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## Note

# A new sesquiterpene ester from the fruits of *Celastrus orbiculatus*

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From the fruits of *Celastrus orbiculatus* Thunb. a new  $\beta$ -dihydroagarofuran sesquiterpene ester named 1 $\beta$ ,2 $\beta$ ,13-triacetoxy-9 $\alpha$ -cinnamoyloxy- $\beta$ -dihydroagarofuran (**1**) has been isolated along with two known compounds, 6 $\alpha$ -acetoxy-1 $\beta$ ,9 $\beta$ -dibenzoyloxy-8 $\beta$ -hydroxy- $\beta$ -dihydroagarofuran (**2**), and 1 $\beta$ , 6 $\alpha$ -diacetoxy-9 $\beta$ -benzoyloxy-8 $\beta$ -hydroxy- $\beta$ -dihydroagarofuran (**3**). Their structures were elucidated on the basis of spectroscopic data.

**Keywords:** *Celastrus orbiculatus*; Sesquiterpene ester; 1 $\beta$ ,2 $\beta$ ,13-Triacetoxy-9 $\alpha$ -cinnamoyloxy- $\beta$ -dihydroagarofuran

## 1. Introduction

*Celastrus orbiculatus*, a medicinal plant widely distributed in China, has activity in tranquilization [1]. Some sesquiterpenes with anti-inflammatory activities from *Celastrus orbiculatus* have been reported [2]. We reported a new  $\beta$ -dihydroagarofuran sesquiterpene ester in previous paper [3]. In extending our research, a new structural elucidation of the new sesquiterpene ester.

## 2. Results and discussion

Compound **1** was isolated as a white powder (mp 207–209°C). HRMS gave a molecular ion peak at  $m/z$  542.2520 [M]<sup>+</sup>, corresponding to a molecular formula of C<sub>30</sub>H<sub>38</sub>O<sub>9</sub> for **1**. The <sup>1</sup>H NMR spectrum gave proton signals at  $\delta$  1.21 (3H, s, H-15), 1.27 (3H, d,  $J = 8.7$  Hz, H-12),

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1.39 (3H, s, H-14), 1.80 (3H, s), 2.10 (3H, s), 2.17 (3H, s). The  $^{13}\text{C}$  NMR spectrum gave three methyl carbon signals at  $\delta$  18.5 (C-12), 24.0 (C-14), 30.0 (C-15), four methylene carbon signals at  $\delta$  30.8 (C-3), 36.1 (C-6), 33.8 (C-8), 65.2 (C-13), five methine carbon signals at  $\delta$  71.1 (C-1), 70.1 (C-2), 39.2 (C-4), 43.4 (C-7), 69.2 (C-9), and three quaternary carbon signals at  $\delta$  86.3 (C-5), 50.4 (C-10), 81.9 (C-11). These spectral data suggest a  $\beta$ -dihydroagarofuran sesquiterpene-type skeleton [4,5].

The  $^{13}\text{C}$  NMR spectrum gave four carbon signals at  $\delta$  71.1 (C-1), 70.1 (C-2), 69.2 (C-9), 65.2 (C-13), indicating the presence of four oxygenated carbons. According to the literatures [4,5], the carbonyl carbon signals at  $\delta$  169.5, 169.8, 170.3 in the  $^{13}\text{C}$  NMR spectrum show that compound **1** contains three acetoxy groups; the aromatic carbon signals at  $\delta$  134.2–128.1, the carbonyl carbon signal at  $\delta$  165.8 and the two carbon signals at  $\delta$  117.9, 145.2 as well as the proton signals at  $\delta$  7.68, 6.38 (each 1H, d,  $J = 15.9$  Hz), 7.35–7.55 showed the presence of one cinnamoyloxy group.

In the HMQC spectrum, the correlations of signals seen at  $\delta$  5.68 (1H, d,  $J = 3.0$  Hz, H-1) with 71.1(C-1),  $\delta$  5.54 (1H, dd,  $J = 6.6, 3.0$  Hz, H-2) with 70.1 (C-2),  $\delta$  5.19 (1H, d,  $J = 6.6$  Hz, H-9) with 69.2 (C-9), and  $\delta$  4.44, 4.82 (each 1H, d,  $J = 12.6$  Hz, H-13) with 65.2 (C-13) are compatible with above conclusion.

