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Y. Xiao<sup>a</sup>; J. -F. Zhao<sup>a</sup>; X. -D. Yang<sup>a</sup>; G. -P. Li<sup>a</sup>; J. -H. Yang<sup>a</sup>; H. -B. Zhang<sup>a</sup>; L. Li<sup>a</sup>

<sup>a</sup> School of Pharmacy, Center for Advanced Studies of Medicinal and Organic Chemistry, Yunnan University, Kunming, China

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## Two new phenyl esters from *Litsea euosma*

Y. XIAO, J.-F. ZHAO, X.-D. YANG, G.-P. LI, J.-H. YANG, H.-B. ZHANG and L. LI\*

School of Pharmacy, Center for Advanced Studies of Medicinal and Organic Chemistry,  
Yunnan University, Kunming 650091, China

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Two new phenyl esters, named as euosmoside A (**1**) and euosmoside B (**2**), have been isolated from the leaves and twigs of *Litsea euosma*. Their structures were elucidated on the basis of spectroscopic methods.

**Keywords:** *Litsea euosma*; Lauraceae; Euosmoside A; Euosmoside B

### 1. Introduction

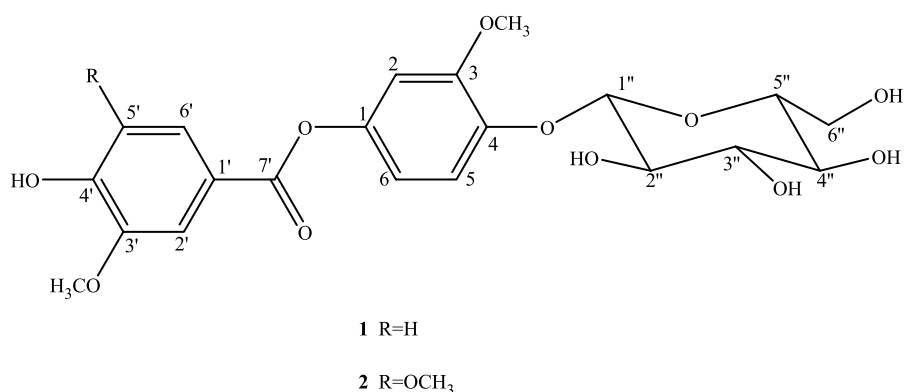
The genus *Litsea* (Lauraceae) has about 72 species, and is distributed in South and Southwest China [1]. Most *Litsea* plants contain alkaloids [2–4], flavonoids [5,6], terpenes [7,8], lactones [9], and volatile oil constituents [10]. *Litsea* plants exhibited a variety of biological activities, including antimicrobial, hypothermic and antitumor [2,11,12]. Although *Litsea euosma* had been used in traditional Chinese medicine, no phytochemical investigation has been carried out previously. As a part of our systematic studies on the chemical constituents of Chinese medicinal plants, we initiated a chemical study on *Litsea euosma*. Two new phenyl esters **1** and **2** have been isolated from the title plant. This paper describes the isolation and structure elucidation of the two compounds.

### 2. Results and discussion

The leaves and twigs of *Litsea euosma* were extracted repeatedly with EtOH, and the ethanolic extract was partitioned between H<sub>2</sub>O and EtOAc. The EtOAc soluble portion was subjected to chromatography over silica gel column, eluting with CHCl<sub>3</sub>-MeOH (20:1–1:1) to afford compounds **1** and **2**.

