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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-C_5-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, curcapicycloside (**2**),[4] capituloside (**3**),[5] breviscaside B (**4**),[9] crassifogenin C (**5**),[10] breviscapin A (**6**),[11] methyl-4-*O*-coumaroylquinate (**7**),[12] orcinol glucoside (**8**)[13,14] and 2,6-dimethoxy-benzioc acid (**9**),[2] from its rhizomes as shown in Figure 1. Their structures were established by spectroscopic analysis, especially using 2D-NMR techniques (^{1}H-^{1}H 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.

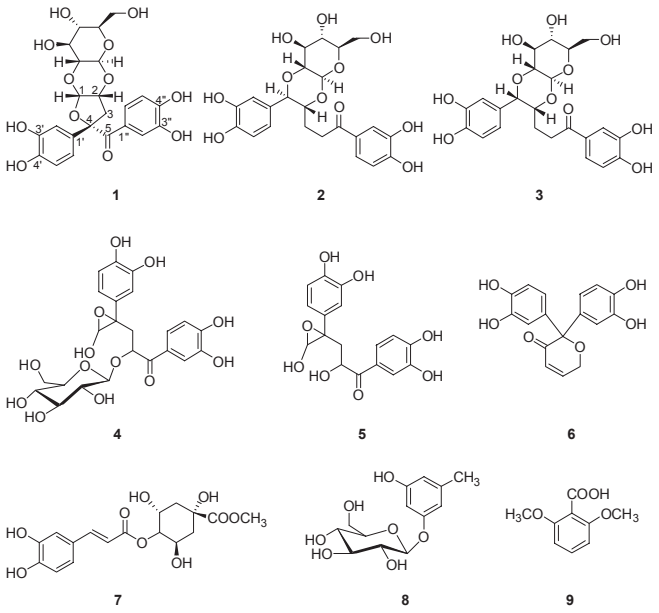

Figure 1. Structures of compounds **1**-**9**.

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 precoated plates (Qingdao Haiyang Chemical Co. Ltd.), and spots were detected by spraying with 5% H_2SO_4 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 H_2O 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-H_2O, 0:1-1:0) to yield two fractions (A_1 and A_2). Fraction A_1 was subjected to further separation on Sephadex LH-20 chromatography (EtOH-acetone, 1:1) and ODS (EtOH-H_2O, 0:1-1:0) to afford **4** (17 mg) and **5** (8 mg). Fraction A_2 was purified by Sephadex LH-20 chromatography (EtOH) and then ODS (EtOH-H_2O, 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-H_2O, 0:1-1:0) to

yield three fractions (B_1-B_3). Fraction B_1 was subjected on ODS (MeOH-H_2O, 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 B_3 by column chromatography on Sephadex LH-20 (EtOH-acetone, 1:1) and then ODS (MeOH-H_2O, 0:1-1:0). The fraction (3.8 g) eluted from 90% MeOH was subjected to chromatography on Sephadex LH-20 (MeOH-H_2O, 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 $CHCl_3$ and H_2O four times. The H_2O-souble fraction was evaporated to dryness. The dried sugar residue was diluted in 1 mL pyridine without water and treated with 0.5 mL trimethyl-chlorsilan (TMCS) and stirred at 60 °C for 5 min. After drying the solution with a stream of N_2, 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. $[\alpha]_D^{21} = -82.1$ (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). ^{1}H- and ^{13}C-NMR data see Table 1. HR-TOF-MS (negative mode): m/z 491.1178 $[M-H]^-$ (calcd. 491.1189 for $C_{23}H_{23}O_{12}$).

Curcapicycloside (2): White powder. ^{1}H-NMR (400 MHz, CD_3OD) 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'"); ^{13}C-NMR (100 MHz, CD_3OD) 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, ^{1}H-NMR (400 MHz, CD_3OD) 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'"); ^{13}C-NMR (100 MHz, CD_3OD) 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'), 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 $[M+H]^+$.

Table 1. ^{1}H-NMR and ^{13}C-NMR data of **1** (400 MHz, in CD_3OD, δ ppm, J in Hz)

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

[a]Values may be interchangeable.

Breviscaside B (4): White powder, ^{1}H-NMR (400 MHz, CD_3OD) 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'"); ^{13}C-NMR (100 MHz, CD_3OD) 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, ^{1}H-NMR (400 MHz, CD_3OD) 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"); ^{13}C-NMR (100 MHz, CD_3OD) 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, ^{1}H-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"); ^{13}C-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*-coumaroylquinate (7): White powder, ^{1}H-NMR (400 MHz, CD_3OD) 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'); ^{13}C-NMR (100 MHz, CD_3OD) 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), ^{1}H-NMR (400 MHz, CD_3OD) δ 2.11(3H, s, CH_3), 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); ^{13}C-NMR (100 MHz, CD_3OD) 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, CH_3); FAB-MS (-) *m/z* 285 $[M-H]^-$.

2,6-Dimethoxy-benzioc acid (9): Colorless needle (EtOH), ^{1}H-NMR (400 MHz, CD_3OD) 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); ^{13}C-NMR (100 MHz, CD_3OD) 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 $C_{23}H_{24}O_{12}$ 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 ^{13}C-NMR (DEPT) spectrum, which was supported by its HR-TOF MS observed at *m/z* 491.1178 $[M-H]^-$ (calcd. 491.1189 for $C_{23}H_{23}O_{12}$). 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 ^{13}C-NMR signal at δ_C 198.0 (Table 1). The ^{1}H 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 ^{1}H 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 ^{13}C 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 ^{1}H and ^{13}C 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 ^{13}C NMR chemical shifts it showed the presence of a β-D-glucosyl unit. All the carbons of the glucosyl moiety were assigned through direct ^{1}H-^{13}C 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 ^{1}H, ^{1}H-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 ^{1}H-^{13}C 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

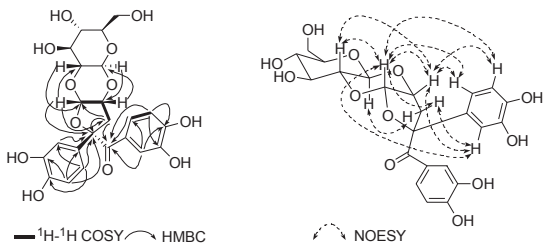

Figure 2. ^{1}H-^{1}H COSY, Key HMBC and NOESY correlations for **1**.

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, curcapicycloside (**2**),[4] capituloside (**3**),[3] breviscaside B (**4**),[9] crassifogenin C (**5**),[10] breviscapin A (**6**),[11] methyl-4-*O*-coumaroylquinate (**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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