

Chemical Constituents from Rhizomes of *Curculigo capitulata*

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The herb *Curculigo capitulata* (Lour.) Ktze is widely distributed in Southern and Southwestern China. It has been used as a tonic and a medicine for the treatment of dysmenorrhea and rheumatism.¹ This species has been reported to be rich in phenolic compounds and norlignan compounds with skeletons Ph-C₅-Ph, which have been found to possess some beneficial pharmacological effects, including anti-arrhythmic properties, antioxidant activity, and vasoconstrictor activity.²⁻⁶

Previously, we reported the chemical constituents from the rhizomes of *C. capitulata* collected in xishuangbanna region of Yunnan Province, China.^{3,7} To compare the chemical constituents' differences of the same *Curculigo* species belonging to different geographical distribution and climatic conditions, we investigated the rhizomes of *C. capitulata* collected in Napo region of Guangxi Province, China. Recently, we reported two novel norlignan derivatives with the rearranged skeletons, named as crassifoside I and sinensigenin C, from this species collected in Napo region of Guangxi Province, China.⁸ To further search more novel compounds, the minor constituents of this plant were investigated. This paper deals with the isolation and structure elucidation of one novel norlignan derivative, named as capituloside B (**1**), together with eight known compounds, curcapicyclo-side (**2**),⁴ capituloside (**3**),⁵ breviscaside B (**4**),⁹ crassifogenin C (**5**),¹⁰ breviscapin A (**6**),¹¹ methyl-4-*O*-coumaroylquininate (**7**),¹²

orcinol glucoside (**8**)^{13,14} and 2,6-dimethoxy-benzioic acid (**9**),² from its rhizomes as shown in Figure 1. Their structures were established by spectroscopic analysis, especially using 2D-NMR techniques (¹H-¹H COSY, HMQC, HMBC, and NOESY) and comparisons of their data with literature values. Compounds **4-7** were isolated for the first time from this plant, and compound **7** was the first example isolated from the family.

Experimental

General experimental procedures. Optical rotation was measured on a Horiba SEPA-300 polarimeter. A UV-2401PC spectrometer was used to obtain the UV spectrum in methanol (MeOH). IR spectra were recorded on Nexus 870-FT-IR spectrophotometer with potassium bromide (KBr) pellets. NMR spectra were measured on a Bruker AM-400 spectrometer with TMS as an internal standard. FAB-MS and HR-TOF-MS were performed on a VG Autospec-3000 spectrometer and API-QSTAR-Pulsar-1 spectrometer, respectively. Column chromatography was carried out on Sephadex LH-20 gel (25 - 100 μm, Pharmacia Fine Chemical Co. Ltd.) and Chromatorex ODS (30 - 50 μm, Fuji Silysia Chemical Co. Ltd.). Thin layer chromatography (TLC) was carried out on silica gel G pre-coated plates (Qingdao Haiyang Chemical Co. Ltd.), and spots were detected by spraying with 5% H₂SO₄ in EtOH followed by heating.

Plant material. The rhizomes of *C. capitulata* were collected in Napo, Guangxi Province, China, in August 2007 and identified by Prof. Dr. Kai-Jin Wang from the School of Life Sciences, Anhui University, where a voucher specimen (No. 20070803) was deposited.

Extraction and isolation. The air-dried and powdered rhizomes of *C. capitulata* (1.25 kg) were extracted with 85% EtOH (3 × 6 L) under reflux for 3 h. The combined organic layer was concentrated in vacuo to achieve a residue (55 g). The residue was suspended in H₂O and then passed through a D101 resin column eluting sequentially with water followed by 30%, 60%, and 90% aqueous MeOH. The fraction (5.3 g) eluted from 30% MeOH was purified by Sephadex LH-20 chromatography (MeOH-H₂O, 0:1-1:0) to yield two fractions (A₁ and A₂). Fraction A₁ was subjected to further separation on Sephadex LH-20 chromatography (EtOH-acetone, 1:1) and ODS (EtOH-H₂O, 0:1-1:0) to afford **4** (17 mg) and **5** (8 mg). Fraction A₂ was purified by Sephadex LH-20 chromatography (EtOH) and then ODS (EtOH-H₂O, 0:1-1:0) to yield **7** (15 mg) and **8** (66 mg). The fraction (5.8 g) eluted from 60% MeOH was purified by Sephadex LH-20 chromatography (MeOH-H₂O, 0:1-1:0) to

