大叶仙茅中一个新的木脂素苷

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摘要:从采自云南西双版纳的大叶仙茅 (Curculigo capitulata) 中分离得到一个新的木脂素苷和 8 个已知化合物,通过光谱方法、化学方法和与参考文献比较(质谱,氢谱和碳谱)的方法鉴定了它们的结构。其中化合物 2~7 为首次从该植物中分离得到。

关键词: 仙茅; 仙茅科; 木质素苷

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A New Lignan Glycoside from Curculigo capitulata

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Abstract: A new lignan glycoside, 4, 4'-dimethoxy-3'-hydroxy-7, 9':7', 9-diepoxylignan-3-O- β -D-glucopyranoside (1), was isolated from the rhizomes of *Curculigo capitulata*, along with eight known compounds (2-9). Their structures were elucidated by spectroscopic and chemical methods and by comparison of their spectral data (MS, 1 H and 13 C) with those reported in the literature. Compounds 2-7 have been obtained from this plant for the first time.

Key words: Curculigo capitulata; Hypoxidaceae; Lignan glycoside

The isolation and identification of some constituents from the rhizomes of *Curculigo capitulata* (Lour.) Ktze have been reported previously (Lee et al, 1996; Chang et al, 1998). In this paper, we wish to report the isolation and structural elucidation of a new lignan glycoside, 4, 4'-dimethoxy-3'-hydroxy-7, 9':7', 9-diepoxylignan-3-O- β -D-glucopyranoside (1), as well as eight known compounds, including 5-hydroxy-2-O- β -D-glucopyranosylbenzyl-2', 6'-dimethoxy benzoate (2) (Kubo et al, 1983; Chen et al, 1999), Orcinol glucoside (3) (Chen et al, 1999), 4', 5, 7-trihydroxy-flavone (4) (Ternai et al, 1976), 3, 5-dihydroxytoluene (5), 6, 15 α -epoxy-1 β , 4 β -dihydroxy eudesmane (6) (Nianbai et al, 1988), 3-(4-hydroxy-3-methoxy-phenyl)-propenal (7) (Heba et al, 1987), daucosterol (8) (Mei et al, 2001) and 4-ethoxy-3-hydroxymethylphenol (9) (Lee et al, 1996; Chang et al, 1998) (Fig. 1).

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Fig. 1 Structure of compounds 1-9

Compound 1 was obtained as white amorphous powder and had a molecular formula of C26 H32 O11 (HRFAB-MS m/z $[M-1]^-$ 519.1877, calcd. 519.1866). According to the UV absorption at λ 279, 228 and 208 nm, and IR absorption at v 1615 and 1515 cm⁻¹, it was evident that compound 1 was an aromatic compound. Inspection of FAB-MS and NMR spectra suggested that compound 1 possessed two phenyl groups, two methylenes, four methines, two methoxys and one glucose unit. HMQC and ¹H - ¹H COSY spectra revealed the presence of the two fragments of -CH₂CHCH - (C - 9 to C-7 and C-9' to C-7'). Analysis of HMBC spectrum (Fig. 2) indicated that compound 1 was a lignan glycoside with a basic skeleton of 7, 9':7', 9-diepoxylignan and had a glucose unit at C-3. Two methoxys were located at C-4 and C-4' of the phenyl groups. On acetylation, the acetate of 1 was subjected to FAB-MS analysis, and showed ion at $m/z 519 + 5 \times 42$ ($[M-1]^- + 5Ac$) (729), which indicated the presence of one free hydroxy group linked with aromatic ring. NMR, HMQC and HMBC spectra showed that C-3' of phenyl group was a quaternary carbon signal at $\delta 147.4$, which revealed the hydroxy group located at C-3'. The stereochemical configuration of compound 1 was verified by a NOESY experiment. The correlations only between H-8 and H-9, H-8' and H-9, H-8 and H-9' and H-8' and H-9' were observed (Fig. 2), but not observed between H-7 and H-8, H-7 and H-8', H-7' and H-8, and H-7' and H-8'. The stereochemical configuration of compound 1 was also verified by the literature (Chiba et al, 1980). In the literature, 13 C

