

Two new α,β -unsaturated butyrolactone derivatives from *Pleione bulbocodioides*

Xin Qiao Liu^a, Wen Yuan Gao^{a,*}, Yuan Qiang Guo^b,
Tie Jun Zhang^c, Lu Lu Yan^a

^aSchool of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China

^bDepartment of Pharmaceutical Sciences, Nankai University, Tianjin 300071, China

^cTianjin Institute of Pharmaceutical Research, Tianjin 300193, China

Received 2 April 2007

Abstract

Two new α,β -unsaturated butyrolactone derivatives, 4-(4''-hydroxybenzyl)-3-(3'-hydroxy-phenethyl)furan-2(5H)-one (**1**) and 3-(3'-hydroxyphenethyl)furan-2(5H)-one (**2**), together with one known phenolic compound (**3**), were isolated from the tubers of *Pleione bulbocodioides* (Franch.) Rolfe. Their structures were elucidated by analysis of spectroscopic data.

© 2007 Wen Yuan Gao. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: *Pleione bulbocodioides*; α,β -Unsaturated butyrolactone; Phenolic compound

The tubers of *Pleione bulbocodioides* (Franch.) Rolfe have been used in Chinese medicine as anti-cancer and anti-bacteria agent. A number of stilbenoids have been isolated from the titled plant [1,2], and various biological activities, such as anti-microbial and anti-allergic activities have been reported [3,4]. In this paper, we reported the isolation of two new α,β -unsaturated butyrolactone derivatives **1** and **2**. Their structures were elucidated by analysis of spectroscopic data.

The air-dried tubers of *P. bulbocodioides* were extracted three times with 95% EtOH under reflux for 3 h. After removal of solvent under reduced pressure, the extract was suspended in water and then partitioned with petroleum ether and EtOAc successively. The EtOAc fraction was subjected to repeated column chromatography on silica gel, Sephadex LH-20 and HPLC to afford compounds **1**, **2** and **3**.

Compound **1** was obtained as oil. Its HR ESI-MS showed $[M-H]^-$ at m/z 309.1128 (calcd. 309.1127), corresponding to the molecular formula $C_{19}H_{18}O_4$. The IR spectrum exhibited absorption at 1754 cm^{-1} , indicating the presence of a carbonyl.

The ^1H NMR spectrum of **1** showed four aromatic protons as an AA'BB' system at δ 6.77 (br d, 2H, $J = 8.0\text{ Hz}$, H-2'', 6''), 6.67 (br d, 2H, $J = 8.0\text{ Hz}$, H-3'', 5''), indicating the presence of a *p*-disubstituted phenyl group, as well as four other aromatic protons at δ 7.08 (t, 1H, $J = 8.0\text{ Hz}$, H-5'), 6.64 (m, 1H, H-4'), 6.62 (m, 1H, H-6'), 6.58 (m, 1H, H-2') which were similar to the signals of *meta*-disubstituted phenyl group [5]. In addition, two methylene, one of which was

* Corresponding author.

E-mail address: pharmgao@tju.edu.cn (W.Y. Gao).

Table 1

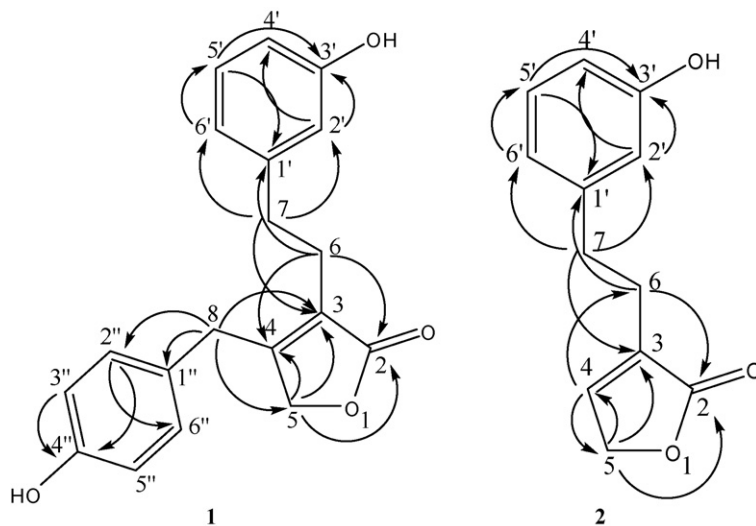
NMR spectral data of compounds **1** and **2** (^1H , 500 MHz; ^{13}C , 125 MHz; in CD_3OD , δ ppm, J Hz)

