NOTE

A New Dibenzyl from *Pleione bulbocodioides*

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A new dibenzyl named 6'-(3''-hydroxyphenethyl)-4'-methoxydiphenyl-2,2',5-triol and two known compounds were isolated from the tubers of *Pleione bulbocodioides* (Franch.) Rolfe. Their structures were elucidated by spectroscopic methods.

Key Words: *Pleione bulbocodioides*, Dibenzyl.

The tubers of *Pleione bulbocodioides* (Franch.) Rolfe have been used in Chinese medicine for the treatment of tumors, burns and frostbite. A number of stilbenoids have been isolated from this plant^{1,2} and various biological activities, such as antiallergic and antimicrobial activities have been reported^{3,4}. Our previous research for anticancer compounds from *P. bulbocodioides* had resulted in the isolation of some dihydrophenanthrofuran^{5,6}. Further investigation of the same source led to the isolation of a new dibenzyl (**1**) named as 6'-(3''-hydroxyphenethyl)-4'-methoxydiphenyl-2,2',5-triol and two known compounds **2**, **3** which were isolated from this plant for the first time.

IR spectra were recorded on a Bio-Rad FTS 6000 infrared spectrometer. NMR spectra were run on Bruker AVANCE-400 and Varian unity INOVA-500 spectrometers, using TMS as an internal standard. Mass spectra were obtained on an IonSpec 7.0T FTMS instrument. Preparative HPLC was carried out on an ODS column (250 mm × 20 mm i.d., YMC) with a JASCO RI-1530 intelligent refractive index detector. Silica gel (200-300 mesh, Qingdao Ocean Chemical Group Co. of China) and Sephadex LH-20 (Merck Co.) for column chromatography as well as silica gel GF₂₅₄ (Qingdao Ocean Chemical Group Co. of China) for TLC were used.

The tubers of *Pleione bulbocodioides* were purchased from Anguo Meiwei Material Medica Cooperation in Hebei province, China, in August 2005. The plant was identified by professor Wen-Yuan Gao, School of Pharmaceutical Science and Technology, Tianjin University. A voucher specimen (No. 20050801) has been deposited at School of Pharmaceutical Science and Technology, Tianjin University, P.R. China.

Extraction and isolation: The tubers of *P. bulbocodioides* (30 kg) 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 partitioned with petroleum ether, EtOAc and *n*-BuOH, successively. The EtOAc-soluble part (500 g) was subjected to column chromatography over silica gel eluting with petroleum ether-EtOAc to EtOAc-MeOH gradient system with increasing amounts of EtOAc and MeOH, respectively, to give seven fractions. Fraction 3 was rechromatographed over a silica gel column eluting with CHCl₃-MeOH (99:1, 98:2, 97:3, 95:5, 9:1) to yield six subfractions. The third and fifth subfractions were further fractionated on a Sephadex LH-20 column (CHCl₃-MeOH, 1:1) and then purified by preparative HPLC column to afford compounds **1** (9 mg), **2** (15 mg), **3** (12 mg).

Compound 6'-(3''-hydroxyphenethyl)-4'-methoxydiphenyl-2,2',5-triol was obtained as oil: Its HR ESI-MS showed [M + Na]⁺ at m/z 375.1204 (calcd. (%) 375.1208), corresponding to the molecular formula C₂₁H₂₀O₅. The IR spectrum exhibited absorption at 3413 cm⁻¹ (OH), 1617, 1583 and 1452 cm⁻¹ (benzenoids). The ¹H NMR spectrum of **1** (Table-1) showed signals of three aromatic protons as an ABX system at δ 6.78 (1H, d, *J* = 8.8 Hz, H-3''), 6.69 (1H, dd, *J* = 8.8, 2.8 Hz, H-4''), 6.54 (d, 1H, *J* = 2.8 Hz, H-6''), suggesting the presence of a 2'',5''-hydroxy-phenyl group and signals of four aromatic protons at δ 6.96 (1H, t, *J* = 8.0 Hz, H-5'), 6.52 (1H, m, H-4'), 6.41 (1H, m, H-2'), 6.39 (1H, m, H-6') which were similar to the signals of 3'-hydroxyphenyl group⁷. In addition, the ¹H NMR spectrum displayed one ethylene at δ 2.56 (4H, m, H-7, 8), one methoxyl group at δ 3.73 (3H, s)