Fig. 2 Key HMBC correlations of compound 1

NMR data, which were sensitive to the stereochemistry of lignan glycoside, were analysed. Thus we determined that H-7 and H-7' were at β orientation and H-8 and H-8' were at α orientation. Therefore, the chemical structure of compound 1 was deduced as 4, 4'-dimethoxy-3'-hydroxy-7, 9':7', 9-diepoxylignan-3-O- β -D-glucopyrano side, which was new according to the literatures we had researched.

Experimental section

General Experimental Procedures $[\alpha]_D$ was carried out on JASCO-20. IR spectra was recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectra was recorded on a UV 210A spectrometer. 1D-and 2D-NMR spectra were run on Bruker AM-400 and DRX-500 instruments with TMS as internal standard. The MS data were recorded on a VG Auto Spec-3000 spectrometer. TLC was carried on silica gel G (MEIJING) precoated plates. Spots were detected by spraying 5% sulfuric acid-ethanol solution followed by heating.

Plant Material Rhizomes of *C. capitulata* were collected from Xishuangbanna Botanical Garden and identified by Prof. Zhou Jun of Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen was deposited in the State Key Laboratory of Phytochemistry and Plant Resources, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation The air-dried and powered rhizomes of C. captulata (3 kg) were extracted with 85% EtOH (3 × 20 L) at room temperature, the combined extracts were evaporated in vacuo. The residue was suspended in H_2 0 and then passed on D101 resin column, in which the column was eluted with 95% EtOH. The EtOH eluent solution was concentrated in vacuo to give a residue (240 g), which was chromatographed on silica gel column (200 – 300 mesh) with CHCl₃-MeOH (7:2) to give 8 fractions. Fractions 1 (10.0 g) and 2 (8.2 g) were chromatographed on silica gel column developed with petroleum-ether/chloroform and petroleum-ether/acetone repeatedly and finally afforded compounds 4 (12 mg), 5 (8 mg), 6 (4 mg), 7 (14 mg), 8 (20 mg) and 9 (13 mg), respectively. Fractions 3 (27.5 g), 4 (9.1 g) and 5 (7.8 g) were subjected to column chromatography and medium pressure column on silica gel with chloroform/acetone and chloroform/methanol as eluent repeatedly to afford compounds 1 (14 mg), 2 (15 mg) and 3 (710 mg).

Acid Hydrolysis of 1 Compound 1 was dotted on the silica gel G plate, placed and hanged in a sealed glass vessel with about 1 ml concentrated HCl at 70° C for an hour for hydrolysis, cooled for a few minutes, the plate was taken out, and the HCl was volatilized with a ventilator. Authentic sugars were dotted to the plate, then the plate was developed with n-butanol-pyridine-water (6:4:3), and 5% sulfuric acid-ethanol solution as spray reagent followed by heating at 120° C. From compound 1 glucose was detected, R_f : glucose 0.40.

Acetylation of 1 Saponin (1 mg) was dissolved in Ac_2 O-pyridine (1:0.5) in a sealed micro-tube. After reacting at 60-70 °C for 6 h, the saponin acetate was subjected to FAB-MS analysis.

4, 4'-dimethoxy-3'-hydroxy-7, 9': 7', 9-diepoxylignan-3-O-β-D-glucopyranoside (1) C_{26} H₃₂ O₁₁, white amorphous powder, $[\alpha]_D^{21} - 54.69^\circ$ (c 0.06, MeOH); IR ν_{max}^{KBr} 3436, 2929, 1615, 1272, 1073 cm⁻¹; UV λ_{max}^{MeOH} 208 (7.64 × 10⁴), 228 (3.39 × 10⁴), 279 (1.26 × 10⁴) nm. ¹H NMR (500 MHz, CD₃ OD) δ: 6.92 (1H, d, J = 1.75 Hz, H - 2), 6.84 (1H, d, J = 1.75 Hz, H - 2'), 7.03 (1H, d, J = 8.35 Hz, H - 5), 6.66 (1H, d, J = 8.35 Hz, H