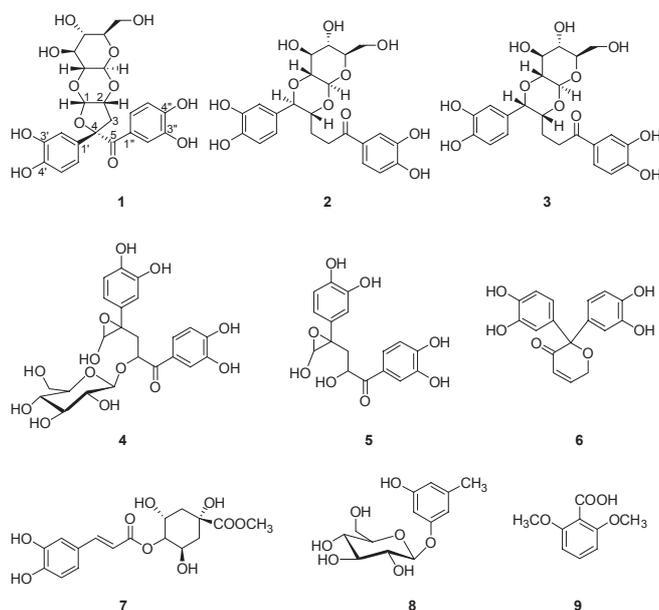


Figure 1. Structures of compounds 1-9.

yield three fractions (B₁-B₃). Fraction B₁ was subjected on ODS (MeOH-H₂O, 0:1-1:0) and then Sephadex LH-20 (EtOH) to afford compounds **1** (23 mg) and **6** (6 mg). Compounds **2** (5 mg) and **3** (9 mg) was obtained from fraction B₃ by column chromatography on Sephadex LH-20 (EtOH-acetone, 1:1) and then ODS (MeOH-H₂O, 0:1-1:0). The fraction (3.8 g) eluted from 90% MeOH was subjected to chromatography on Sephadex LH-20 (MeOH-H₂O, 0:1-1:0, then EtOH) to yield compound **9** (21 mg).

Acidic hydrolysis of compound 1. Compound **1** (23 mg) was refluxed with 2 mol L⁻¹ HBr-dioxane (1:1, v/v, 2 mL) on a water bath for 6 h. The reaction mixture was evaporated to dryness. The dry reaction mixture was extracted with CHCl₃ and H₂O four times. The H₂O-soluble fraction was evaporated to dryness. The dried sugar residue was diluted in 1 mL pyridine without water and treated with 0.5 mL trimethyl-chlorosilan (TMCS) and stirred at 60 °C for 5 min. After drying the solution with a stream of N₂, the residue was extracted with ether (1 mL). The ether layer was analyzed by GC with the following conditions: HP AC-5 quartz capillary column (30 m × 0.32 mm); detector: FID (250 °C); injection temperature: 250 °C; column temperature: 180 - 280 °C; rate: 3 °C/min; and retention times (min): the derivative of D-glucose (7.22).

Capituloside B (1): White powder. [α]_D²¹ = -82.1 (*c* = 0.12, MeOH); IR (KBr) ν_{\max} cm⁻¹: 3419 (OH), 2924, 1665 (C=O), 1600, 1522, 1440, 1375, 1294, 1201, 1107, 1032, 872, 808, 784; UV (MeOH) λ_{\max} nm (log ϵ): 204 (4.35), 232 (3.97), 284 (3.79), 314 (3.69). ¹H- and ¹³C-NMR data see Table 1. HR-TOF-MS (negative mode): *m/z* 491.1178 [M-H]⁻ (calcd. 491.1189 for C₂₃H₂₃O₁₂).

