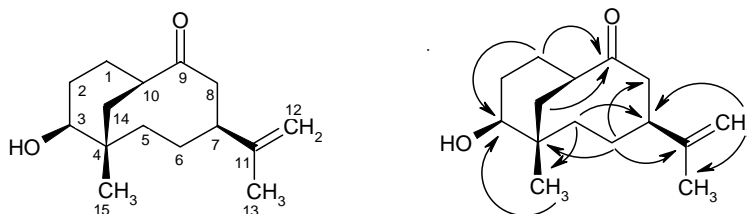
Abstract: A new sesquiterpene with a unusual modified germacrane skeleton was isolated from the ethanol extracts of the roots of *Biondia hemsleyana* and its structure was elucidated as 3 β -hydroxy-4,14-cyclogermacra-11-en-9-one by the spectroscopic methods and X-ray crystallography.

Keywords: *Biondia hemsleyana*, Asclepiadaceae, sesquiterpene, modified germacrane.

Biondia hemsleyana (Warb.) Tsiang (Asclepiadaceae), an endemic plant mainly distributed in southwestern China, is used as a folk medicine for the treatment of stomachache^{1,2}. Five new pregnane glycosides, biondianosides A~E, had been isolated from these two closely related species, *B. hemsleyana*^{3,4} and *B. chinensis*⁵. A new sesquiterpene derived from a germacrane skeleton⁶ was isolated from the ethanol extracts of the roots of *B. hemsleyana* by repeated chromatography on normal and reversed phase silica gel. The unusual modified germacrane skeleton has not been reported from the species of Asclepiadaceae until now.

Compound **1** was obtained as colorless prisms from 95% EtOH (15 mg), mp 126-128°C, $[\alpha]_D^{25} + 8.0$ (CHCl₃, *c* 0.08). Its molecular formula C₁₅H₂₄O₂ was deduced from HR-ESI-MS ($[M+H]^+$ *m/z* 237.1852, calcd. 237.1854). The IR spectrum indicated the presence of hydroxyl (3380 cm⁻¹) and carbonyl (1670 cm⁻¹) groups. The ¹³C NMR spectrum showed fifteen carbon signals, DEPT analysis indicated the presence of two primary, seven secondary, three tertiary and three quaternary carbons. In order to determine its structure, X-ray crystallography has been carried out. The structure of compound **1** was confirmed unambiguously by investigation of X-ray diffraction⁷ since it

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



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was difficult to determine the linkages of carbon, hydrogen and oxygen atoms only by the HMBC spectrum (**Figure 1**). A computer-generated drawing of the final X-ray model of **1** is given in **Figure 2**.

The assignment for all carbons, as well as for all hydrogens of **1** was initiated from the long-range coupling networks observed between the methyl protons of isopropylene bonded to C-7 with the adjacent carbons in an HMBC experiment together with HSQC spectrum (**Table 1**). Because bicyclo [5.3.1] undecane derivatives were early recognized as potential anti-Bret's-rule candidates and the absolute configuration had been deduced from the data of stereochemical analysis⁸, the structural framework of the new sesquiterpene can be identified reasonably as 3 β -hydroxy-4,14-cyclogermacra-11-en-9-one.

Figure 2 The X-ray crystal structure for **1**

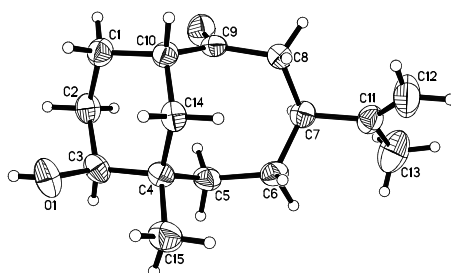


Table 1 The ¹H (600 MHz) and ¹³C NMR (150 MHz) spectral data of **1** (CDCl₃, δ ppm)

No.	δ_C	δ_H J (Hz)	HMBC(H \rightarrow C)
1	18.0(t)	2.13(1H, dt, 13.4, 2.2), 1.59(1H, tt, 13.4, 4.8)	C-2, 3, 9, 10
2	25.5(t)	1.99(1H, tt, 14.0, 3.0), 1.49(1H, br. d, 14.0)	C-1, 3, 4, 10
3	74.4(d)	3.34(1H, br. s)	C-1, 2, 4, 5, 14
4	38.7(s)		
5	33.9(t)	1.26(1H, t, 16.0), 1.09(1H, dd, 16.0, 7.6)	C-4, 6, 7, 14, 15
6	27.7(t)	1.70(1H, t, 13.0), 1.45(1H, dd, 13.0, 7.6)	C-4, 5, 7, 8, 11
7	50.5(d)	2.41(1H, br. t, 12.0)	C-11
8	44.5(t)	2.90(1H, t, 12.0), 2.19(1H, br. d, 8.5)	C-6, 7, 9, 10, 11
9	215.7(s)		
10	47.0(d)	2.35(1H, br. s)	C-1, 2, 4, 9, 14
11	149.8(s)		
12	109.6(t)	4.76(1H, s), 4.73(1H, s)	C-7, 11, 13
13	21.1(q)	1.77(3H, s)	C-7, 11, 12
14	29.3(t)	2.17(1H, d, 14.6), 1.93(1H, dd, 14.6, 5.4)	C-3, 4, 9, 10, 15
15	25.3(q)	0.91(3H, s)	C-3, 4, 5, 14

A suitable crystal that formed in the orthorhombic space group P212121 was selected for the study and mounted on glass fibers, coated with epoxy, and placed on a Simens P4 diffractometer. The accurate lattice constants were $a = 6.068$ (1), $b = 11.124$ (2), $c = 20.103$ (4) Å, $V = 1356.9$ (4) Å³ and $Z = 4$ with four molecules (C₁₅H₂₄O₂) in the asymmetric unit. Its calculated density was $D_c = 1.157$ g/cm³. All unique diffraction maxima with $2.03 < \theta < 27.00^\circ$ were collected in ω -scan mode with graphite-monochromated Mo K α radiations (0.71073 Å). A total of 1887 unique reflections was collected, and of those 1734 were judged observed [$I > 2\sigma(I)$] and used in subsequent calculations. The structure was phased using direct methods (SHELXTL) and refined using full-matrix least-squares techniques with anisotropic heavy atoms and isotropic riding hydrogens to conventional crystallographic residual of 0.0366 ($R_w = 0.0779$) for the observed data.

Acknowledgments

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