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-5'), 6.80 (1H, dd, J=1.75, 8.35 Hz, H-6), 6.70 (1H, dd, J=1.75, 8.35 Hz, H-6'), 4.64 (1H, d, J=3.10 Hz, H-7), 4.59 (1H, d, J=4.35 Hz, H-7'), 3.01 (1H, m, H-8), 3.01 (1H, m, H-8'), 4.12 (2H, m, H-9), 3.75 (2H, m, H-9'), 3.76 (3H, s, CH₃O-4), 3.74 (3H, s, CH₃O-4'), 4.74 (1H, d, J=6.00 Hz, Glc. H-1), 3.20-3.40 (4H, m, Glc. H-2-5), 3.58 (1H, m, Glc. H-6a), 3.75 (1H, m, Glc. H-6b); the data of ¹³C NMR (125 MHz, CD₃OD) are shown in Table 1. FAB-MS m/z: 519 [M-1]⁻, 357 [M-Glc]⁻.

Table 1 ¹³C NMR spectral data of compound 1 (CD₃OD, 125 MHz)

	¹³ C NMR		¹³ C NMR
1	137.5s	8*	55.5d
1'	133.8s	8′*	55.3d
2	111.7d	9	72.7t
2'	111.0d	9′	72.7t
3	147.5s	4-0CH ₃	56.8q
3′	147.4s	4'-OCH ₃	56.4q
4	151.0s		_
4′	149.1s	Glucose	
5	118.0d	1	102.8d
5′	116.1d	2	74.9d
6	119.8d	3	77.8d
6′	120.0d	4	71.3d
7	87.0d	5	78.2d
7'	87.5d	6	62.5t

^{*} data are changed.

5-hydroxy-2-O-β-D-glucopyranosylbenzyl -2', 6'-dimethoxybenzoate (curculigoside I) (2) $C_{22} H_{26} O_{11}$, colorless needles (MeOH), mp 158 – 160°C, FAB+ MS m/z: 467 [M+1]+, 305 [M-glc]+; ¹H NMR (500 MHz, CD₃OD) δ: 6.97 (1H, d, J=8.85 Hz, H-3), 6.59 (1H, dd, J=3.05, 8.85 Hz, H-4), 6.82 (1H, d, J=3.05 Hz, H-6), 6.56 (2H, d, J=8.55 Hz, H-3' and H-5'), 7.23 (1H, t, J=8.55 Hz, H-4'), 3.70 (6H, s, OCH₃ × 2), 5.36 (1H, ABd, J=13.45 Hz, phCH₂O-Ha), 5.29 (1H, ABd, J=13.40 Hz, phCH₂O-Hb), 4.65 (1H, d, J=7.30 Hz, H-1"), 3.36 (1H, m, H-2"), 3.37 (1H, m, H-3"), 3.20 (1H, m, H-4"), 3.27 (1H, m, H-5"), 3.60 (1H, dd, J=5.00, 12.20 Hz, Ha-6"), 3.77 (1H, dd, J=2.15, 12.25 Hz, Hb-6"); ¹³ C NMR (125 MHz,

CD₃ OD) δ : 128.8 (s, C-1), 153.9 (s, C-2), 118.9 (d, C-3), 116.2 (d, C-4), 149.6 (s, C-5), 116.3 (d, C-6), 56.5 (q, OCH₃ × 2), 63.2 (t, phCH₂O-), 168.5 (s, C=O), 114.2 (s, C-1'), 158.7 (s, C-2'), 105.1 (d, C-3'), 132.6 (d, C-4'), 105.1 (d, C-5'), 158.7 (s, C-6'), 104.3 (d, C-1"), 75.0 (d, C-2"), 78.1 (d, C-3"), 71.4 (d, C-4"), 78.0 (d, C-5"), 62.6 (t, C-6").

