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# 中华青荚叶的一个新环烯醚萜甙*

来国防[1,2], 王易芬[1], 王 梅[2], 罗士德[1]
(1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室, 云南 昆明 650204;
2 云南省药物研究所, 云南 昆明 650011)

**摘要**: 从山茱萸科中华青荚叶 (*Helwingia chinensis*) 的乙酸乙酯部份分离得到一个新环烯醚萜和三个已知环烯醚萜化合物, 通过现代波谱技术, 确定其结构为 10-*O*-trans-cinnamoyl oleoside (**1**), 10-hydroxyoleoside 11-methyl ester (**2**), jasminoside (**3**) and 10-hydroxyoleuropein (**4**)。

**关键词**: 中华青荚叶; 山茱萸科; 环烯醚萜甙
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# A New Secoiridoid Glycoside from *Helwingia chinensis* (Cornaceae)

LAI Guo-Fang[1,2], WANG Yi-Fen[1], WANG Mei[2], LUO Shi-De[1]
(1 *State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences*, Kunming 650204, China; 2 *Yunnan Institute for Food and Drug Control*, Kunming 650011, China)

**Abstract**: A new secoiridoid glycoside, together with tree secoiridoid glycosides were isolated from the AcOEt fraction of the aerial part of *Helwingia chinensis*. Their structures were elucidated to be 10-*O*-trans-cinnamoyl oleoside (**1**), 10-hydroxyoleoside 11-methyl ester (**2**), jasminoside (**3**) and 10-hydroxyoleuropein (**4**) by detailed spectroscopic analysis.
**Key words**: *Helwingia chinensis*; Cornaceae; Iridoid glycoside; Oleoside

*Helwingia chinensis* Batal (Cornaceae) is distributed in the western and southern regions of China. The aerial part of this plant has long been used to treat dysentery, hematochezia, swelling, etc (Wu *et al*, 1990). Our previous investigation of the plant reported the isolation and characterization of three new triterpenoids (Lai *et al*, 2003). In continuation of our work on this genus, a new secoiridoid glycoside (10-*O*-trans-cinnamoyl oleoside, **1**) and three know secoiridoid glycosides (10-hydroxyoleoside 11-methyl ester, jasminoside and 10-hydroxyoleuropein, **2**-**4**) (Shen *et al*, 1990; Kenichiro *et al*, 1982) were obtained from *H. chinensis*. In this paper, we describe the structures elucidation by various NMR spectra analysis.

## Results and Discussion

Compound **1**, white powder, $[\alpha]_D^{20}$ - 246 (*c* 0.50, $CHCl_3$), showed a molecular ion peak at *m/z* 535 $[M-H]^+$ in the negative FAB mass spectrum. In combination with $^1H$ and $^{13}C$ NMR spectra (see Table 1), its molecular formula was deduced to be $C_{25}H_{28}O_{13}$, which was consistent with the data of negative high-resolution TOFMS at *m/z* 535.1452 $[M-H]^+$

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作者简介: 来国防 (1972-) 男, 博士, 主管药师, 主要从事植物化学及药品质量标准的研究。