Compound **1** was obtained as a colorless oil. The molecular formula, C<sub>21</sub>H<sub>24</sub>O<sub>11</sub>, was determined by HR-FABMS, consistent with 10 degrees of unsaturation. The <sup>13</sup>C NMR and DEPT spectra indicated that there were two methoxy, one ester carbonyl and one glucosyl groups, in addition to 12 aromatic carbons in the molecule. <sup>1</sup>H NMR spectrum displayed two

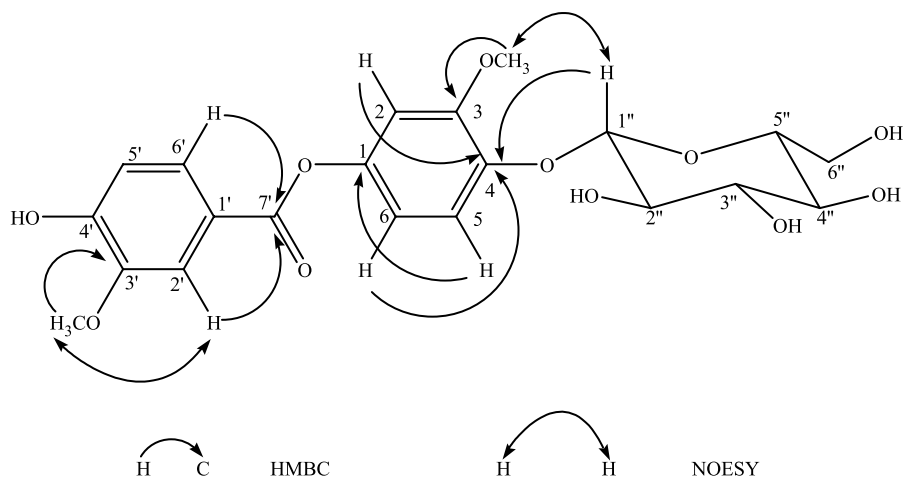
\*Corresponding author. Tel.: + 86-871-5033644, Fax: + 86-871-5035538. E-mail: liliang5758@hotmail.com

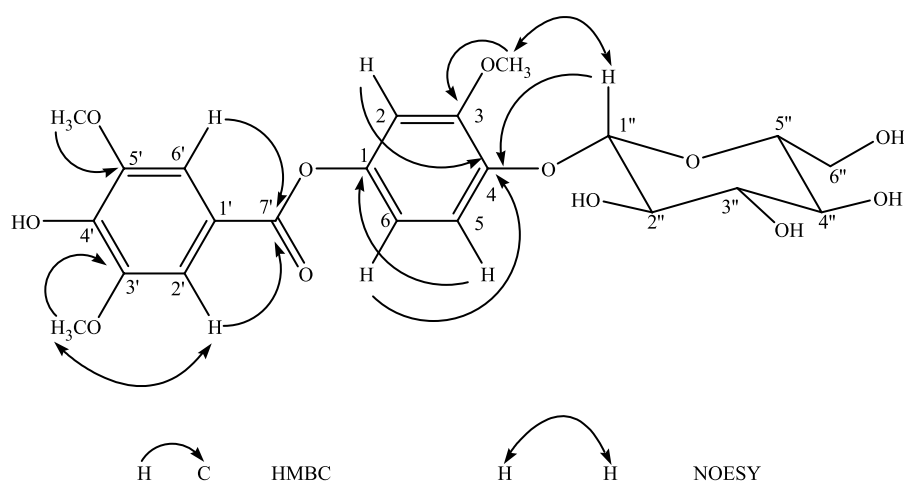
Figure 1. Structures of compounds **1–2**.