Position	1		2	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}
2		178.3		173.7
3		126.2		132.4
4		164.1	7.25 (m)	147.2
5	4.50 (s)	72.9	4.77 (m)	70.9
6	2.58 (t, 7.5)	26.6	2.55 (t, 7.5)	26.7
7	2.73 (t, 7.5)	34.5	2.80 (t, 7.5)	33.2
8	3.38 (s)	33.1		
1'		143.9		142.5
2'	6.58 (m)	116.8	6.63 (m)	115.1
3'		158.6		157.3
4'	6.64 (m)	114.1	6.61 (m)	112.9
5'	7.08 (t, 8.0)	130.5	7.08 (t, 8.0)	129.3
6'	6.62 (m)	121.0	6.66 (m)	119.5
1''		128.5		
2''	6.77 (br d, 8.0)	130.8		
3''	6.67 (br d, 8.0)	116.6		
4''		157.5		
5''	6.67 (br d, 8.0)	116.6		
6''	6.77 (br d, 8.0)	130.8		

oxygenated, at δ 4.50 (s, 2H, H-5), 3.38 (s, 2H, H-8), together with one ethylene at δ 2.73 (t, 2H, $J = 7.5$ Hz, H-7), 2.58 (t, 2H, $J = 7.5$ Hz, H-6) were observed.

The ^{13}C NMR spectrum (Table 1) combined with HSQC spectrum exhibited the signals for 19 carbons. Four of them (δ 178.3, 164.1, 126.2, 72.9) were similar to the signals of α,β -unsaturated butenolide [6]. And other 15 carbons consisted of 1 ethylene, 1 methylene and 12 aromatic carbons (8 protonated carbons, 2 quaternary carbons and 2 oxygenated carbons) which were consistent with the assumption of the *p*-disubstituted phenyl group and the *meta*-disubstituted phenyl group.

In the HMBC spectrum (Fig. 1), the long range correlations of H-6 (δ 2.58) to C-1'; H-7 (δ 2.73) to C-6', C-2'; H-2' (δ 6.58) to C-3', C-4', C-6'; H-6' (δ 6.62) to C-5', C-4'; H-5' (δ 7.08) to C-1', C-3' revealed the presence of a *meta*-hydroxyphenethyl group. Correspondingly, the HMBC correlations of H-8 (δ 3.38) to C-1'', C-2''; H-2'' (δ 6.77)

Fig. 1. The key HMBC (H \rightarrow C) correlations of compounds **1** and **2**.

to C-4'', C-6''; H-3'' (δ 6.67) to C-1'', C-4'', C-5'' revealed the presence of a *p*-hydroxybenzyl group. In addition, the HMBC correlations of H-5 (δ 4.50) to C-2, C-3, C-4; H-6 (δ 2.58) to C-2, C-4; H-7 (δ 2.73) to C-3; H-8 (δ 3.38) to C-3, C-5 confirmed α,β -unsaturated butenolide skeleton and the linkage sites of the skeleton and the above two groups. Therefore, the structure of compound **1** was elucidated as 4-(4''-hydroxybenzyl)-3-(3'-hydroxyphenethyl)furan-2(5H)-one.

Compound **2** was obtained as oil. Its HR ESI-MS showed $[M-H]^-$ at m/z 203.0718 (calcd. 203.0709), corresponding to the molecular formula $C_{12}H_{12}O_3$. The IR spectrum exhibited absorption at 1745 cm^{-1} , indicating the presence of a carbonyl. The ^1H and ^{13}C NMR spectrum of **2** showed that its structure is similar to that of **1** (Table 1) except for that the *p*-hydroxybenzyl group (δ 157.5, 130.8, 130.8, 128.5, 116.6, 116.6, 33.1) of **1** was replaced by a proton at δ 7.25 (m, 1H, H-4). The long-range correlations of this proton (δ 7.25) to C-3, C-5 and C-6 confirmed its assignment. And the other ^1H and ^{13}C signals were attributed by analysis of the HMBC and HSQC spectrum (Table 1 and Fig. 1). Therefore, the structure of **2** was elucidated as 3-(3'-hydroxyphenethyl)furan-2(5H)-one.

The structure of one known compound was identified as 3-hydroxybenzoic acid (**3**) [7] which was isolated from the tubers of *P. bulbocodioides* for the first time.

References

- [1] L. Bai, N. Maxukawa, M. Yamaki, S. Takagi, *Phytochemistry* 47 (8) (1998) 1637.
- [2] L. Bai, N. Maxukawa, M. Yamaki, S. Takagi, *Phytochemistry* 48 (2) (1998) 327.
- [3] S. Takagi, M. Yamaki, K. Inoue, *Phytochemistry* 22 (4) (1983) 1011.
- [4] M. Hisashi, M. Toshio, H.H. Xie, Y. Masayuki, *Planta Med.* 70 (9) (2004) 847.
- [5] K.P. Manfredia, V. Vallurupallia, M. Demidovaa, *Phytochemistry* 58 (2001) 153.
- [6] D. Rajasekhar, G.V. Subbaraju, *Tetrahedron* 54 (1998) 3227.
- [7] R. Bemini, A. Coratti, G. Provenzano, *Tetrahedron* 61 (7) (2005) 1821.