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Three New Diarylpropanes from *Dioscorea composita*

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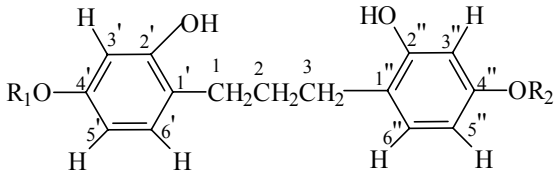
Abstract: Three new diarylpropanes were isolated from the dried rhizomes of *Dioscorea composita* Hemsl., and their structures were determined as 1, 3-bis-(2-hydroxy-4-methoxyphenyl) propane (**1**), 1, 3-bis-(2, 4-dihydroxyphenyl)propane (**2**), 1-(2′-hydroxy-4′-O-β-D- glucopyranosy-phenyl)-3-(2″, 4″-dihydroxyphenyl)propane (**3**), by spectroscopic analysis, respectively.

Keywords: *Dioscorea composita*, diarylpropane, chemical constituents.

Dioscorea composita Hemsl.(Dioscoreaceae) has been used as a source of diosgenin for the preparation of steroid hormones, which is original native in Mexico and cultivated at Xishuangbanna of Yunnan Province in China in 1978, for the output and the amounts of diosgenin[1]. Previously, the isolation and structural elucidation of several steroidal saponins, as the precursors of diosgenin, from the rhizomes of it have been reported[2-3]. It is present in different amounts and constituents in the same plant growing in different localities, in the present study, we describe the isolation and structures determination of three new diarylpropanes from a dried rhizomes of a cultivated *D. composita* at Xishuangbanna. These compounds have not been reported from the plants of *Dioscorea*.

The methanol extracts of dried rhizomes of *D. composita* Hemsl., which were collected in Xishuangbanna of Yunnan Province in January 2002, were subjected to repeated column chromatography of normal and reverse silica gel yielded compounds **1**-**3**.

Compound **1** was isolated as a colorless crystal, mp 68～72°C. Its molecular formula ($C_{17}H_{20}O_4$) was determined by ^{13}C NMR DEPT NMR and EIMS, which showed at *m/z* 288 $[M]^+$. The UV spectrum of **1** exhibited absorptions at 280, 204 nm, which



1 R_1, R_2=CH_3 **2** R_1, R_2=H **3** R_1=Glc, R_2=H

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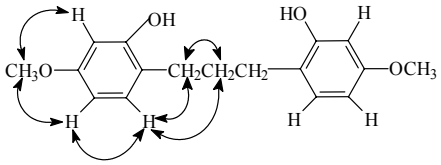
Figure 1 Key ROESY correlations of compound **1**



