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Two Quinones from the Aerial Parts of *Sphallerocarpus gracillis*

Neng Yu CHEN*, Jun SHI, Tao CHEN

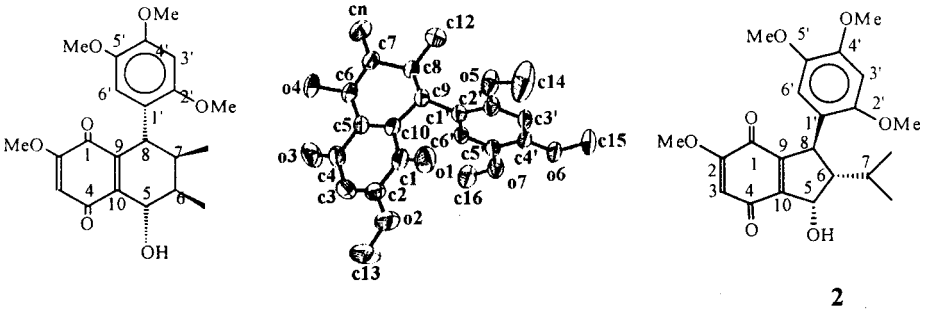
Institute of Organic Chemistry, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000

Abstract: Two new quinones were isolated from the aerial parts of *Sphallerocarpus gracillis*. Their structure were determined by spectroscopic methods (HRMS,2D NMR) and finally confirmed by X-ray crystallography.

Keywords: Quinones; *Sphallerocarpus gracillis*.

Sphallerocarpus gracillis (Boss) K-Pol. is the only species of the genus *Sphallerocarpus*, mainly distributed in northeastern and northwestern parts of China. It has been used in traditional Chinese medicine since ancient times[1]. In this paper, we report the structure elucidation of two new quinones isolated from the aerial parts of *Sphallerocarpus gracillis*.

X-ray structure of **1**



2

Compound **1** was obtained as brown-yellow needles, m.p. 202-204°C. Its HRMS showed the molecular ion peak [M^+] at m/z=402.1680, which allowed for a $C_{22}H_{26}O_7$ molecular formula (calcd. 402.1679). The color reactions with NaOH and $(CH_3COO)_2Mg$ indicated it to be a hydroxyquinone[2], which was further supported by the absorption in the IR spectrum at 1686, 1646cm-1 (quinone)[3,4] and at 3499cm^{-1} (OH). Its ^1H NMR spectra showed the presence of four methoxy groups (δ 3.67, 3.72, 3.75, 3.78), two aromatic protons at δ6.43 (1H, s, H-3') and δ6.42 (1H, s, H-6'), two methyls at δ1.13 (3H, d, J=6.0Hz, H-12) and δ0.90 (3H, d, J=6.0Hz, H-13), an olefinic proton at 5.77 (1H, s, H-3). In the ^{13}C NMR spectra of **1**, there are two methyls and four methines, and

signals for a phenyl group and two quinone carbonyl carbons. The ^{1}H NMR and ^{13}C NMR data (**Table 1**) were assigned by ^{1}H-^{1}H COSY, ^{13}C-^{1}H COSY and ^{13}C-^{1}H COLOC correlations of δH 5.77 (H-3) to δC 181.1 (C-4) and 141.6 (C-10), δH 4.44 (H-5) to δC 181.1 (C-4), 141.6 (C-10) suggesting the hydroxy is at C-5. At the same time, δH 1.13 (H-11) to δC 71.6 (C-5), 39.3 (C-6) and 41.1 (C-7) indicated two methyls are at C-6 and C-7, the phenyl is at C-8. The structure of compound **1** was finally confirmed by X-ray analysis.

Compound **2** was obtained as brown-red prism, m.p. 196-198°C. Its IR spectrum showed absorption bands at 3520cm^{-1} (hydroxy), 1681,1654 (quinone), 1612, 1514, 1454cm^{-1} (phenyl). The HRMS (402.1674) determined the molecular formula to be $C_{22}H_{26}O_7$ (calcd. 402.1679). Its ^{1}H NMR and ^{13}C NMR spectra are very similar to those of compound **1**. It was evident that there is an isopropyl group in the structure of compound **2** (supported by ^{1}H-^{1}H COSY, ^{13}C-^{1}H COLOC). The small coupling constant of H-5 (d, J=2.4Hz) indicated that the hydroxy at C-5, and isopropyl at C-6 are *cis*, while the coupling constants of H-6 (ddd, J=9.8, 7.6, 2.4Hz) suggested that the isopropyl (C-6) and phenyl (C-8) are *trans*. Thus, the structure of compound **2** was determined.

Table 1 ^{1}H (400MHz) and ^{13}C-NMR (100MHz) data of Compound **1** and **2** ($CDCl_3$, δ, ppm, TMS)

No.	^{1}H NMR				^{13}C NMR			
	1		**2**		**1**		**2**	
1					190.0		187.4	
2					158.8		158.9	
3	5.77,s		5.84, s		106.8		106.5	
4					181.1		182.2	
5	4.44, dq(8.8,1.5)		4.63,d(2.4)		71.6		65.1	
6	1.42m		1.85,ddd(9.8,7.6,2.4)		39.3		35.6	
7	1.44m		1.39,m		41.1		38.6	
8	3.73,overlapped		3.72,overlapped		43.2		43.2	
9					141.6		141.3	
10					144.0		143.6	
Me	1.13,d(6.0)		1.11,d(6.8)		15.2		15.0	
Me	0.90,d,(6.0)		0.92,d(6.8)		16.1		16.6	
1'					123.3		123.6	
2'					151.6		151.4	
3'	6.43,s		6.46,s		98.7		98.9	
4'					148.6		148.5	
5'					143.3		143.9	
6'	6.42,s		6.62,s		113.9		114.2	
OMe	3.67,s	3.72,s	3.70,s	3.75,s	56.02	56.03	56.28	56.12
	3.75,s	3.78,s	3.80,s	3.81,s	56.28	57.01	56.89	56.89

a. Coupling constants in parentheses in Hz.

Acknowledgment

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