(calcd. for 535.1451). The UV absorption maxima (270 nm) and IR bands (1700 and 1635 $cm^{-1}$) suggested the presence of a ferulic chromophore (Shen *et al*, 1997). The $^1H$ NMR spectrum indicated the presence of a *trans*-double bond at δ 6.31 (1H, d, $J$ = 16.0 Hz), 7.56 (1H, d, $J$ = 16.0 Hz), a mono-substituted benzene ring at δ 7.40 (2H, dd, $J$ = 3.6, 6.6 Hz), 7.25 (2H, m), 7.41 (1H, m), two olefinic protons at δ 7.40 (1H, s) and 6.08 (1H, t, $J$ = 6.4 Hz), a anomeric proton signal at δ 4.71 (1H, d, $J$ = 7.7 Hz). The $^{13}C$ NMR spectrum exhibited signals for 25 carbons, while the DEPT NMR spectrum showed the presence of 3 methylene carbons, 16 methine carbons, 6 quaternary carbons (including three carbonyl groups). On based above data **1** showed typical signals from a 10-hydroxyoleoside except for the signals of a trans-cinnamoyl moiety and a glucoside (Shen *et al*, 1996). Careful investigation of the $^1H$ and $^{13}C$ NMR spectroscopic data of **1** revealed its structure to be very similar to that reported for jasminoside (Shen *et al*, 1990), except that **1** was the absence of methoxyl group. The HMBC spectrum displayed correlations of the signals at δ 2.80 (1H, dd, $J$ = 3.9, 14.7 Hz, H-6α), 2.32 (1H, dd, $J$ = 10.2, 14.7 Hz, H-6β) in the $^1H$ NMR spectrum with that at δ 173.5 (COOH), so the additional carboxyl group should be located at C-6. Meantime the ROESY spectrum showed the correlations of the signals at δ 3.91 (1H, dd, 3.8, 9.8 Hz, H-5) with those at 5.76 (1H, s, H-1), 2.32 (1H, dd, $J$ = 10.2, 14.7 Hz, H-6β), 4.82 (1H, dd, $J$ = 5.5, 13.4 Hz, H-10α), 4.75 (1H, dd, $J$ = 1.2, 13.4 Hz, H-10β), which indicated the α-$CH_2COOH$ substitution in C-5. On basis of above discussion, the structure of **1** was determined to be 10-*O*-trans-cinnamoyl oleoside (named Chinenicside A).

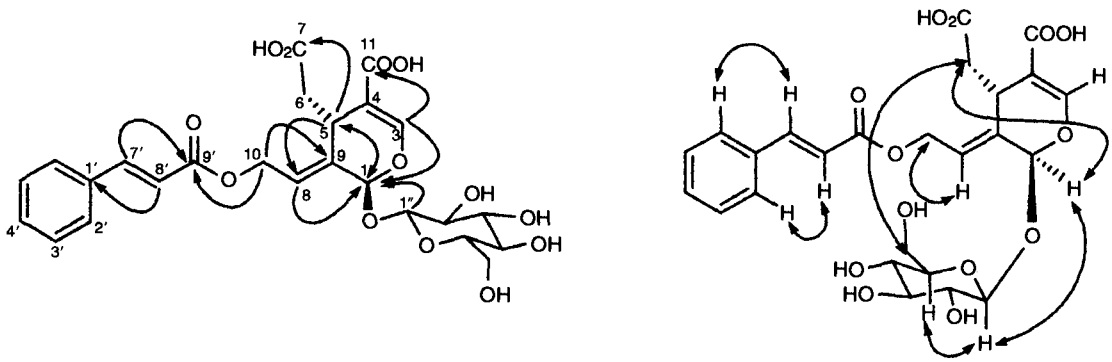


Fig. 1 The key HMBC (left) and ROESY (right) correlations of compound **1**

## Experimental

**General experimental procedures** Optical rotation was taken on a SEPA-300 polarimeter. The IR (KBr) spectra were obtained on a Bio-Rad FTS-135 spectrometer, $\nu$ in $cm^{-1}$. UV spectra were obtained on a Shimadzu double-beam 210A spectrophotometer, $\lambda_{max}$ in nm. FABMS data were obtained on a VG AutoSpec-3000 spectrometers. $^1H$-, $^{13}C$-, and 2D-NMR spectra were recorded on a Bruker AM 400 NMR and a DRX-500 spectrometer with TMS as internal standard. Silica gel (200-300 mesh, or silica gel H, 10-40 μm) for column chromatography and silica gel plate ($GF_{254}$) for thin-layer chromatography (TLC) were obained from the Qingdao Marine Chemical Factory, Qingdao, Shandong Province China.

**Plant material** The aerial parts of *Helwingia chinensis* were collected in xishuangbanna, Yunnan, P. R. China in July 2002 (Lai *et al*, 2003).

