# A New Prenylated Xanthone from Root Barks of *Cudrania cochinchinensis*

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**Abstract:** **Objective** To study the chemical constituents from the root barks of *Cudrania cochinchinensis*. **Methods** The chemical constituents were isolated and purified by silica gel column chromatography. The structures of the compounds were identified on the basis of spectral data (MS, $^{1}$H-NMR, $^{13}$C-NMR, and 2D NMR) and by the comparison of spectroscopic data with the reported values in the literatures. **Results** A new xanthone, 1,6,7-trihydroxy-4-(1,1-dimethylallyl)-3-methoxyxanthone (**1**) and a known prenylated xanthone 1,5,6-trihydroxy-4-(1,1-dimethylallyl)-3-methoxyxanthone (isocudraniaxanthone B, **2**) were isolated from the root barks of *C. cochinchinensis*. **Conclusion** Compound **1** is a new prenylated xanthone. Isomers **1** and **2** are obtained from this plant for the first time.

**Key words:** *Cudrania cochinchinensis*; isocudraniaxanthone B; prenylated xanthone; 1,5,6-trihydroxy-4-(1,1-dimethylallyl)-3-methoxyxanthone; 1,6,7-trihydroxy-4-(1,1-dimethylallyl)-3-methoxyxanthone

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## Introduction

*Cudrania cochinchinensis* (Lour.) Kudo et Masam. is a deciduous shrub distributed over southern China, Korea, and Japan. The roots of *C. cochinchinensis* are known as *Chuanposhi* along with the roots of *C. tricuspidata* (Carr.) Bur. in folk medicine for the treatment of humid jaundice, gastric carcinoma, dysmenorrhea, scabies, bruising, etc (Song and Hu, 1999). Previous phytochemical studies have reported that the extract from the root of the plants in genus *Cudrania* Trec. contained various flavonoids and prenylated xanthones (Chang *et al*, 1995; Liang *et al*, 2007), prenylated benzophenones (Hou *et al*, 2001), prenylated isoflavones (Han *et al*, 2009), and so on. Certain prenylated xanthones showed the strong antifungal and antimicrobial activities (Fukai *et al*, 2003; 2005), and cytotoxicity to human tumor cell lines (Zou *et al*, 2004). In order to find some new bioactive constituents, the roots of *C. cochinchinensis*, collected from Longan (Guangxi, China) were investigated. Herein, we reported the work on the isolation and identification of a new prenylated xanthone **1** and its isomer **2** (Fig. 1) from the root barks of *C. cochinchinensis*.

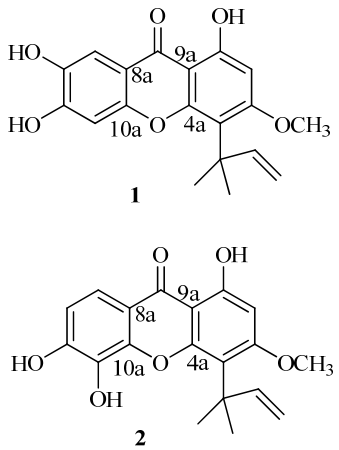


**Fig. 1 Structures of prenylated xanthone 1 and isomer 2**

## Materials and methods

### General

Melting points were determined on an X4 Micro Apparatus. Infrared spectra were measured with a Nicolet

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FT—360 Spectrophotometer. The $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker AV—300 Spectrometer with TMS as internal standard, $\delta$ and $J$ in Hz were recorded. HR-ESI-MS was recorded on a Waters Xevo G2 QT of MS Instrument. TLC was performed on silica gel GF254 plates (Qingdao Marine Chemical Co., Ltd., China). For column chromatography (CC), silica gel (300—400 meshes, Qingdao Marine Chemical Co., Ltd., China) and polyamide (60—100 meshes) were used.