Curcapiacycloside (2): White powder. ¹H-NMR (400 MHz, CD₃OD) δ 4.61 (1H, d, *J* = 6.0 Hz, H-1), 4.54 (1H, m, H-2), 2.07 (1H, m, H-3a), 1.86 (1H, m, H-3b), 3.07 (2H, m, H-4), 6.98 (1H, d, *J* = 1.8 Hz, H-2'), 6.80 (1H, d, *J* = 8.2 Hz, H-5'), 6.86 (1H, dd, *J* = 8.1, 2.0 Hz, H-6'), 7.44 (1H, d, *J* = 2.0 Hz, H-2''), 6.85 (1H, d, *J* = 8.8 Hz, H-5''), 7.44 (1H, dd, *J* = 8.7, 2.0 Hz, H-6''), 4.84 (1H, d, *J* = 8.5 Hz, H-1'''), 3.44 (1H, m, H-2'''), 3.66 (1H, m, H-3'''), 3.54 (1H, m, H-4'''), 3.35 (1H, m, H-5'''), 3.91 (1H, dd, *J* = 12.0, 2.0 Hz, Ha-6'''), 3.74 (1H, dd, *J* = 12.0, 5.4 Hz, Hb-6'''); ¹³C-NMR (100 MHz, CD₃OD) δ 79.5 (d, C-1), 79.9 (d, C-2), 27.6 (t, C-3), 34.7 (t, C-4), 200.9 (s, C-5), 131.9 (s, C-1'), 116.2 (d, C-2'), 146.4 (s, C-3'), 146.4 (s, C-4'), 116.2 (d, C-5'), 120.8 (s, C-6'), 130.5 (s, C-1''), 116.0 (s, C-2''), 146.5 (s, C-3''), 152.1 (s, C-4''), 115.8 (d, C-5''), 123.1 (d, C-6''), 97.4 (d, C-1'''), 73.9 (d, C-2'''), 76.0 (d, C-3'''), 71.9 (d, C-4'''), 75.6 (d, C-5'''), 62.6 (t, C-6'''); FAB-MS (+) *m/z* 479 [M+H]⁺.

Capituloside (3): White powder, ¹H-NMR (400 MHz, CD₃OD) δ 4.92 (1H, d, *J* = 3.6 Hz, H-1), 4.20 (1H, m, H-2), 2.19 (1H, m, Ha-3), 1.53 (1H, m, Hb-3), 2.91 (2H, m, H-4), 6.88 (1H, d, *J* = 2.0 Hz, H-2'), 6.79 (1H, d, *J* = 8.4 Hz, H-5'), 6.73 (1H, dd, *J* = 8.4, 2.0 Hz, H-6'), 7.39 (1H, d, *J* = 2.0 Hz, H-2''), 6.83 (1H, d, *J* = 8.0 Hz, H-5''), 7.38 (1H, dd, *J* = 8.0, 2.0 Hz, H-6''), 4.64 (1H, d, *J* = 7.6 Hz, H-1'''), 3.23 (1H, dd, *J* = 9.6, 8.4 Hz, H-2'''), 3.69 (1H, m, H-3'''), 3.43 (1H, m, H-4'''), 3.49 (1H, m, H-5'''), 3.93 (1H, dd, *J* = 12.0, 2.0 Hz, Ha-6'''), 3.75 (1H, dd, *J* = 12.0, 5.2 Hz, Hb-6'''); ¹³C-NMR (100 MHz, CD₃OD) δ 80.4 (d, C-1), 79.2 (d, C-2), 21.3 (t, C-3), 34.7 (t, C-4), 201.1 (s, C-5), 130.5 (s, C-1'), 115.7 (d, C-2'), 146.3 (s, C-3'), 145.7 (s, C-4'),

