SUPPLEMENTARY MATERIAL

NMR Solution Structure Study of One Saturated Sulphur-containing Amides from *Glycosmis lucida*

Zhu-Feng Geng^{a,b}, Kai Yang^a, Yin-Ping Li^c, Shan-Shan Guo^a, Chun-Xue You^a, Wen-Juan Zhang^a, Zhe Zhang^a and Shu-Shan Du^{a*}

^aState Key Laboratory of Earth Surface Processes and Resource Ecology, Beijing Normal University, No.19 Xijiekouwai Street, Haidian District, Beijing 100875, China;

^bAnalytic and Testing Center, Beijing Normal University, No.19 Xijiekouwai Street, Haidian District, Beijing 100875, China.

^cCollege of Chemistry, Beijing Normal University, No.19 Xijiekouwai Street, Haidian District, Beijing 100875, China.

Abstract: One sulphur-containing amides (N-[2-(4-Hydroxyphenyl)-ethyl]-3-methanesulfonyl-N-methyl-propionamide) which was isolated from *Glycosmis lucida* Wall ex Huang had a different NMR profile with this kind of compound's normal case. Based on the information obtained by Nuclear Magnetic Resonance Spectroscopy (NMR) and Mass Spectrometry (MS), its configurations in solution were investigated. The results indicated that the compound would have two stable configurations in solution as the double bond switched between C-N and C-O in an appropriate rate. This phenomenon was clearly exposed by the one dimension selective NOE (1D-NOE) experiments. This conclusion would play an active role in the structure analysis work of this kind of compounds.

Keywords: NMR; NOE; sulphur-containing amides; solution structure

* Corresponding authors. Email: dushushan@bnu.edu.cn (S.S. Du).

Experimental

Fresh leaves of *G. lucida* were collected in October 2011 in Xishuangbanna, Yunnan province, China (northern latitude: 21°08'~22°36'; east longitude: 99°56'~101°50'). The species was identified by Dr. Zhang, L.X., Yunnan branch of the Institute of Medicinal Plant Development (IMPLAD), Chinese Academy of Medical Sciences, Yunnan province, China. The voucher specimen (BNU-Dushushan-2011-11-12-006) was deposited at the Herbarium of the College of Resources Science and Technology, Beijing Normal University.

The leaf powder of *G. lucida* (2.27 kg) was extracted three times with MeOH (10 L) for each at room temperature. The extract liquor were collected, filtered and concentrated. Then 70.2 g of the crude dark green viscous material was obtained as the methanol extracts. By chromatography, the methanolic extracts were separated on a silica gel column (column length 60 cm, i.d. 5.5 cm) with a gradient solvent system of PE/EtOAc (petroleum ether, 50:1, 20:1, 10:1, 5:1, 1:1 and MeOH) to afford 60 fractions (1000 ml/Fr.). All fractions were then evaluated with the thin layer chromatography (TLC) and the chromogenic reaction to obtain several fractions which contained alkaloids compounds. Among them, seven fractions were chromatographed on a silica gel column based on the different polarity and then successively permeated through a Sephadex LH-20 column (column length 50 cm, i.d. 2.5 cm; column length 35 cm, i.d. 2 cm) previously equilibrated with methanol. Compound 1 was obtained from Fr. 47.

The 1D and 2D NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer (Bruker-Biospin, USA) using a broadband probe equipped with a z-gradient coil. The NMR sample had a volume of 500μL and was run in standard 5 mm NMR tubes at 298K. Pulse programs used for the Bruker Avance III 500 MHz NMR spectrometer were standard sequences taken from the Bruker Topspin 3.2 pulse sequence library. ¹H and ¹³C chemical shifts were calibrated relative to the solvents and TMS. ESI-MS and HR-ESI-MS were performed on a Bruker Q-TOF mass spectrometer.

Figure S1. Structure of N-[2-(4-Hydroxyphenyl)-ethyl]-3-methanesulfonyl-N-methylpropionamide.

Figure S2. ^1H NMR (a) and ^{13}C NMR (b) spectra of Compound 1 (DMSO- d_6 , 500 MHz).

Figure S3. ^1H NMR spectra of Compound 1 at different temperatures (a: 298K; b: 318K; c: 338K; d: 358K; DMSO- d_6 , 500 MHz).

Figure S4. Sections of ¹H NMR (a) and 1D- NOE (excited position at b: δ_H2.83; c: δ_H2.93; d: δ_H2.99) spectra of Compound 1 (DMSO-d₆, 500 MHz).

Figure S5. The enlarged drawing of HMBC spectrum of Compound 1.

Figure S6. ^1H NMR spectra of Compound 1 in different concentration and different deuterated solvent (a: lower concentration; b: higher concentration; c: deuterated solvent was MeOD-d_4 ; d: deuterated solvent was pyridine-d_5).

Analysis Info		Acquisition Date	9/19/2014 9:22:10 AM
Analysis Name	D:\Data\EC\2014\2014-00\0010\Gly-47-12-5-5_000001.d	Operator	
Method	4_23_Sensitivity_4.7T	Instrument	solarix
Sample Name	Gly-47-12-5-5		
Comment			

Acquisition Parameter			
Acquisition Mode	Single MS	Acquired Scans	4
Polarity	Positive	No. of Cell Fills	1
Broadband Low Mass	57.8 m/z	Source Accumulation	0.001 sec
Broadband High Mass	1000.0 m/z	Ion Accumulation Time	0.100 sec
		Calibration Date	Mon Sep 15 08:57:39
		Data Acquisition Size	2044576
		Data Processing Size	2097152
		Apodization	Sine-Bell Multiplication

Figure S7. The HR-ESI-MS spectrum of Compound 1.

Table S1. ^1H -NMR (δ , ppm; J, Hz) and ^{13}C -NMR (δ , ppm) data of Compound 1 in DMSO- d_6 .

Position	Compound 1(A)		Compound 1(B)	
	^1H	^{13}C	^1H	^{13}C
1	-	169.1	-	169.0
2	2.74(t, 7.4)	26.6	2.56(t, 7.4)	25.9
3	3.31(t, 7.4)	50.3	3.18(t, 7.4)	50.5
-SCH ₃	2.99(s)	40.8	2.94(s)	40.7
-NCH ₃	2.93(s)	35.6	2.83(s)	33.7
1'	3.43(t, 7.9)	49.9	3.48(t, 7.2)	51.3
2'	2.62(t, 7.4)	32.6	2.71(t, 7.4)	33.4
3'	-	129.1		129.6
4'	7.00(d, 8.3)	130.0	7.03(d, 8.0)	130.3
5'	6.68(d, 7.2)	115.6	6.69(d, 7.9)	115.7
6'	-	156.1	-	156.3
7'	6.68(d, 7.2)	115.6	6.69(d, 7.9)	115.7
8'	7.00(d, 8.3)	130.0	7.03(d, 8.0)	130.3
-OH	9.18(s)	-	9.23(s)	-