**Extraction and Isolation** The air-dried aerial parts (40 kg) were extracted twice with 95% EtOH/$H_2O$ at r.t.. The solvent was evaporated at 50℃ to give a deep-brown waxy residue, which was suspended in $H_2O$ and extracted with AcOEt (3 × 2000 ml). The AcOEt extract (374 g) was fractionated by CC (silica gel (200-300 mesh, $CHCl_3$/MeOH 100:1, 50:1, 20:1, 10:1) to afford several fractions (A-G). The fraction C was rechromatographed (silica gel (200-300 mesh), $CHCl_3$/MeOH 50:1 to 10:1) to afford three sub-fractions. The second fraction (2.1 g) was purified by repeated CC (silica gel; $CHCl_3$/MeOH 50:1, 30:1) and then Sephadex LH-20 eluted by MeOH to give

pure **1** (1.1 g) and **2** (24 mg). The third fraction (1.5 g) was purified by CC (silica gel; $CHCl_3$/MeOH 20:1) and then Sephadex LH-20 (MeOH) to give pure **3** (900 mg) and **4** (33 mg).

Chinenicside A (**1**): white powder, molecular formula: $C_{25}H_{28}O_{13}$, $[\alpha]_D^{20} = -246°$ (*c* 0.5, $CHCl_3$), IR (KBr) $\nu_{max}$: 3432, 2926, 2651, 2021, 1700, 1635, 1496, 1450, 1399, 1333, 1312, 1282, 1204, 1176, 1075, 1042, 990, 770, 685, 576, 484 $cm^{-1}$; negative FABMS: 535 $[M-H]^+$ (100), 473 (13), 312 (8); $^1H$ NMR and $^{13}C$ NMR (table 1).

Table 1 $^1H$ and $^{13}C$ NMR spectral data of compound **1** (in Pyridine, 500 MHz and 125 MHz, respectively, *J* in Hz)

| NO. | $\delta_H$ | $\delta_C$ | NO. | $\delta_H$ | $\delta_C$ |
|---|---|---|---|---|---|
| 1 | 5.76s | 93.3d | 2″,6″ | 7.40dd (3.6,6.6) | 127.9d |
| 3 | 7.40s | 153.8d | 3″,5″ | 7.25m | 128.7d |
| 4 | | 107.8s | 4″ | 7.41m | 130.3d |
| 5 | 3.91dd (3.8,9.8) | 32.3d | 7″ | 7.56d (16.0) | 145.3d |
| 6 | 2.80dd (3.9,14.7) | 39.9t | 8″ | 6.31d (16.0) | 117.2d |
| | 2.32dd (10.2,14.7) | | 9″ | | 168.3s |
| 7 | | 173.5s | 1′ | 4.71d (7.7) | 99.6d |
| 8 | 6.08t (6.4) | 123.1d | 2′ | 3.30m | 72.9d |
| 9 | | 132.2s | 3′ | 3.40 (1H,t,8.8) | 76.3d |
| 10 | 4.82dd (5.5,13.4) | 60.7t | 4′ | 3.33 (1H,t,7.9) | 69.6d |
| | 4.75dd (1.2,13.4) | | 5′ | 3.22m | 76.1d |
| 11 | | 167.0s | 6′ | 3.77dd (2.0,12.4) | 61.4t |
| 1″ | | 134.0s | | 3.60dd (5.3,12.4) | |

10-Hydroxyoleoside 11-methyl ester (**2**): white powder, molecular formula: $C_{17}H_{24}O_{12}$, negative FAB MS *m/z* (%): 419 $[M-H]^+$ (100); $^1H$ NMR (400 MHz, $CD_3OD$) δ: 5.90 (1H, br s, H-1), 7.62 (1H, br s, H-3), 3.65 (1H, dd, *J* = 9.0, 5.8 Hz, H-5), 2.16 (1H, dd, *J* = 13.8, 9.0 Hz, H-6a), 2.62 (1H, dd, *J* = 13.8, 5.8 Hz, H-6b), 6.04 (1H, br t, *J* = 6.5 Hz, H-8), 3.65 (3H, OMe), 4.86 (1H, d, *J* = 7.5 Hz, H-1′); $^{13}C$ NMR (100 MHz, $CD_3OD$) δ: 95.0 (d, C-1), 154.9 (d, C-3), 110.2 (s, C-4), 32.9 (d, C-5), 43.6 (t, C-6), 178.2 (s, C-7), 128.8 (d, C-8), 131.9 (s, C-9), 60.0 (t, C-10), 168.9 (s, C-11), 52.8 (q, OMe), 101.2 (d, C-1′), 74.5 (d, C-2′), 78.2 (d, C-3′), 71.4 (d, C-4′), 77.8 (d, C-5′), 62.7 (t, C-6′).

