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A New Di-(*p*-hydroxybenzyl) Hydroxylamine from *Gastrodia eleta* Bl.

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Abstract: It is the first reported that a new nitrogen-containing non-amino acid type organic component **1** isolated from one of the well known traditional chinese herb medicines, *Gastrodia eleta* Bl. Structure elucidation and unambiguous NMR assignments for the title compound were carried out mainly on the basis of 1D and 2D NMR experiments.

Keywords: *Gastrodia eleta* Bl.; di-(*p*-hydroxybenzyl) hydroxylamine; 1D NMR; 2D NMR.

Gastrodia eleta Bl. is a prominent traditional chinese herb medicine[1]. Studies on the chemical constituents of this plant were started twenty years ago[2, 3] and since then many papers have been published[2-7]. However, previous work mostly reported the isolations of phenol compounds including their glycosides[2-7]. During our re-investigating on this plant, di-(*p*-hydroxybenzyl) hydroxylamine **1** (**Figure 1**) was isolated and its structure was elucidated on the basis of HRFABMS (high resolution fast atom bombardment mass spectroscopy), and 1D and 2D NMR experiments.

Positive HRFABMS m/z 246.1084 (M^+), calcd for $C_{14}H_{16}NO_3$. UV (MeOH) λ_{max} (logε) 238 (4.4), 279 (3.5) and 282.5 (3.4) nm indicate that **1** is an aromatic compound. IR (KBr pallet) signals at 1612, 1596, 1515, 1457 cm^{-1} support the above suggestion. It was deduced from its ^{13}C NMR spectrum and mass data that **1** can be a symmetric structure because fourteen carbons only afford five carbon signals. The ^1H NMR signals at δ 6.789 (d, J=8.3Hz) and 7.151 (d, J=8.3Hz) together with the ^{13}C NMR and DEPT signals at δ 116.68 (CH), 122.22 (C), 132.65 (CH) and 159.81 (C) suggested that **1** has 1,4-disubstituted phenyl moiety. Hence, **1** is likely a symmetric molecule with two 1,4-disubstituted phenyl sub-units. DEPT experiment indicated that the ^{13}C NMR signal at δ 57.43 should be a methylene group. HMBC and DEPT experiments revealed *p*-hydroxyl benzyl group is the only carbon building-unit in **1**. The two protons at the methylene group of **1** form a AB system in ^1H NMR spectrum induced to propose that the connection point of the two identical parts of **1** is a chiral or pro-chiral center. Protons at δ 3.837 and 4.034 that attribute to methylene group gave long-range correlation with carbon at δ 57.43 confirmed the above proposal. On the basis of NMR spectra, HRFABMS data clearly reveal that a hydroxylated amino group is

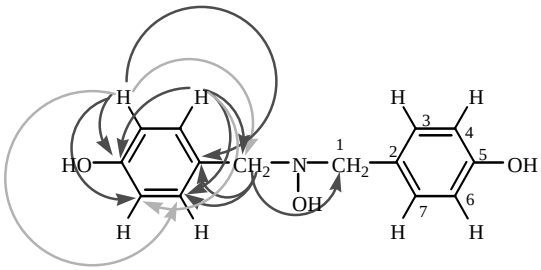
the symmetric center having pro-chirality **1**. Therefore, **1** was determined as the title compound. The unambiguous NMR assignments for **1** are listed in **Table 1**.

Table 1. The ^{1}H, ^{13}C NMR assignments for **1**[a].

position	^{1}H NMR data	^{13}C NMR data
1/1'	3.837, d, J=13.1Hz, 4.034, d, J=13.1Hz AB system	57.43 (CH_2)
2/2'	N/A	122.22 (C)
3/3'	7.151, d, J=8.3Hz	132.65 (CH)
4/4'	6.789, d, J=8.3Hz	116.68 (CH)
5/5'	N/A	158.91 (C)
6/6'	6.789, d, J=8.3Hz	116.68 (CH)
7/7'	7.151, d, J=8.3Hz	132.65 (CH)

[a] ^{1}H NMR and ^{13}C NMR spectra were obtained at 400 MHz and 100 MHz, and recorded in CD_3OD at room temperature, respectively.

Figure 1*. The long-range ^{1}H-^{13}C correlations for **1****



*Grey curves symbolize weak long-range ^{1}H-^{13}C correlations compared to the normal ones illustrated with black curves.
**HMBC spectrum was obtained at 500 Mhz and recorded in CD_3OD at room temperature.

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