Table 1. ¹H-NMR and ¹³C-NMR data of **1** (400 MHz, in CD₃OD, δ ppm, *J* in Hz)

position	δ (C)	δ (H)	HMBC (H→C)
1	98.5 (<i>d</i>)	5.46 (<i>d</i> , <i>J</i> = 3.7)	C-3, C-4, Glc.C-2
2	77.1 (<i>d</i>)	4.60 (<i>td</i> , <i>J</i> = 9.2, 3.6)	C-3, C-4, Glc.C-1
3	36.6 (<i>t</i>)	3.56 (<i>dd</i> , <i>J</i> = 12.9, 9.7) 2.11 (<i>dd</i> , <i>J</i> = 13.0, 8.7)	C-1, C-2, C-4, C-5
4	93.6 (<i>s</i>)		
5	198.0 (<i>s</i>)		
1'	135.5 (<i>s</i>)		
2'	112.7 (<i>d</i>)	6.82 (<i>d</i> , <i>J</i> = 1.6)	C-4, C-1', C-3'
3'	146.1 (<i>s</i>)		
4'	146.8 (<i>s</i>)		
5'	116.73 (<i>d</i>) ^a	6.74 (<i>d</i> , <i>J</i> = 8.4)	C-4, C-1', C-3'
6'	116.71 (<i>d</i>) ^a	6.71 (<i>dd</i> , <i>J</i> = 8.4, 1.6)	C-4, C-1', C-2', C-4'
1''	127.9 (<i>s</i>)		
2''	119.3 (<i>d</i>)	7.48 (<i>d</i> , <i>J</i> = 2.0)	C-5, C-3'', C-4'', C-6''
3''	145.6 (<i>s</i>)		
4''	151.6 (<i>s</i>)		
5''	115.2 (<i>d</i>)	6.64 (<i>d</i> , <i>J</i> = 8.4)	C-5, C-1'', C-3'', C-4''
6''	126.2 (<i>d</i>)	7.43 (<i>dd</i> , <i>J</i> = 8.4, 2.0)	C-5, C-2'', C-4''
Glc.			
1	94.1 (<i>d</i>)	4.65 (<i>d</i> , <i>J</i> = 7.9)	C-2
2	77.4 (<i>d</i>)	3.06 (<i>dd</i> , <i>J</i> = 9.1, 8.2)	C-1
3	74.7 (<i>d</i>)	3.40 (<i>m</i>)	
4	71.8 (<i>d</i>)	3.32 (<i>m</i>)	
5	79.6 (<i>d</i>)	3.35 (<i>m</i>)	
6	62.6 (<i>t</i>)	3.86 (<i>dd</i> , <i>J</i> = 12.0, 1.8) 3.68 (<i>dd</i> , <i>J</i> = 12.0, 5.4)	

^aValues may be interchangeable.

116.2 (d, C-5'), 118.3 (s, C-6'), 130.4 (s, C-1''), 114.2 (s, C-2''), 146.3 (s, C-3''), 152.0 (s, C-4''), 115.9 (d, C-5''), 123.0 (d, C-6''), 93.9 (d, C-1'''), 81.9 (d, C-2'''), 75.0 (d, C-3'''), 72.1 (d, C-4'''), 79.9 (d, C-5'''), 62.6 (t, C-6'''); FAB-MS (+) *m/z* 479 [M+H]⁺.

Breviscaside B (4): White powder, ¹H-NMR (400 MHz, CD₃OD) δ 5.56 (1H, s, H-1), 2.05 (1H, dd, *J* = 13.4, 3.0 Hz, Ha-3), 3.57 (1H, dd, *J* = 14.0, 6.4 Hz, Hb-3), 4.21 (1H, m, H-4), 7.01 (1H, d, *J* = 2.0 Hz, H-2'), 6.71 (1H, d, *J* = 8.4 Hz, H-5'), 6.87 (1H, dd, *J* = 8.4, 2.0 Hz, H-6'), 7.52 (1H, d, *J* = 2.0 Hz, H-2''), 6.65 (1H, d, *J* = 8.4 Hz, H-5''), 7.46 (1H, dd, *J* = 8.4, 2.0 Hz, H-6''), 4.30 (1H, d, *J* = 7.6 Hz, H-1'''), 3.13-3.39 (4H, m, Glc.H), 3.87 (1H, dd, *J* = 12.0, 2.0 Hz, Ha-6'''), 3.70 (1H, dd, *J* = 12.4, 5.2 Hz, Hb-6'''); ¹³C-NMR (100 MHz, CD₃OD) δ 104.0 (d, C-1), 94.7 (s, C-2), 43.1 (t, C-3), 86.0 (d, C-4), 200.6 (s, C-5), 136.1 (s, C-1'), 113.3 (d, C-2'), 145.7 (s, C-3'), 146.4 (s, C-4'), 116.4 (d, C-5'), 117.3 (d, C-6'), 128.2 (s, C-1''), 119.4 (d, C-2''), 145.5 (s, C-3''), 151.1 (s, C-4''), 115.1 (d, C-5''), 126.2 (d, C-6''), 103.7 (d, C-1'''), 74.9 (d, C-2'''), 77.8 (d, C-3'''), 71.4 (d, C-4'''), 77.9 (d, C-5'''), 62.6 (t, C-6'''); FAB-MS (-) *m/z* 509 [M-H]⁻.