and two aromatic protons at δ 6.33 (1H, m, H-4), 6.34 (1H, m, H-6). The ^{13}C NMR spectrum (Table-1) combined with HSQC, HMBC spectrum exhibited the signals for 21 carbons: one ethylene, one methoxyl along with 12 unsaturated carbons (seven protonated carbons, two quaternary carbons and three oxygenated carbons) which were consistent with the assumption of the two phenyl group and other six carbons remaining (δ 143.1, 117.6, 155.6, 99.1, 160.1, 106.3) was similar to the signals of a 1,2,3,5-tetrasubstituted benzene (C-3 and C-5 were oxygenated unsaturated carbons)³. In the HMBC spectrum (Fig. 1), the correlations of H-7 (δ 2.56) to C-1, C-2, C-6, H-6'' (δ 6.54) to C-2, H-6 (δ 6.34) to C-1, C-4, C-5, C-7 and H-4 (δ 6.33) to C-2, C-3, C-5 confirmed that C-1, C-2, C-3, C-4, C-5, C-6 formed a 1,2,3,5-tetrasubstituted benzene and C-7 was linked to C-1, C-1'' was linked to C-2. The correlations of H-6' to C-8 and H-8 (δ 2.46) to C-2', C-6' indicated that the 3'-hydroxyphenyl group was linked to C-8. The methoxyl (δ 3.73) was linked to C-5 because of its clear HMBC correlation to C-5. The other ^1H and ^{13}C signals could be attributed by analysis of the HMBC and HSQC spectrum (Table-1 and Fig. 1). Therefore compound **1** was elucidated as the structure shown in Fig. 1. In order to compare the spectral data with those of other bibenzyls, we used the bibenzyl numbering system instead of the systematic nomenclature. Thus compound (**1**) should be called 6'-(3''-hydroxyphenethyl)-4'-methoxydiphenyl-2,2',5-triol.

Fig. 1. Key HMBC (H $\rightarrow$ C) correlations of compound **1**

Compound 1: Amorphous powder, $\text{C}_{21}\text{H}_{20}\text{O}_5$; IR (KBr, ν_{max} , cm^{-1}): 3413, 1617, 1583, 1452; ^1H NMR (CD_3OD , 400 MHz) and ^{13}C NMR (CD_3OD , 100 MHz) spectral data: see Table-1; HRESIMS (positive) m/z : 375.1204 [$\text{M} + \text{Na}$] $^+$ (calcd. (%) for $\text{C}_{25}\text{H}_{23}\text{O}_6$, 375.1208).

The structures of two known compounds **2**, **3** were identified as *p*-hydroxy benzaldehyde⁸ and *p*-hydroxybenzoic acid⁹, which were isolated from the tubers of *P. bulbocodioides* for the first time.

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No.	δ_{H}	δ_{C}	HMBC
1	—	143.1	—
2	—	117.6	—
3	—	155.6	—
4	6.33 (m)	99.1	H-4/C-2, 3, 5
5	—	160.0	—
6	6.34(m)	106.3	H-6/C-1, 2, 4, 5, 7
7	2.56 (m)	36.6	H-7/C-1, 2, 6, 8
8	2.56 (m)	37.1	H-8/C-1', 2', 6', 7
1'	—	144.0	—
2'	6.41 (m)	115.0	H-2'/C-8, 3', 6'
3'	—	157.0	—
4'	6.52 (m)	112.4	H-4'/C-2', 6', 3'
5'	6.96 (t, 8.0)	128.9	H-5'/C-3', 1', 6'
6'	6.39 (m)	119.6	H-6'/C-8, 1', 4', 5'
1''	—	124.6	—
2''	—	148.1	—
3''	6.78 (d, 8.8)	116.3	H-3''/C-5'', 1'', 2''
4''	6.69 (dd, 8.8, 2.8)	115.2	H-4''/C-2'', 5'', 6''
5''	—	149.9	—
6''	6.54 (d, 2.8)	118.7	H-6''/C-2, 5'', 2''
OCH_3	3.73 (s)	54.4	H/C-5