indicated the presence of a group of substituted phenyl groups. The IR spectrum (KBr) of **1** showed strong absorptions at 3423 (O-H), 2922 (C-H) and 1619, 1517 (phenyl), 1290 (C-O) and 829 (1, 2, 4-trisubstituted phenyl)[5] cm^{-1}. The ^1H NMR spectrum (**Table 1**) of **1** showed six aromatic H-atom signals at δ 7.00 (d, 2H, *J*=8.3 Hz), 6.41 (dd, 2H, *J*=2.4, 8.3 Hz) and 6.36 (d, 2H, *J*=2.4 Hz) ppm, which exhibited as an ABX-type coupling system and indicated that they were 1, 2, 4-trisubstituted phenyl groups; as well as three signals at δ 2.56 (t, 4H, *J*=7.5 Hz), 1.88 (dd, 2H, *J*=7.8 Hz) and 3.72 (s, 6H) ppm, indicated two methenes and two methoxyl groups. The ^{13}C NMR spectrum of **1** (**Table 1**) showed nine signals, they were recognized as three aromatic methines, three aromatic quaternary carbons including two oxygen-bearing carbons, one methoxyl and two methenes. On the basis of these spectroscopic studies, it showed that the substance was a 1, 3-diarypropane with two hydroxyl and two –OMe groups distributed at positions C-2 and C-4[4]. In the HMQC spectrum of **1**, the H-atoms resonating at δ 2.56 (H-1/3), 1.88 (H-2), 3.72 (MeO-4′/4″), 6.36 (H-3′/3″), 6.41 (H-5′/5″) and 7.00 (H-6′/6″) were found to be coupled with δ 28.9 (C-1/3), 30.4 (C-2), 55.3 (MeO-4′/4″), 101.9 (C-3′/3″), 106.0 (C-5′/5″), and 130.6 (C-6′/6″), respectively. The HMBC experiment showed long-range coupling of H-1/3 (δ 2.56) with C-2 (δ 30.4), C-1′/1″ (δ 120.5), C-6′/6″ (δ 130.6) and C-2′/2″ (δ 154.2). The H-2 (δ 1.88) was found to be coupled with C-1/3 (δ 28.9), C-1′/1″(δ 120.5). The proton of MeO-4′/4″ (δ 3.72) showed coupling with C-4′/4″ (δ 158.8). Similarly, H-6′/6″ (δ 7.00) showed couplings with C-1/3 (δ 28.9), C-3′/3″ (δ 101.9), C-5′/5″ (δ 106.0), C-6′/6″(δ 130.6), C-2′/2″ (δ 154.2) and C-4′/4″ (δ 158.8), the couplings of H-5′/5″ (δ 6.41) with C-3′/3″(δ 101.9), C-1′/1″ (δ 120.5), 154.2 (C-2′/2″) and C-4′/4″ (δ 158.8), while H-3′/3″ (δ 6.36) with C-5′/5″ (δ 106.0), C-1′/1″ (δ 120.5), C-2′/2″ (δ 154.2) and C-4′/4″ (δ 158.8). The ROESY spectrum of **1** (**Figure 1**) exhibited couplings between H-3′/3″ (δ 6.36) and protons of MeO-4′/4″ (δ 3.72), H-5′/5″ (δ 6.41) and MeO-4′/4″ (δ 3.72), H-6′/6″ (δ 7.00). The proton signal at δ 7.00 (H-6′/6″) correlated with the proton signals H-1/3 (δ 2.56), H-2 (δ 1.88), H-5′/5″ (δ 6.41), and the proton signals at δ 1.88 (H-2) with H-6′/6″ (δ 7.00), H-1/3 (δ 2.56) and the proton signals at δ 2.56 (H-1/3) with H-6′/6″ (δ 7.00), H-2 (δ 1.88). The EIMS spectrum of **1** exhibited the fragment ion at *m/z* 137 (100, $-CH_2C_6H_3(OH)OCH_3$), 164, 151. Thus, the structure of **1** was determined as 1, 3-bis-(2-hydroxy-4- methoxyphenoyl)propane.

Compound **2** was obtained as a yellow needle crystal, mp 179~181°C. Its molecular formula was analyzed as $C_{15}H_{16}O_4$ from EIMS spectrum, in which the quasi-molecular ion peak at *m/z* 260 (96%, M^+). Comparing its ^1H and ^{13}C NMR spectra with those of **1** (**Table 1**) indicated that both compounds were very similar, instead of a methoxyl attached at C-4′/4″ of **1**, a hydroxyl unit attached at C-4′/4″ of **2**, from the strong mass spectral

fragment ions at *m/z* 123 (base peak, $ArCH_2^+$), the absence of methoxyl signals in the ^1H and ^{13}C NMR spectra, the absorptions at 282, 257, 207 nm in UV spectrum and the strong absorptions at 3386 (O-H), 2926 (C-H) and 1621, 1516 (phenyl), 1223 (C-O) and 843 cm^{-1} in the IR (KBr) spectrum. On the basis of these spectroscopic studies, it was concluded that the compound **2** is 1, 3-bis-(2, 4-dihydroxyphenyl)propane.

Compound **3** was obtained as a yellow powder, mp 207~209°C, $[\alpha]_D^{21.9}$ –40.89 (C 0.0038, CH_3OH), with a molecular formula $C_{21}H_{26}O_9$, determined by negative ion FABMS and ^{13}C DEPT NMR data. The negative-ion FABMS spectrum of **3** exhibited a molecular ion peak at *m/z* 421 $[M-H]^-$, and the fragment ions at *m/z* 265 $[M-H-C_6H_3(OH)_2CH_2CH_2-H_2O-H]^-$ (base peak), 311 $[M-H-C_6H_4(OH)_2]^-$. The UV spectrum of **3** exhibited absorptions at 280, 205 nm. The IR(KBr) spectrum showed strong absorptions at 3386 (O-H), 2926 (C-H) and 1615, 1505 (phenyl), 1275 (C-O) and 843, 834 cm^{-1} (1, 2, 4-trisubstituted phenyl)[5]. The signals of **3** were very similar to those of **2** except the sugar moiety. The ^1H and ^{13}C NMR spectra of **3** (**Table 2**) exhibited an anomeric proton signal at δ 4.83 (d, 1H, *J*=10.1 Hz) and anomeric carbon signal at δ 102.4，respectively. In the HMQC spectra of **3**, the H-atoms resonating at δ 4.83 (H-1‴), 3.48 (H-2‴), 3.46 (H-3‴), 3.42 (H-4‴), 3.39 (H-5‴), 3.90 (H-6‴), 3.71 (H-6‴), were found to be coupled with δ 102.4 (C-1‴), 75.0 (C-2‴), 78.0 (C-3‴), 71.3 (C-4‴), 78.2 (C-5‴), 62.5 (C-6‴), respectively. In the HMBC spectra of **3** (**Figure 2**), the following correlation signals was observed: δ 4.83 (anomer of glucose) to 157.2 (C-4′ of the aglycone), which confirmed the sequence and its linkage position to the aglycone. Thus, the structure of **3** was determined as 1-(2′-hydroxy-4′-O-β-D-glucopyranosyphenyl)-3-(2", 4"-dihydroxy-phenyl) propane.