Crassifogenin C (5): White powder, ¹H-NMR (400 MHz, CD₃OD) δ 5.42 (1H, s, H-1), 1.84 (1H, dd, *J* = 13.7, 2.8 Hz, Ha-3), 3.49 (1H, dd, *J* = 6.2, 13.7 Hz, Hb-3), 4.08 (1H, m, H-4), 6.93 (1H, d, *J* = 1.9 Hz, H-2'), 6.67 (1H, d, *J* = 8.3 Hz, H-5'), 6.75 (1H, dd, *J* = 8.3, 2.0 Hz, H-6'), 7.49 (1H, d, *J* = 1.9 Hz, H-2''), 6.62 (1H, d, *J* = 8.4 Hz, H-5''), 7.45 (1H, dd, *J* = 8.4, 1.9 Hz, H-6''); ¹³C-NMR (100 MHz, CD₃OD) δ 105.5 (d, C-1), 93.3 (s, C-2), 45.5 (t, C-3), 77.8 (d, C-4), 200.4 (s, C-5), 136.7

(s, C-1'), 113.3 (d, C-2'), 145.7 (s, C-3'), 146.5 (s, C-4'), 116.5 (d, C-5'), 117.3 (s, C-6'), 128.7 (s, C-1''), 119.6 (s, C-2''), 145.5 (s, C-3''), 151.2 (s, C-4''), 115.2 (d, C-5''), 126.4 (d, C-6''); FAB-MS (-) m/z 347 [M-H]⁻.

Breviscapin A (6): Black powder, ¹H-NMR (400 MHz, acetone-*d*₆) δ 6.14 (1H, dt, J = 10.4, 2.2 Hz, H-4), 7.13 (1H, dt, J = 10.4, 2.8 Hz, H-5), 4.34 (1H, dd, J = 2.8, 2.3 Hz, H-6), 6.72 (1H, d, J = 2.0 Hz, H-2'), 6.76 (1H, d, J = 8.0 Hz, H-5'), 6.60 (1H, dd, J = 8.0, 2.0 Hz, H-6'), 6.72 (1H, d, J = 2.0 Hz, H-2''), 6.76 (1H, d, J = 8.0 Hz, H-5''), 6.60 (1H, dd, J = 8.0, 2.0 Hz, H-6''); ¹³C-NMR (100 MHz, acetone-*d*₆) δ 88.3 (s, C-2), 196.2 (s, C-3), 128.1 (d, C-4), 150.2 (d, C-5), 62.8 (t, C-6), 133.5 (s, C-1'), 117.3 (d, C-2'), 146.2 (s, C-3'), 146.6 (s, C-4'), 116.2 (d, C-5'), 121.3 (d, C-6'), 133.5 (s, C-1''), 117.3 (d, C-2''), 146.2 (s, C-3''), 146.6 (s, C-4''), 116.2 (d, C-5''), 121.3 (d, C-6''); FAB-MS (-) m/z 313 [M-H]⁻.