**Plant materials**

*Cudrania cochinchinensis* (Lour.) Kudo et Masam. was collected from Longan, Guangxi in October 2010, and identified by Prof. LIANG Zi-ning in Guangxi University of Chinese Medicine (Nanning, China). The specimen (201001) was deposited at the Laboratory 120 of College of Chemistry and Chemical Engineer, Guangxi University (Nanning, China).

**Extraction and isolation**

The fresh root barks (4 kg) were extracted with 95% EtOH at room temperature for three times and filtered. The filtrate was evaporated *in vacuo* and then suspended in water and partitioned successively with petroleum ether (PE), PE-EtOAc (1:1), EtOAc, and *n*-BuOH. The PE-EtOAc extract (36 g) was subjected to silica gel CC eluted with PE-acetone (10:1→1:1) to yield seven fractions (Frs. 1—7). Fr. 3 was repeatedly separated over silica gel CC to give compound **2** (184 mg). A mixture containing compound **2** from Fr. 3 (1.67 g) was further separated by polyamide CC eluted with $CDCl_3$-MeOH (15:1) as the eluent to obtain compound **1** (8 mg).

## Results

Compound **1**: mp 174—176 ℃, was isolated as yellow powder and the formula was established as $C_{19}H_{18}O_6$ (Fig. 2) based on HR-ESI-MS $[M + H]^+$ at *m/z* 343.1214 (calculated for $C_{19}H_{19}O_6$, 343.1182) and NMR data. The IR spectrum showed the presence of hydroxyl groups (3412 cm$^{-1}$), a conjugated carbonyl group (1652 cm$^{-1}$), and benzene rings. The $^1$H-NMR spectrum showed signals for a hydroxyl group $\delta$ 13.58 (1H, s) formed hydrogen bond with carbonyl, an aromatic methoxyl 3.91 (3H, s) and three uncoupled singlet aromatic protons $\delta$ 7.53 (1H, s), 6.93 (1H, s), and 6.37 (1H, s). Moreover, the $^1$H-NMR spectrum of compound **1** showed signal of a 1,1-dimethylallyl group $\delta$ 6.32 (1H, dd, $J$ = 10.5, 17.7 Hz), 4.95 (1H, d, $J$ = 17.7 Hz), 4.87 (1H, d, $J$ = 10.5 Hz), and 1.65 (6H, s). The $^{13}$C-NMR spectrum revealed the presence of 19 carbons (Table 1), including one carbonyl group, two aromatic rings with six oxygenated carbons, and a 5C group, corresponding to a prenylated and tetraoxylated xanthone. Based upon the above findings, it was deduced that one aromatic ring of the xanthone was tri-substituted while the other was 6,7-di-substituted. The position of substituents on the xanthone skeleton was determined on the basis of HSQC and HMBC spectral analysis. In the HMBC spectrum, the hydrogen-bonded hydroxyl group at $\delta$ 13.57 (OH-1) correlated with C-1 ($\delta$ 162.1), C-2 ($\delta$ 95.1), and C-9a ($\delta$ 102.9). The aromatic proton at $\delta$ 6.37 (H-2) correlated with C-1, C-3 ($\delta$ 165.0), C-4 ($\delta$ 116.5), and C-9a. The olefinic proton at $\delta$ 6.32 (H-2′) and the methyl groups at $\delta$ 1.65 (H-4′, 5′) showed cross-peaks with C-4. In addition, the HMBC spectrum also displayed the correlations between $\delta$ 7.53 (H-8) and C-6 ($\delta$ 153.6), C-7 ($\delta$ 143.2), C-9 ($\delta$ 180.4); $\delta$ 6.93 (H-5) and C-6, C-7 C-8a ($\delta$ 112.3) respectively. As a result, it could be confirmed that these two hydroxyl groups were ortho-substituted at the C-6, 7 of compound **1**. While the correlations between the aromatic proton H-2 ($\delta$ 6.37) and C-1, C-4, C-9a and between 3-$OCH_3$ ($\delta$ 3.91) and C-3 ($\delta$ 165.0) indicated the aromatic proton and 3-$OCH_3$ was located at positions C-2 and C-3, respectively. Thus, the structure of compound **1** was determined as 1,6,7-trihydroxy-4-(1,1-dimethylallyl)-3-methoxyxanthone.

