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Note

Isolation of 4,4'-Dihydroxybenzyl Sulfoxide from *Gastrodia elata*

Hye Sook Yun-Choi and Mi Kyung Pyo

Natural Products Research Institute, Seoul National University, Seoul 110-460, Korea

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In the course of continous work on tubers of *Gastrodia elata*, a new constituent, 4,4'-dihydroxybenzyl sulfoxide was isolated from the ethyl acetate soluble fraction prepared from the methanol extract. The structure of the compound was identified from the elemental analytical and spectroscopic data in comparison with those of non-substituted benzyl sulfoxide.

Key words : *Gastrodia elata*, 4,4'-Dihydroxybenzyl sulfoxide

INTRODUCTION

The steamed and dried tubers of *Gastrodia elata* Blume (Orchidaceae) have been considered as one of the very important herb medicines and used for the treatment of headaches, migraine, dizziness, childhood convulsions, epilepsy, rheumatism, neuralgia and other neuralgic and nervous affections in oriental traditional or folk medicines (Bensky and Gamble, 1986, Tang and Eisenbrand, 1992). In the course of our search for plants with anti-platelet and/or anti-thrombotic potentials, several solvent fractions prepared from the MeOH extract of the tubers of *G. elata* attenuated the thrombotic symptoms in both mouse and rat models of thrombosis (Paik *et al.*, 1995). In this paper, we report the isolation of a novel plant constituent 4,4'-dihydroxybenzyl sulfoxide (**1**) from the EtOAc fraction which is one of the solvent fractions with anti-thrombotic activities.

MATERIALS AND METHODS

Melting point was determined on a Mitamura-Riken melting point apparatus and uncorrected. IR spectra was recorded on a Jasco FT/IR-5300 spectrometer and ^{1}H- and ^{13}C-NMR spectra were taken at 300 MHz and 75.5 MHz respectively on a Varian Gemini-2000 spectrometer with tetramethylsilane as the internal standard. Mass spectra were taken with a VG Analytical VG70-VSEQ and the elemental analysis was performed with a GmbH Vario EL Elemental Analysensystem by Seoul Branch Analytical Lab, Korea Basic Science Institute. Benzyl sulfoxide (**2**), the reference compound, was purchased from Aldrich Chem. Comp.

Correspondence to: Hye Sook Yun-Choi, Natural Products Research Institute, Seoul National University, Seoul 110-460, Korea

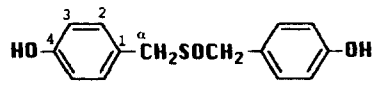
Plant materials

Steamed and dried tubers of *Gastrodia elata* was purchased from a crude drug market in Seoul and were identified by Prof. Hyung Joon Chi, Natural Products Research Institute, Seoul National University.

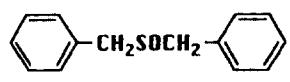
Isolation of 4,4'-dihydroxybenzyl sulfoxide

The steamed and dried tubers of *Gastrodia elata* (6 Kg) was refluxed with methanol three times for six hours each. The concentrated MeOH extract was partitioned between $CHCl_3$ and H_2O and the H_2O layer was further extracted with EtOAc to obtain EtOAc soluble fraction (40 g). 25 g of the EtOAc fr. was chromatographed on a silica gel (2.5 Kg) column eluting with $CHCl_3$ containing increasing proportions of MeOH. The subfraction eluted with $CHCl_3$:MeOH= 20:1 afforded 70 mg of compound **1** as beige colored cubic crystal.

mp 185-187°C (from MeOH-EtOAc), Anal. calcd. for $C_{14}H_{14}SO_3$: C, 64.09; H, 5.39; S, 12.22, found: C,



1. 4,4'-Dihydroxybenzyl sulfoxide



2, Benzyl sulfoxide

Table I. Comparison of spectral data of comp. 1 and comp. 2

	^{1}H-NMR (CD_3CO), δ (*J* values in Hz)		^{13}C-NMR (CD_3OD), δ			
	1	2	1		2	
			found	calcd*	found	s.e.**
1			122.481	122.259	129.559	+1.059
2	7.174, 7.196	7.322	132.925	133	131.6	+3.1
3	(4H each, d, *J*=2.3)	-7.418	116.908	117.333	130.033	+1.533
4		(10H, m)	159.274	159.016	132.116	+3.616
OH	8.454 (s)					
α	3.976 (2H, d, *J*=13)	4.121 (2H, d, *J*=13)	57.568		58.253	
	3.756 (2H, d, *J*=13)	3.880 (2H, d, *J*=13)				

*calculated from substituent effects of OH and CH_2SO.
**substituent effect of CH_2SO

63.66; H, 5.37; S, 12.29; IR ν_{max} (KBr) cm^{-1}; 3,400, 1613, 1514; EI-MS *m/z*; 246 (M^+-16), 212,137,107 (base peak), 78.

RESULTS AND DISCUSSION

Compound 1, mp 185-187°C, was obtained as cubic crystal with pale beige color. Its IR spectrum showed the presence of hydroxyl (3400 cm^{-1}) and aromatic C=C (1613 cm^{-1}) groups. The elemental analytical result indicated that it was a sulfur-containing compound with the molecular formular of $C_{14}H_{14}SO_3$. ^{1}H-NMR spectrum showed signals ascribable to 1,4-disubstituted aromatic protons (doublets at δ 7.174 and 7.196) and a peak (δ 8.454) due to the phenolic hydroxyl protons. A pair of doublets were also shown at δ 3.976 and 3.756 with *J*=13 Hz. When examining the NMR spectrum of non-hydroxylated benzyl sulfoxide (**2**), it was noticed that the two benzylic protons appeared as a singlet when the spectrum was taken at 60 MHz (Pouchert, 1983), however as a AB quartet when taken at 300 MHz (Pouchert and Behnke,1993). Two doublets were obtained at δ 4.121 and 3.880 with same *J* values as those from comp. **1** when ^{1}H-NMR spectrum was taken in CD_3CO, the identical solvent used for the spectrum of comp. **1**. ^{13}C-NMR spectrum exhibited five peaks, one of which appeared in the region characteristic of phenolic carbon (δ 159.274), three peaks in the region of the regular aromatic carbons, two of which are from methine carbons (δ 132.925 and 116.908) and one of which is from non-protonated carbons (δ 122.481). The twelve aromatic carbons of **2** obtained in $CDCl_3$ integrated into three peaks in ^{13}C-NMR spectra (Pouchert and Behnke,1993). However four separated peaks for aromatic carbons could be obtained when the spectra was taken by dissolving **2** in CD_3OD. The shifts for the aromatic carbons of the structure of comp **1** could be approximated (Silverstein *et al.*, 1991) from the substituent effects of OH and of CH_2SO estimated from the spectra of comp. **2**. The ^{13}C-NMR data for the aromatic carbons obtained with comp. **1** were fairly well matched to the calculated values as shown in Table 1. The Mass spectrum of **1** displayed a base peak at *m/z* 107 corresponding to the hydroxybenzyl fragment, however the molecular ion at *m/z* 262 was not detected. The data were comparable to those for comp. **2** showing the base peak at *m/z* 91 for the benzyl fragment. The structure of comp. **1** was identified as 4,4'-dihydroxybenzyl sulfoxide on the basis of the above discussed data.

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