Methyl-4-O-coumaroylquinatate (7): White powder, ¹H-NMR (400 MHz, CD₃OD) δ 2.19 (1H, m, Ha-2), 2.04 (1H, m, Hb-2), 4.27 (1H, m, H-3), 4.83 (1H, dd, J = 8.8, 2.7 Hz, H-4), 4.29 (H, m, H-5), 2.20 (1H, m, Ha-6), 2.06 (1H, m, Hb-6), 3.76 (3H, s, H-8), 7.08 (1H, d, J = 2.0 Hz, H-2'), 6.79 (1H, d, J = 8.2 Hz, H-5'), 6.98 (1H, dd, J = 8.0, 2.0 Hz, H-6'), 7.64 (1H, d, J = 15.9 Hz, H-7'), 6.73 (1H, d, J = 15.9 Hz, H-8'); ¹³C-NMR (100 MHz, CD₃OD) δ 76.5 (s, C-1), 42.2 (t, C-2), 65.8 (d, C-3), 78.6 (d, C-4), 69.1 (d, C-5), 38.5 (t, C-6), 175.7 (s, C-7), 53.0 (q, C-8), 127.9 (s, C-1'), 115.2 (d, C-2'), 149.6 (s, C-3'), 146.9 (s, C-4'), 116.5 (d, C-5'), 123.0 (d, C-6'), 147.2 (d, C-7'), 115.4 (d, C-8'), 169.0 (s, C-9'); FAB-MS (-) m/z 365 [M-H]⁻.

Orcinol glucoside (8): Colorless needle (MeOH), ¹H-NMR (400 MHz, CD₃OD) δ 2.11(3H, s, CH₃), 6.31 (1H, s, H-2), 6.27 (1H, s, H-4), 6.19(1H, s, H-6), 4.74 (1H, d, J = 7.6 Hz, H-1'), 3.20-3.36 (4H, m, Glc H), 3.61 (1H, dd, J = 12.08, 4.80 Hz, Ha-6'), 3.79 (1H, dd, J = 12.08, 1.48 Hz, Hb-6'), 10.09 (1H, br. s, C-3-OH); ¹³C-NMR (100 MHz, CD₃OD) δ 158.7 (s, C-1), 100.8 (d, C-2), 157.8 (s, C-3), 108.4 (d, C-4), 139.9 (s, C-5), 109.8 (d, C-6), 100.8 (d, C-1'), 73.5 (d, C-2'), 76.7 (d, C-3'), 70.0 (d, C-4'), 76.6 (d, C-5'), 61.1 (t, C-6'), 20.3 (q, CH₃); FAB-MS (-) m/z 285 [M-H]⁻.

2,6-Dimethoxy-benzioc acid (9): Colorless needle (EtOH), ¹H-NMR (400 MHz, CD₃OD) δ 3.79 (6H, s, 2, 6-OMe), 6.67 (2H, d, J = 8.4 Hz, H-3, 5), 7.17 (1H, t, J = 8.4 Hz, H-4); ¹³C-NMR (100 MHz, CD₃OD) δ 115.1 (s, C-1), 157.8 (s, C-2, 6), 104.8 (d, C-3, 5), 131.4 (d, C-4), 56.2 (q, 2, 6-OMe), 167.0 (s, C=O); EI-MS m/z 182 [M]⁺.

Results and Discussion

Capituloside B (**1**) was obtained as white amorphous powder. Its molecular formula C₂₃H₂₄O₁₂ with twelve unsaturation degrees was determined from a quasi-molecular ion peak at m/z 491 [M-H]⁻ in its FAB-MS mass spectrum and the ¹³C-NMR (DEPT) spectrum, which was supported by its HR-TOF MS observed at m/z 491.1178 [M-H]⁻ (calcd. 491.1189 for C₂₃H₂₃O₁₂). The IR spectrum indicated absorptions of OH groups at 3419, a conjugated carbonyl group at 1665 and aromatic rings at 1600, 1522 and 1440 cm⁻¹. The conjugated carbonyl IR band was confirmed by the ¹³C-NMR signal at δ_C 198.0 (Table 1). The ¹H NMR spectrum (Table 1) exhibited signals for one methylene