ABX-type signals at  $\delta_{\text{H}}$  6.88 (d,  $J = 8.0$ , H-5'), 7.56 (dd,  $J = 1.9, 8.0$ , H-6') and 7.53 (d,  $J = 1.9$ , H-2'), and  $\delta_{\text{H}}$  6.94 (d,  $J = 8.7$ , H-5), 6.13 (dd,  $J = 2.7, 8.7$ , H-6) and 6.43 (d,  $J = 2.7$ , H-2), suggesting the presence of two catechol-type aromatic rings. Coupling constant ( $J = 7.8$ ) of the anomeric proton of glucose at  $\delta_{\text{H}}$  4.68 (H-1'') indicated the anomeric configuration was  $\beta$ -oriented. In HMBC spectrum (figure 2), the obvious correlations of H-1'' ( $\delta_{\text{H}}$  4.68) and H-6 ( $\delta_{\text{H}}$  6.13) and H-2 ( $\delta_{\text{H}}$  6.43) to C-4 ( $\delta_{\text{C}}$  140.4) suggested that glucosyl was linked to C-4, and H-5 ( $\delta_{\text{H}}$  6.94) to C-1 ( $\delta_{\text{C}}$  154.5) indicated the ester carbonyl was linked at C-1. Furthermore, the correlations of H-6' ( $\delta_{\text{H}}$  7.56) and H-2' ( $\delta_{\text{H}}$  7.53) to C-7' ( $\delta_{\text{C}}$  167.5) suggested that C-7' was linked at C-1'. On the other hand, the correlations between OCH<sub>3</sub>-3' ( $\delta_{\text{H}}$  3.85) to C-3' ( $\delta_{\text{C}}$  148.3) and OCH<sub>3</sub>-3 ( $\delta_{\text{H}}$  3.77) to C-3 ( $\delta_{\text{C}}$  151.6) indicated that two methoxy were substituted at C-3' and C-3. NOESY experiments were also conducted and the key correlations were indicated in figure 2.

On the basis of the above evidence, compound **1** was established as 3-methoxy-4-(3,4,5-trihydroxy-6-(hydroxymethyl)-tetrahydro-2*H*-pyran-2-yloxy)phenyl 4-hydroxy-3-methoxybenzoate.

Compound **2** was obtained as a colorless oil. The molecular formula, C<sub>22</sub>H<sub>26</sub>O<sub>12</sub>, was determined by HR-FABMS, consistent with 10 degrees of unsaturation. In comparison with **1**,

Figure 2. Key HMBC and NOESY correlations of **1**.

Figure 3. Key HMBC and NOESY correlations of **2**.

the spectra data of **2** ( $^1\text{H}$ ,  $^{13}\text{C}$ , COSY, NOESY, HMQC and HMBC) were quite similar to those of **1** except one more methoxy signal in **2**. By analysis of the HMBC spectrum, the correlation of  $\text{OCH}_3\text{-}5'$  ( $\delta_{\text{H}}$  3.84) with  $\text{C-}5'$  ( $\delta_{\text{C}}$  149.1) indicated that the methoxy was linked at  $\text{C-}5'$ . So, compound **2** was elucidated as 3-methoxy-4-(3,4,5-trihydroxy-6-(hydroxymethyl)-tetrahydro-2H-pyran-2-yloxy)phenyl 4-hydroxy-3,5-dimethoxybenzoate.

### 3. Experimental

#### 3.1 General experimental procedures

UV spectra were recorded on a shimadzu-2401PC spectrophotometer;  $\lambda_{\text{max}}$  in nm. Optical rotations were measured on a Jasco-20 MC Polarimeter. IR spectra were taken on a Nicolet AVATAR-360 spectrophotometer,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured with a Bruker AV 300 (300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$ ) spectrometer. Chemical shifts ( $\delta$ ) are in ppm (TMS as internal standard), and coupling constants ( $J$ ) in Hz. The FABMS was obtained on a VG-Autospec 3000 mass spectrometers. Commercial Si gel plates (Qingdao Haiyang Chemical Group Co.) were used for TLC.

#### 3.2 Plant material

The sample was collected from Xishuangbanna county of Yunnan province in April 2003 and identified by Professor Zh.-H. Hu of the Department of Botany, Yunnan University. A voucher specimen is deposited in the School of Pharmacy, Yunnan University.

