

## 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; 木脂素苷

**中图分类号:** Q 946 **文献标识码:** A **文章编号:** 0253-2700(2003)06-0711-05

## 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-diepoxylicignan-3-O- $\beta$ -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,  $^1\text{H}$  and  $^{13}\text{C}$ ) 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-diepoxylicignan-3-O- $\beta$ -D-glucopyranoside (**1**), as well as eight known compounds, including 5-hydroxy-2-O- $\beta$ -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 $\alpha$ -epoxy-1 $\beta$ , 4 $\beta$ -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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收稿日期: 2003-07-23, 2003-07-30 接受发表

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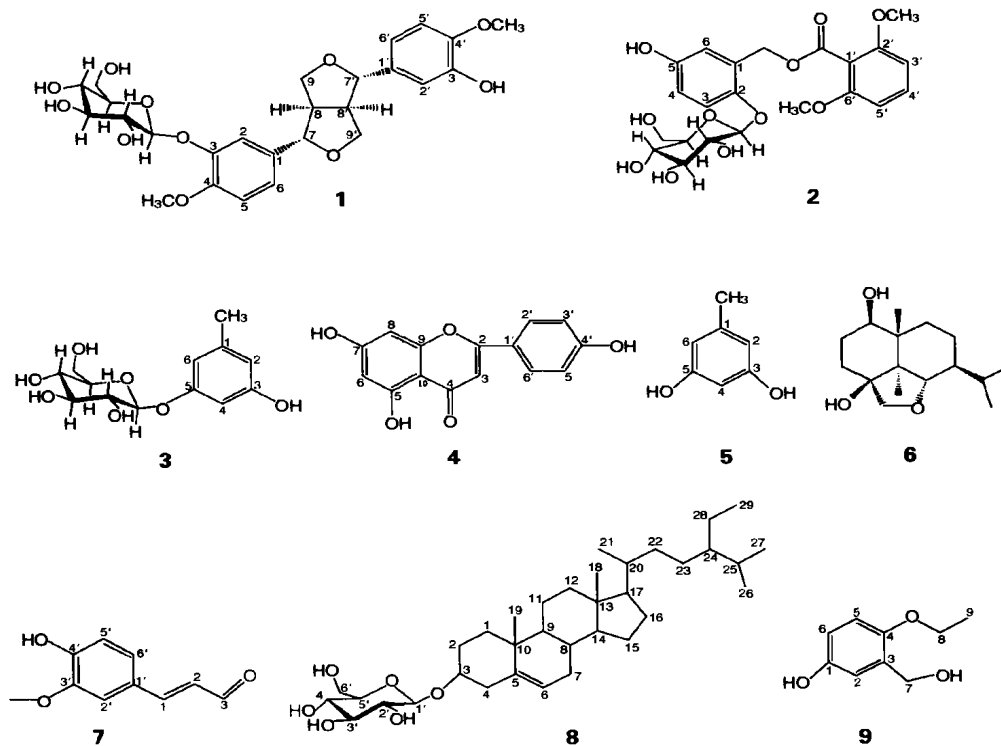


Fig. 1 Structure of compounds 1-9

Compound 1 was obtained as white amorphous powder and had a molecular formula of  $C_{26}H_{32}O_{11}$  (HRFAB-MS  $m/z$   $[M-1]^-$  519.1877, calcd. 519.1866). According to the UV absorption at  $\lambda$  279, 228 and 208 nm, and IR absorption at  $\nu$  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  $-CH_2CHCH-$  (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-diepoxy lignan 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 configura-



-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, CH<sub>3</sub>O-4), 3.74 (3H, s, CH<sub>3</sub>O-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 <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD) are shown in Table 1. FAB-MS  $m/z$ : 519 [M-1]<sup>-</sup>, 357 [M-Glc]<sup>-</sup>.

Table 1 <sup>13</sup>C NMR spectral data of compound

1 (CD <sub>3</sub> OD, 125 MHz)			
<sup>13</sup> C NMR		<sup>13</sup> 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-OCH <sub>3</sub>	56.8q
3'	147.4s	4'-OCH <sub>3</sub>	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.

CD<sub>3</sub>OD)  $\delta$ : 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, OCH<sub>3</sub>  $\times$  2), 63.2 (t, phCH<sub>2</sub>O-), 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<sub>13</sub>H<sub>18</sub>O<sub>7</sub>, colorless needles (MeOH), mp 132-133°C, FAB-MS  $m/z$ : 285 [M-1]<sup>-</sup>, 123 [M-glc]<sup>-</sup>; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$ : 2.11 (3H, s, CH<sub>3</sub>), 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, C<sub>3</sub>-OH). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$ : 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, CH<sub>3</sub>).

**4', 5, 7-trihydroxyflavone (4)** C<sub>15</sub>H<sub>10</sub>O<sub>5</sub>, EI-MS  $m/z$ : 270 [M]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ : 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'); <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ : 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<sub>7</sub>H<sub>8</sub>O<sub>2</sub>, EI-MS  $m/z$ : 124 [M]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, Me<sub>2</sub>CO-d<sub>6</sub>)  $\delta$ : 3.09 (3H, s, H-7), 6.05 (2H, s, H-2, H-6), 8.03 (1H, s, H-4); <sup>13</sup>C NMR (100 MHz, Me<sub>2</sub>CO-d<sub>6</sub>)  $\delta$ : 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 $\alpha$ -epoxy-1 $\beta$ , 4 $\beta$ -dihydroxyeudesmane (6)** C<sub>15</sub>H<sub>26</sub>O<sub>3</sub>, EI-MS  $m/z$ : 254 [M]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 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

-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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 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  $[\text{M}]^+$  (15.1), 239  $[\text{M}-\text{Me}]^+$  (6.2), 236  $[\text{M}-\text{H}_2\text{O}]^+$  (3.9), 222  $[\text{M}-\text{MeOH}]^+$  (43.6), 209 (18.7), 206 (25.2), 180 (36.0), 81 (100).

**3-(4-hydroxy-3-methoxy-phenyl)-propenal (7)**  $\text{C}_{10}\text{H}_{10}\text{O}_3$ , EI-MS  $m/z$ : 178  $[\text{M}]^+$ .  $^1\text{H}$  NMR (400 MHz,  $\text{Me}_2\text{CO}-d_6$ )  $\delta$ : 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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{Me}_2\text{CO}-d_6$ )  $\delta$ : 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)**  $\text{C}_{35}\text{H}_{60}\text{O}_6$ , white amorphous powder. FAB $^-$ -MS  $m/z$ : 576  $[\text{M}]^-$ , EI-MS  $m/z$  (%): 414  $[\text{M}-162]^+$  (5), 396 (100), 382 (27), 231 (10), 187 (7), 147 (24).

**4-ethoxy-3-hydroxymethylphenol (9)**  $\text{C}_9\text{H}_{12}\text{O}_3$ , EI-MS  $m/z$ : 168  $[\text{M}]^+$ .  $^1\text{H}$  NMR (400 MHz,  $\text{Me}_2\text{CO}-d_6$ )  $\delta$ : 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, C $_7$ -OH), 7.72 (1H, br s, C $_1$ -OH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{Me}_2\text{CO}-d_6$ )  $\delta$ : 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).

**Acknowledgements:** The authors are grateful to the staffs of the analytical group at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences for their measuring spectral data.

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