group at δ 3.56 (dd, J = 12.9, 9.7 Hz), 2.11 (dd, J = 13.0, 8.7 Hz), and two methine protons at δ 5.46 (d, J = 3.7 Hz), and 4.60 (td, J = 9.2, 3.6 Hz). The ¹H NMR spectrum of **1** also appeared six aromatic protons, three of them were assigned to H-2' at δ 6.82 (d, J = 1.6 Hz), H-5' at δ 6.74 (d, J = 8.4 Hz), and H-6' at δ 6.71 (dd, J = 8.4, 1.6 Hz), which suggested the existence of 1,3,4-trisubstituted benzene ring; the remaining three aromatic protons were assigned to H-2'' at δ 7.48 (d, J = 2.0 Hz), H-5'' at δ 6.64 (d, J = 8.4 Hz), and H-6'' at δ 7.43 (dd, J = 8.4, 2.0 Hz) in another 1,3,4-trisubstituted benzene ring, in which H-2'' and H-6'' were shifted downfield due to an *ortho* carbonyl group (IR ν_{CO} 1665 cm⁻¹ and δ_C 198.0). The ¹³C NMR (DEPT) spectrum (Table 1) showed one methylene carbon at δ 36.6 (C-3), two methine carbons at δ 77.1 (C-2), and 98.5 (C-1), one quaternary carbon at δ 93.6 (C-4), a conjugated carbonyl carbon at δ 198.0 (C-5), four oxygen bearing aromatic carbons at δ 145.6 (C-3'), 146.1 (C-3''), 146.8 (C-4'), and 151.6 (C-4''), six aromatic CH at δ 112.7 (C-2'), 115.2 (C-5''), 116.71 (C-6'), 116.73 (C-5'), 119.3 (C-2''), and 126.2 (C-6''), two aromatic quaternary carbons at δ 127.9 (C-1'), and 135.5 (C-1'') together with six carbons of one glucosyl moiety. The ¹H and ¹³C NMR spectra indicated the presence of a glucosyl moiety. The anomeric proton signal appeared as a doublet at δ 4.65 (d, J = 7.9 Hz) suggested a β-configured glucose unit. Acid hydrolysis of **1** with 2 mol L⁻¹ HBr under refluxing produced D-glucose as sugar residue determined by GC analysis. Incorporating ¹³C NMR chemical shifts it showed the presence of a β-D-glucosyl unit. All the carbons of the glucosyl moiety were assigned through direct ¹H-¹³C correlations in the HMQC spectrum and were situated between δ 62.6 and 79.6 except for that at the anomeric position, which was assigned to the signal at δ 94.1.

The ¹H, ¹H-COSY correlations (Figure 2) of H-1/H-2, and H-2/H-3 showed the connectivity C(1)-C(2)-C(3), which was further confirmed by HMBC correlations of H-1/C-3, H-3/C-1, H-2/C-3, and H-3/C-2. The HMBC correlations (Figure 2) of H-2/C-4 and H-3/C-4 showed the linkage of C-3 to C-4. The linkage of C-1 and C-4 to an O-atom was established by the HMBC correlations of H-1/C-4 and the low-field chemical shift of C-1 and C-4, at δ_C = 98.5 and 93.6, respectively (Table 1), thus, a tetrahydrofuran ring moiety was established. The benzoyl was established by the HMBC correlations H-2''/C-5, H-5''/C-5, and H-6''/C-5. The HMBC experiments showed the long-range couplings of H-2'/C-4, H-5'/C-4, H-6'/C-4, and H-3/C-5, which suggested that the phenyl and the benzoyl were connected with C-4, respectively. The long range ¹H-¹³C correlations of GlcH-1/C-2, H-2/GlcC-1, GlcH-2/C-1, and H-1/GlcC-2, confirmed that the fused glucosyl moiety was GlcH-1 ether-linked to C-2 and

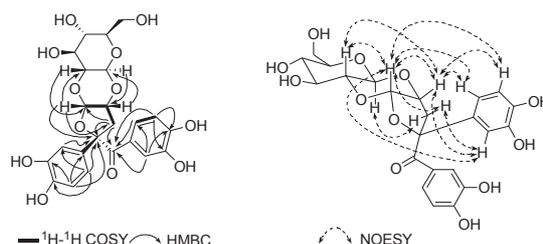


Figure 2. ¹H-¹H COSY, Key HMBC and NOESY correlations for **1**.