#### 3.3 Extraction and isolation

The powdered leaves and twigs of *Litsea euosma* (8 kg) were repeatedly extracted with 95% EtOH ( $4 \times 20\text{L}$ ) at room temperature. The extract was then concentrated under reduced pressure to give a black syrup, which was suspended in water, and then extracted with  $\text{Et}_2\text{O}$ , EtOAc and *n*-BuOH, successively, to afford  $\text{Et}_2\text{O}$  fraction (70 g), EtOAc fraction (20 g) and *n*-BuOH fraction (80 g). The EtOAc fraction was subjected to silica gel column chromatography washing with  $\text{CHCl}_3\text{-MeOH}$  (20:1–1:1), by which five fractions (I–V)

Table 1.  $^1\text{H}$  (300 MHz) and  $^{13}\text{C}$  NMR (75 MHz) data of **1** and **2** in  $\text{CD}_3\text{OD}$  ( $\delta$  in ppm).

No.	<b>1</b>		<b>2</b>	
	$^{13}\text{C}$	$^1\text{H}$ (J, Hz)	$^{13}\text{C}$	$^1\text{H}$ (J, Hz)
1'	122.0 s		120.8 s	
2'	113.2 d	7.53 d (1.9)	108.8 d	7.31 d (1.8)
3'	148.3 s		149.1 s	
4'	152.4 s		143.3 s	
5'	115.5 d	6.88 d (8.0)	149.1 s	
6'	124.8 d	7.56 dd (1.9, 8.0)	108.8 d	7.31 d (1.8)
7'	167.5 s		167.2 s	
1	154.5 s		155.4 s	
2	101.4 d	6.43 d (2.7)	102.8 d	6.41 d (2.7)
3	151.6 s		152.1 s	
4	140.4 s		141.4 s	
5	120.1 d	6.94 d (8.7)	119.8 d	6.91 d (8.7)
6	107.0 d	6.13 dd (2.7, 8.7)	107.8 d	6.09 dd (2.7, 8.7)
3'-OCH <sub>3</sub>	56.0 q	3.85 s	56.7 q	3.84 s
3-OCH <sub>3</sub>	56.0 q	3.77 s	56.4 q	3.76 s
5'-OCH <sub>3</sub>			56.7 q	3.84 s
1''	103.7 d	4.68 d (7.8)	104.4 d	4.66 d (7.4)
2''	74.5 d	3.68 m	75.5 d	3.66 m
3''	75.1 d	3.45 m	76.1 d	3.45 m
4''	71.6 d	3.48 m	72.3 d	3.47 m
5''	77.3 d	3.50 m	78.8 d	3.48 m
6''	64.6 t	4.71 d (2.2), 4.39 m	65.7 t	4.71 d (1.9), 4.39 m

were obtained. Fraction II (4 g) was further subjected to silica gel column chromatography ( $\text{CHCl}_3\text{-MeOH-H}_2\text{O}$  in order of increasing polarity) to yield compounds **1** (50 mg) and **2** (20 mg), respectively.

**3.3.1 Compound 1.** A colorless oil,  $[\alpha]_D^{25} - 32.03$  (c 0.007,  $\text{CH}_3\text{OH}$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm): 271 (lg $\epsilon$  4.0); IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3411, 2934, 1699, 1513, 1287, 1214, 1027, 765.9, 625.8;  $^1\text{H}$  and  $^{13}\text{C}$  NMR (see table 1). HR-FABMS:  $m/z$  475.1212 [ $\text{M} + \text{Na}$ ] $^+$  (calcd for  $\text{C}_{21}\text{H}_{24}\text{O}_{11}$ , + Na 475.1216).

**3.3.2 Compound 2.** A colorless oil,  $[\alpha]_D^{25} - 25.77$  (c 0.003,  $\text{CH}_3\text{OH}$ ); UV ( $\text{CH}_3\text{OH}$ )  $\lambda_{\text{max}}$  (nm): 274 (lg $\epsilon$  4.6); IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3431, 2934, 1699, 1512, 1217, 1073, 806, 761;  $^1\text{H}$  and  $^{13}\text{C}$  NMR (see table 1). HR-FABMS:  $m/z$  505.1317 [ $\text{M} + \text{Na}$ ] $^+$  (calcd for  $\text{C}_{22}\text{H}_{26}\text{O}_{12}$ , + Na 505.1321).

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