

Curculigoside C, a New Phenolic Glucoside from Rhizomes of *Curculigo orchioides*

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Abstract: A new phenolic glucoside, curculigoside C (**3**), was isolated from the rhizomes of *Curculigo orchioides* Gaertn., together with three known compounds, curculigoside (**1**), curculigoside B (**2**), and 2,6-dimethoxyl benzoic acid (**4**). The structure of the new compound (**3**) was elucidated as 5-hydroxy-2-O- β -D-glucopyranosyl benzyl-3'-hydroxy-2', 6'-dimethoxybenzoate by using spectroscopic methods.

Key words: *Curculigo orchioides*; Hypoxidaceae; rhizomes; phenolic glucoside

Curculigo orchioides is a tiny herbal plant widely distributed in China, India, Malaya, Japan and Australia. Its rhizomes having the properties of warming kidney, invigorating yang, expelling cold and eliminating dampness are used as traditional Chinese medicine "Xianmao" to cure impotence, enuresis, cold sperm, cold pain of back and knee, and numbness of the limb (Liu, 2001). In India, the tuberous roots of this plant are considered to be tonic, alterative, demulcent, diuretic, and restorative, and are used as a poultice for itch and skin diseases (Shri *et al.*, 1989). Previous phytochemical investigations on the rhizomes of this species revealed the presence of curculigoside (Li *et al.*, 2003), curculigoside B (Xu and Xu, 1992a), orcinol glycosides (Li *et al.*, 2003), 2,6-dimethoxyl benzoic acid (Chen *et al.*, 1999), curculigines A–C (Chen *et al.*, 1999), curculigol (Triguna *et al.*, 1990), curculigosaponins A–M (Xu and Xu, 1992b), 2,3,4,7-tetramethoxyxanthone, 1,3,7-trimethylxanthine, daucosterol (Li *et al.*, 2003), and aliphatic long-chain ketones (Triguna *et al.*, 1984). In the current study, a new phenolic glucoside, curculigoside C (**3**), together with three known compounds, curculigoside (**1**), curculigoside B (**2**) and 2,6-dimethoxyl benzoic acid (**4**), was isolated. The structure of curculigoside C was elucidated on the basis of spectral data.

1 Results and Discussion

Compound **3**, colorless needles, had a molecular formula of $C_{22}H_{26}O_{12}$ as established by its ESI-MS and NMR data. The IR spectrum resembled those of compounds **1** and **2**, showing absorptions for hydroxyl groups, an ester carbonyl group, and aromatic rings. The 1H -NMR spectrum showed proton signals for two phenolic hydroxyl groups at δ 9.19 and 9.06 (each 1H, s, D_2O -exchangeable),

an oxygenated methylene group at δ 5.33 (2H, s), two methoxyl groups at δ 3.71 and 3.70 (each 3H, s), and an anomeric proton of the glucose moiety at δ 4.63 (1H, d, $J = 6.6$ Hz). The configuration at C-1'' of the sugar moiety was determined to be β -oriented as judged by the coupling constant of H-1''. Moreover, three aromatic proton signals at δ 6.99 (1H, d, $J = 8.8$ Hz), 6.82 (1H, d, $J = 2.3$ Hz), and 6.65 (1H, dd, $J = 2.3, 8.8$ Hz) assignable to the A ring and two aromatic doublets at δ 6.88 (1H, d, $J = 8.9$ Hz) and 6.67 (1H, d, $J = 8.9$ Hz) attributable to the B ring were also observed. The ^{13}C -NMR spectrum resolved 22 carbon signals, corresponding to a benzylbenzoate skeleton bearing two methoxyl groups and the β -glucose moiety. By comparing the NMR spectral data of compounds **1**, **2** and **3** (Tables 1 and 2), it could be inferred that compounds **1–3** had the same substitution pattern in the A ring, and compound **3** attached one more hydroxyl group at C-3' in the B ring than compound **1** (Fig. 1).