Jasminoside (**3**): white powder, molecular formula: $C_{26}H_{30}O_{13}$, negative FAB MS *m/z* (%): 549 (95), 402 (26), 222 (16), 147 (100); $^1H$ NMR (400 MHz, $C_5D_5N$) δ: 2.70 (1H, dd, *J* = 5.9, 15.5 Hz, H-6), 3.18 (1H, dd, *J* = 3.2, 15.5 Hz, H-6), 3.49 (3H, s, COOMe), 4.04 (1H, dd, *J* = 3.2, 5.9 Hz, H-5), 6.49 (1H, br s, H-1), 6.58 (1H, t, *J* = 6.5 Hz, H-8), 6.65 (1H, d, *J* = 16.0 Hz, -CH= CH-Φ), 7.83 (1H, d, *J* = 16.0 Hz, -CH = CH-Φ), 7.94 (1H, s, H-3), 5.55 (1H, d, *J* = 7.8 Hz, H-1′), 7.59 (2H, m, H-4′, 8″), 7.36 (2H, m, H-5′, 7″); $^{13}C$ NMR (100 MHz, $C_5D_5N$) δ: 93.9 (d, C-1), 153.6 (d, C-3), 109.8 (s, C-4), 32.2 (d, C-5), 40.5 (t, C-6), 172.2 (s, C-7), 123.7 (d, C-8), 134.4 (s, C-9), 61.5 (t, C-10), 168.9 (s, C-11), 101.6 (d, C-1′), 74.9 (d, C-2′), 79.1 (d, C-3′), 71.5 (d, C-4′), 78.5 (d, C-5′), 62.6 (t, C-6′), 51.7 (q, OMe), 166.7 (s, CO), 145.3 (d, C-1″), 118.7 (d, C-2″), 135.0 (s, C-3″), 128.7 (d, C-4″), 129.5 (d, C-5″), 130.9 (d, C-6″), 128.7 (d, C-7″), 129.5 (d, C-8″).

10-Hydroxyoleuropein (**4**): white powder, molecular formula: $C_{25}H_{32}O_{14}$, negative FAB MS *m/z* (%): 555 $[M-H]^+$ (100); $^1H$ NMR (100 MHz, $CD_3OD$) δ: 5.95 (1H, br s, H-1), 7.54 (1H, br s, H-3), 2.51 (1H, dd, *J* = 9.4, 14.6 Hz, H-6a), 2.74 (1H, dd, *J* = 4.2, 14.6 Hz, H-6b), 6.16 (1H, br t, *J* = 6.4 Hz, H-8), 3.60 (3H, OMe), 4.85 (1H, d, *J* = 7.6 Hz, H-1″); $^{13}C$ NMR (100 MHz, $CD_3OD$) δ: 94.7 (d, C-1), 155.8 (d, C-3), 110.0 (s, C-4), 32.2 (d, C-5), 41.2 (t, C-6), 173.2 (s, C-7), 129.4 (d, C-8), 130.9 (s, C-9), 59.5 (t, C-10), 168.5 (s, C-11), 66.8 (t, C-1′), 35.4 (t, C-2′), 130.9 (s, C-3′), 116.3 (d, C-4′), 146.3 (s, C-5′), 144.8 (s, C-6′), 117.0 (d, C-7′), 124.4 (d, C-8′), 52.5 (q, OMe), 101.2 (d, C-1″), 74.4 (d, C-2″), 78.2 (d, C-3″), 71.5 (d, C-4″), 77.8 (d, C-5″), 62.7 (t, C-6″).

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