orcinol glucoside (3) $C_{13}H_{18}O_7$, colorless needles (MeOH), mp 132-133 °C, FAB-MS m/z: 285 [M - 1]⁻, 123 [M - glc]⁻; ¹H NMR (400 MHz, CD₃OD) δ : 2.11 (3H, s, CH₃), 6.32 (1H, S, H - 2), 6.27 (1H, s, H - 4), 6.19 (1H, s, H - 6), 4.74 (1H, d, J = 7.28 Hz, H - 1'), 3.20 - 3.36 (4H, m, glc. H), 3.61 (1H, dd, J = 4.80, 12.08 Hz, Ha - 6'), 3.79 (1H, dd, J = 1.48, 12.08 Hz, Hb - 6'), 10.09 (1H, brs, C₃-OH). ¹³C NMR (100 MHz, CD₃OD) δ : 160.4 (s, C - 1), 102.6 (d, C - 2), 159.6 (s, C - 3), 110.1 (d, C - 4), 141.6 (s, C - 5), 111.6 (d, C - 6), 102.5 (d, C - 1'), 75.3 (d, C - 2'), 78.4 (d, C - 3'), 71.7 (d, C - 4'), 78.3 (d, C - 5'), 62.9 (t, C - 6'), 22.1 (q, CH₃).

- 4′, 5, 7-trihydroxyflavone (4) $C_{15}H_{10}O_5$, EI-MS m/z: 270 [M]⁺. ¹H NMR (400 MHz, C_5D_5N) δ : 6.15 (1H, d, J=2.00 Hz, H-6), 6.34 (1H, s, H-3), 6.50 (1H, d, J=2.00 Hz, H-8), 6.82 (2H, d, J=8.80 Hz, H-3′ and H-5′), 7.75 (2H, d, J=8.80 Hz, H-2′ and H-6′); ¹³ C NMR (100 MHz, C_5D_5N) δ : 166.1 (s, C-2), 104.1 (d, C-3), 183.0 (s, C-4), 158.7 (s, C-5), 100.2 (d, C-6), 164.8 (s, C-7), 95.1 (d, C-8), 163.4 (s, C-9), 105.2 (s, C-10), 122.5 (s, C-1′), 129.1 (d, C-2′), 117.1 (d, C-3′), 162.9 (s, C-4′), 117.1 (d, C-5′), 129.1 (d, C-6′).
- 3, 5-dihydroxytoluene (orcinol)(5) $C_7H_8O_2$, EI-MS m/z: 124 [M]⁺. ¹H NMR (400 MHz, Me₂CO-d₆) δ : 3.09 (3H, s, H-7), 6.05 (2H, s, H-2, H-6), 8.03 (1H, s, H-4); ¹³C NMR (100 MHz, Me₂CO-d₆) δ : 140.5 (s, C-1), 108.3 (d, C-2, C-6), 159.3 (s, C-3, C-5), 100.6 (d, C-4), 21.5 (q, C-7).
- 6, 15 α -epoxy-1 β , 4 β -dihydroxyeudesmane (6) $C_{15} H_{26} O_3$, EI-MS m/z: 254 [M]⁺. ¹H NMR (400 MHz, CDCl₃) δ : 0.90 (3H, d, J=7.04 Hz, H-13), 0.96 (3H, d, J=7.04 Hz, H-12), 1.03 (3H, s, H