Table 1 ^1H and ^{13}C NMR data of compounds **1** and **2** (δ ppm)

Position	**1**		**2**	
	δ_C	δ_H	δ_C	δ_H
1,3	28.9t	2.56 (t, 4H, *J*=7.5 Hz)	30.5t	2.52 (tt, 4H, *J*=7.6 Hz)
2	30.4t	1.88 (tt, 2H, *J*=7.8, 7.5 Hz)	31.9t	1.77 (t, 2H, *J*=7.9, 7.6 Hz)
1′,1″	120.5s		121.6s	
2′,2″	154.2s		156.9s	
3′,3″	101.9d	6.36 (d, 2H, *J*=2.4 Hz)	103.4d	6.86 (d, 2H, *J*=8.1 Hz)
4′,4″	158.8s		157.0s	
5′,5″	106.0d	6.41 (dd, 2H, *J*=8.3, 2.4 Hz)	107.2d	6.23 (dd, 2H, *J*=8.1, 2.4 Hz)
6′,6″	130.6d	7.00 (d, 2H, *J*=8.3 Hz)	131.3d	6.28 (d, 2H, *J*=2.4 Hz)
OMe	55.3q	3.72 (s, 6H)		

^1H (^{13}C)NMR spectra were obtained at 400 (100) MHz and recorded in CD_3OD.

Figure 2 Key HMBC correlations of compound **3**

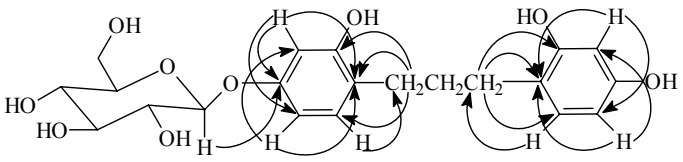


Table 2 ^{1}H and ^{13}C NMR data of compound **3** (δ ppm)

Position	δ_C	δ_H
1	30.4t	2.62 (m, 2H), 2.50(t, 2H, *J*=8.4 Hz)
2	32.1t	1.77 (tt, 2H, *J*=7.8 Hz)
3	30.4t	2.56 (m, 1H), 2.49 (t, 1H *J*=7.3 Hz)
1′	124.3s	
2′	156.7s	
3′	103.9d	6.61 (d, 1H, *J*=2.4 Hz)
4′	157.4s	
5′	109.8d	6.38 (dd, 1H, *J*=2.4, 8.2 Hz)
6′	131.4d	6.85 (d, 1H, *J*=8.2 Hz)
1″	121.7s	
2″	157.0s	
3″	103.5d	6.26 (d, 1H, *J*=2.4 Hz)
4″	157.2s	
5″	107.4d	6.21 (dd, 1H, *J*=2.4,8.2 Hz)
6″	131.2d	6.91 (d, 1H, *J*=8.2 Hz)
Glc 1‴	102.4d	4.83 (d, 1H, *J*=10.1 Hz)
2‴	75.0d	3.48 (t, 1H, *J*=8.3 Hz)
3‴	78.0d	3.46 (t, 1H, *J*=8.6 Hz)
4‴	71.3d	3.42 (d, 1H, *J*=4.8 Hz)
5‴	78.2d	3. 39 (m, 1H)
6‴	62.5t	3.90 (d, 1H, *J*=11.5 Hz)
		3.71 (dd, 1H, *J*=12, 4.7 Hz)

^{1}H (^{13}C)NMR spectra were obtained at 500 (125) MHz and recorded in CD_3OD.

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