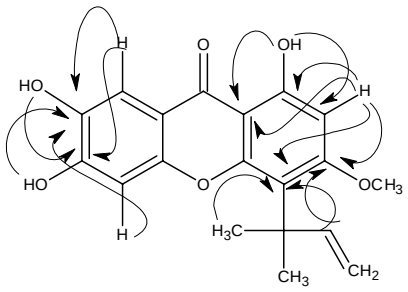


**Fig. 2 HMBC of compound 1**

Compound **2**: mp 229—231 ℃, was obtained as yellow powder. HR-ESI-MS $[M + H]^+$ signal is corresponding to the molecular formula of $C_{19}H_{18}O_6$ at

*m/z* 343.1215 $[M + H]^+$ (calculated 343.1182). The $^1$H-NMR and $^{13}$C-NMR spectral data of compound **2** were similar with those of compound **1** except for two hydroxyl substituted at the C-5, 6 because of two aromatic protons at $\delta$ 6.96 (1H, H-7) and $\delta$ 7.71 (1H, H-8) with $J$ = 8.7 Hz. Compound **2** was characterized to be isocudraniaxanthone B [1,5,6-trihydroxy-4-(1,1-dimethylallyl)-3-methoxy xanthone] (Kobayashi *et al*, 1997). The $^1$H-NMR and $^{13}$C-NMR data of compounds **1** and **2** were shown in Table 1.

**Table 1 $^1$H-NMR (300 MHz) and $^{13}$C-NMR (75 MHz) data of compounds 1 and 2 (TMS, $\delta$, $J$ in Hz)**

| Position | Compound **1** (Acetone-$d_6$) | | Compound **2** ($CDCl_3$) | |
|---|---|---|---|---|
| | $\delta_H$ | $\delta_C$ | $\delta_H$ | $\delta_C$ |
| 1 | 13.57 (1H, s, OH) | 162.1 | 13.36 (1H, s, OH) | 162.5 |
| 2 | 6.37 (1H, s) | 95.1 | 6.42(1H, s) | 95.6 |
| 3 | | 165.0 | | 165.2 |
| 4 | | 116.5 | | 113.6 |
| 4a | | 155.3 | | 156.9 |
| 5 | 6.93 (1H, s) | 102.4 | | 131.1 |
| 6 | 9.06 (1H, s, OH) | 153.6 | | 149.1 |
| 7 | 9.01 (1H, s, OH) | 143.2 | 6.97 (1H, d, 8.7) | 112.7 |
| 8 | 7.53 (1H, s) | 108.0 | 7.71 (1H, d, 8.7) | 117.5 |
| 8a | | 112.3 | | 113.2 |
| 9 | | 180.4 | | 180.9 |
| 9a | | 102.9 | | 103.0 |
| 10a | | 151.6 | | 144.7 |
| 1′ | | 41.0 | | 41.6 |
| 2′ | 6.32 (1H, dd, 10.5, 17.7) | 150.9 | 6.75 (1H, dd, 10.5, 17.7) | 154.0 |
| 3′ | 4.95 (1H, d, 17.7); 4.87 (1H, d, 10.5) | 106.4 | 5.26 (1H, d, 17.7); 5.06 (1H, d, 10.5) | 103.2 |
| 4′ | 1.65 (3H, s) | 29.0 | 1.63 (3H, s) | 27.8 |
| 5′ | 1.65 (3H, s) | 29.0 | 1.63 (3H, s) | 27.8 |
| $OCH_3$ | 3.91 (3H, s) | 55.3 | 3.92 (3H, s) | 55.7 |

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