On the basis of HMQC, HMBC and NOESY spectral analysis, the structure of compound **3** was further determined, and all the proton and carbon signals were fully assigned. In the HMBC spectrum, the proton at δ 4.63 (1H, d, $J = 6.6$ Hz, H-1'') coupled with C-2 (δ 147.6), and the hydroxyl group at δ 9.06 correlated with C-4 (δ 114.9), C-5 (δ 152.3), and C-6 (δ 114.6), suggesting that the β -glucose moiety and the hydroxyl group were located at C-2 and C-5, respectively (Fig. 2). The hydroxyl and methoxyl groups in the B ring were also assigned by the HMBC correlations. The linkage of two aromatic parts was verified by the HMBC cross peaks of H₂-7 at δ 5.33 (2H, s) with C-2, C-6, and C-7' (δ 165.3). The structure of compound **3** was also confirmed by the NOESY experiment (Fig. 3). Compound **3** was therefore elucidated as 5-hydroxy-2-O- β -D-glucopyranosyl

Table 2 ^{13}C -NMR assignments for compounds **1–3** (in DM SO-d_6)

Position	1	2	3
1	127.7	127.4	126.5
2	147.9*	148.0*	147.6
3	117.7	117.8	117.2
4	115.2	115.2	114.9
5	152.8*	152.7*	152.3
6	114.9	114.9	114.6
7	61.8	61.3	61.5
1'	104.8	102.7	118.7
2'	157.1	156.1	144.6
3'	113.2	111.4	143.8
4'	131.7	131.7	117.6
5'	113.2	109.0	107.3
6'	157.1	157.9	148.5
7'	165.9	166.6	165.3
2' (OCH ₃)	56.3		60.5
6' (OCH ₃)	56.3	56.2	56.1
1''	103.1	103.1	102.5
2''	73.8	73.8	73.3
3''	77.5	77.4	77.0
4''	70.3	70.3	69.8
5''	77.0	76.9	76.5
6''	61.4	61.7	60.8

*, the assignments for the C-2 and C-5 of compounds **1** and **2** were reversed in the literature (Xu and Xu, 1992a; Li *et al.*, 2003), and were revised in this paper.

gel column developed with CH_3Cl -MeOH (10:1, 9:1, 8:1, 7:1, 6:1, 5:1 and 4:1) to give seven fractions (G_1 - G_7). Each fraction was purified repeatedly by column chromatography over Sephadex LH-20 eluted with aqueous MeOH to afford compounds **1** (1.8g), **2** (40mg), **3** (20mg) and **4** (800 mg).

2.4 Identification

Compound 1 Colorless needles (MeOH), $\text{C}_{22}\text{H}_{26}\text{O}_{11}$, mp 159–161 °C. IR (KBr) $\nu_{\text{max}} \text{ cm}^{-1}$: 3370 (OH), 2922, 1724 (ester), 1598 (aromatic ring). ESI-MS m/z : 484 $[\text{M}+\text{NH}_4]^+$, 489 $[\text{M}+\text{Na}]^+$. See Tables 1 and 2 for ^1H -NMR and ^{13}C -NMR data.

Compound 2 Colorless needles (MeOH), $\text{C}_{21}\text{H}_{24}\text{O}_{11}$, mp 210–211 °C. IR (KBr) $\nu_{\text{max}} \text{ cm}^{-1}$: 3375 (OH), 2920, 1724 (ester), 1598 (aromatic ring). ESI-MS m/z : 470 $[\text{M}+\text{NH}_4]^+$,

475 $[\text{M}+\text{Na}]^+$. See Tables 1 and 2 for ^1H -NMR and ^{13}C -NMR data.

Compound 3 Colorless needles (MeOH), $\text{C}_{22}\text{H}_{26}\text{O}_{12}$, mp 107–108 °C. IR (KBr) $\nu_{\text{max}} \text{ cm}^{-1}$: 3380 (OH), 2923, 1724 (ester), 1598 (aromatic ring). ESI-MS m/z : 500 $[\text{M}+\text{NH}_4]^+$, 505 $[\text{M}+\text{Na}]^+$. See Tables 1 and 2 for ^1H -NMR and ^{13}C -NMR data.

Compound 4 Colorless needles (MeOH), $\text{C}_9\text{H}_{10}\text{O}_4$. ESI-MS m/z : 183 $[\text{M}+\text{H}]^+$. ^1H -NMR δ (in DMSO-d_6): 3.75 (6H, s, 2 \times OCH₃), 6.68 (2H, d, $J = 8.4$ Hz, H-3, 5), 7.30 (1H, t, $J = 8.4$ Hz, H-4), 12.88 (1H, br s, COOH). ^{13}C -NMR δ (in DMSO-d_6): 116.9 (C-1), 156.9 (C-2, 6), 104.9 (C-3, 5), 131.2 (C-4), 168.7 (COOH), 56.5 (OCH₃).

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