GlcH-2 to C-1.

NOESY correlations of H-1 with H-2, H-1 and H-2 with Glc. H-2, H-1 and H-2 with H-3a [δ 2.11 (*dd*, $J = 13.0, 8.7$)], and Glc. H-1 with H-3b [δ 3.56 (*dd*, $J = 12.9, 9.7$)] as shown in Figure 2, indicated the *cis* relationship of H-1, H-2, H-3a and the Glc. H-2. The NOESY spectrum also exhibited cross-peaks of H-3a with H-2', H-1 and H-2 with H-2', H-5' and H-6', respectively, but not between H-1, H-2, and H-3a with protons of the benzoyl, indicated the *cis* relationship of H-1, H-2, H-3a and the phenyl, and the *trans* relationship of H-1, H-2, and H-3a with the benzoyl. Incorporating the known stereochemistry of the β -D-glucosyl unit would require 1*R*, 2*S* and 4*R* stereochemistry in **1**. Therefore, the structure of **1** was deduced as a glucosyl-fused norlignan derivative, named capituloside B (Fig. 1).

Eight known compounds, curcapiocycloside (**2**),⁴ capituloside (**3**),³ breviscaside B (**4**),⁹ crassifogenin C (**5**),¹⁰ breviscapin A (**6**),¹¹ methyl-4-*O*-coumaroylquininate (**7**),¹² orcinol glucoside (**8**)^{13,14} and 2,6-dimethoxy-benzioc acid (**9**),² were also isolated from the Rhizomes of *C. capitulata*. Their structures were elucidated by spectral data and their comparison with literature values. Compounds **4-7** were isolated for the first time from this plant, and compound **7** was the first example isolated from the family.

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References

1. Lee, S. S.; Chang, W. L.; Chen, C. H. *Tetrahedron Lett.* **1996**, *37*, 4405.
2. Chang, W. L.; Lee, S. S. *Phytochemistry* **1998**, *49*, 2133.
3. Li, N.; Chen, J. J.; Zhao, Y. X.; Zhou, J. J. *Asian Nat. Prod. Res.* **2005**, *7*, 189.
4. Chang, W. L.; Chen, C. H.; Lee, S. S. *J. Nat. Prod.* **1999**, *62*, 734.
5. Chang, W. L.; Su, M. J.; Lee, S. S. *J. Nat. Prod.* **1997**, *60*, 76.
6. Cometa, M. F.; Palazzino, G.; Galeffi, C.; Palmery, M. *Il Farmaco* **2001**, *56*, 353.
7. Li, N.; Chen, J. J.; Zhou, J. J. *Asian Nat. Prod. Res.* **2005**, *7*, 279.
8. Wang, K. J.; Zhu, C. C.; Di, L.; Li, N.; Zhao, Y. X. *Fitoterapia* **2010**, *81*, 869.
9. Li, N.; Zhu, C. C.; Xiao, H. M.; Wang, K. J. *Fitoterapia* **2010**, *81*, 528.
10. Wang, K. J.; Li, N. *Arch. Pharm. Res.* **2008**, *31*, 1313.
11. Zhu, C. C.; Wang, K. J.; Wang, Z. Y.; Li, N. *Bull. Korean Chem. Soc.* **2010**, *31*, 224.
12. Liu, Y. Z.; Yi, C. R.; Feng, W. S.; Xie, J. X. *Chin. Tradit. Herbal. Drugs* **1989**, *20*, 9.
13. Xu, J. P.; Dong, Q. Y. *Chin. Tradit. Herbal. Drugs* **1986**, *17*, 8.
14. Wu, Q.; Fu, D. X.; Hou, A. J.; Lei, G. Q.; Liu, Z. J.; Chen, J. K.; Zhou, T. S. *Chem. Pharm. Bull.* **2005**, *53*, 1065.