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 $\begin{array}{l} -14),\ 1.18\ (1H,\ d,\ J=12.08\ Hz,\ H-5),\ 1.23\ (1H,\ m,\ H-7),\ 1.77\ (1H,\ m,\ Ha-2),\ 1.94\ (1H,\ m,\ Hb-2),\ 3.37\ (1H,\ dd,\ J=4.28,\ 11.04\ Hz,\ H-1),\ 3.61\ (1H,\ d,\ J=9.32\ Hz,\ Ha-15),\ 3.72\ (1H,\ d,\ J=9.32\ Hz,\ Hb-15),\ 3.73\ (1H,\ dd,\ J=2.28,\ 12.08\ Hz,\ H-6);\ ^{13}\ C\ NMR\ (100\ MHz,\ CDCl_3)\ \delta;\ 80.5\ (d,\ C-1),\ 28.0\ (t,\ C-2),\ 39.7\ (t,\ C-3),\ 77.2\ (s,\ C-4),\ 57.5\ (d,\ C-5),\ 75.6\ (d,\ C-6),\ 51.1\ (d,\ C-7),\ 22.2\ (t,\ C-8),\ 33.2\ (t,\ C-9),\ 39.1\ (s,\ C-10),\ 29.5\ (d,\ C-11),\ 18.5\ (q,\ C-12),\ 20.7\ (q,\ C-13),\ 12.8\ (q,\ C-14),\ 80.4\ (t,\ C-15).\ EI-MS\ m/z\ (\%);\ 254\ [M]^+\ (15.1),\ 239\ [M-Me]^+\ (6.2),\ 236\ [M-H_2O]^+\ (3.9),\ 222\ [M-MeOH]^+\ (43.6),\ 209\ (18.7),\ 206\ (25.2),\ 180\ (36.0),\ 81\ (100). \end{array}$

3-(4-hydroxy-3-methoxy-phenyl)-propenal (7) C_{10} H_{10} O_3 , EI-MS m/z: 178 [M]⁺. ¹H NMR (400 MHz, Me₂CO-d₆) δ : 3.05 (3H, s, OMe), 5.78 (1H, dd, J=7.80, 15.60 Hz, H-2), 6.03 (1H, dd, J=2.85, 8.04 Hz, H-6'), 6.32 (1H, d, J=8.00 Hz, H-5'), 6.68 (1H, d, J=2.85 Hz, H-2'), 7.20 (1H, d, J=15.60 Hz, H-1), 8.76 (1H, d, J=7.80 Hz, H-3); ¹³ C NMR (100 MHz, Me₂CO-d₆) δ : 154.0 (d, C-1), 116.2 (d, C-2), 193.8 (d, C-3), 127.3 (s, C-1'), 116.7 (d, C-2'), 148.7 (s, C-3'), 150.9 (s, C-4'), 111.5 (d, C-5'), 127.0 (d, C-6'), 56.3 (q, OMe). EI-MS m/z (%): 178 (100), 167 (62), 149 (80), 137 (72), 119 (38), 107 (67), 91 (41).

daucosterol (8) C_{35} H₆₀ O₆, white amorphous powder. FAB⁻-MS m/z: 576 [M]⁻, EI-MS m/z (%): 414 [M-162]⁺ (5), 396 (100), 382 (27), 231 (10), 187 (7), 147 (24).

4-ethoxy-3-hydroxymethylphenol (9) $C_9H_{12}O_3$, EI-MS m/z: 168 [M]⁺. ¹H NMR (400 MHz, Me₂CO-d₆) δ: 1.14 (3H, t, J=7.04 Hz, H-9), 3.01 (2H, s, H-7), 3.49 (2H, q, J=7.04 Hz, H-8), 6.53 (1H, dd, J=3.02, 8.50 Hz, H-6), 6.60 (1H, d, J=8.50 Hz, H-5), 6.70 (1H, d, J=3.02 Hz, H-2), 7.62 (1H, br s, C₇OH), 7.72 (1H, br s, C₁-OH); ¹³C NMR (100 MHz, Me₂CO-d₆) δ: 148.7 (s, C-1), 115.3 (d, C-2), 126.3 (s, C-3), 151.1 (s, C-4), 115.7 (d, C-5), 116.5 (d, C-6), 69.0 (t, C-7), 66.3 (t, C-8), 15.5 (q, C-9).

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