In the HMBC spectrum, the proton signal of H-1 at  $\delta$  5.68 (1H, d,  $J = 3.0$  Hz) shows long-range correlations with the carbon signals at  $\delta$  70.1 (C-2), 30.8 (C-3), 86.3 (C-5), 50.4 (C-10), 65.2 (C-13) and 169.5. Long-range correlations of signals at  $\delta$  5.54 (1H, dd,  $J = 6.6, 3.0$  Hz, H-2) with 71.1 (C-1), 30.8 (C-3), 39.2 (C-4), 50.4 (C-10), 169.8, and  $\delta$  4.44, 4.82 (each 1H, d,  $J = 12.6$  Hz, H-13) with 71.1 (C-1), 50.4 (C-10), 69.2 (C-9), 86.3 (C-5), 170.3 were also observed; hence the three acetoxy groups are at C-1, C-2, C-13 respectively. The proton signal at  $\delta$  5.19 (1H, d,  $J = 6.6$  Hz, H-9) show long-range correlations with the carbon signals at  $\delta$  33.8 (C-8), 43.4 (C-7), 50.4 (C-10), 65.2 (C-13), 71.1 (C-1), 86.3 (C-5), 165.8, therefore one cinnamoyloxy group is linked at C-9.

The configurations of the substituted groups of the dihydroagarofuran skeleton were determined by the coupling constants of protons ( $J_{1,2} = 3.0$  Hz,  $J_{8,9} = 6.6$  Hz) compared with those reported in previously [4–6]. Thus, compound **1** was identified as  $1\beta,2\beta,13$ -triacetoxy- $9\alpha$ -cinnamoyloxy- $\beta$ -dihydroagarofuran (figure 1).

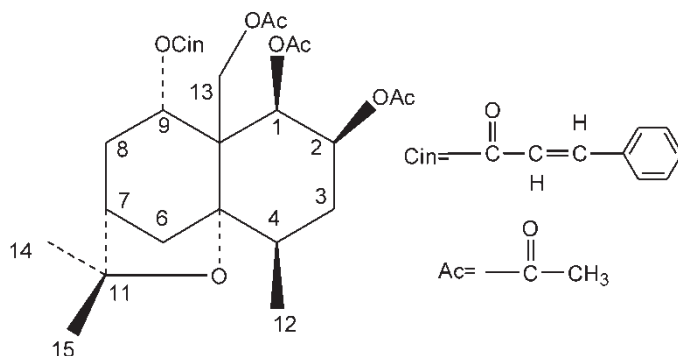


Figure 1. Structure of compound **1**.

### 3. Experimental

#### 3.1 General experimental procedures

Melting points were measured on a Yamaco-hot-stage and are uncorrected. All NMR spectra were recorded on a Bruker-ARX-300 spectrometer, using TMS as an internal standard. The UV spectrum was recorded on a Shimadzu UV-260 UV–Vis spectrometer. ESI-MS was performed on a VG-70SE mass spectrometer. The optical rotation was measured on a Perkin–Elmer 241 polarimeter. Silica gel for chromatography was produced by the Qingdao Ocean Chemical Group Co. of China. The HPLC system used a Shimadzu CTO-6A equipped with a UV detector, and a Shimadzu SPD-6A column (Shimadzu Shim-pack PREP-ODS, i.d. 2.5 × 21.6 cm). The boiling point range of light petroleum was 60–90°C.

#### 3.2 Plant material

The plant material was collected in Shenyang city, Liaoning Province, China, and was identified by Professor Guo Yunzheng (Department of Pharmacognosy, Shenyang Pharmaceutical University, China). A voucher specimen (200115) has been deposited in the Herbarium of the Research Department of Natural Medicine, Shenyang Pharmaceutical University, China.

#### 3.3 Extraction and isolation

Dried fruits (10 kg) of *Celastrus orbiculatus* were extracted with 95% ethanol. The EtOH extract was concentrated *in vacuo*, and then the residue was extracted with light petroleum, EtOAc and n-BuOH successively. A portion (160 g) of the light petroleum extract was subjected to column chromatography on silica gel and eluted with light petroleum–acetone (100:6) to yield compound **1** (5 mg); light petroleum–acetone (100:7) provided fraction 5,

Table 1. <sup>1</sup>H and <sup>13</sup>C NMR data for **1** in CDCl<sub>3</sub>.

No.	δ <sub>C</sub>	δ <sub>H</sub>	HMBC
1 <sup>a</sup>	71.1	5.68 (1H, d, <i>J</i> = 3.0 Hz)	C-2, C-3, C-5, C-10, C-13
2 <sup>a</sup>	70.1	5.54 (1H, dd, <i>J</i> = 6.6, 3.0 Hz)	C-1, C-3, C-4, C-10
3	30.8	1.76 (1H, dd, <i>J</i> = 15.1, 1.8 Hz) 2.45 (1H, ddd, <i>J</i> = 15.1, 6.8, 3.4 Hz)	C-2, C-5, C-1, C-4
4	39.2	1.94 (1H, m)	C-12, C-2, C-3, C-5, C-10, C-6
5	86.3		
6	36.1	2.28 (2H, m)	C-4, C-5, C-7, C-8, C-10, C-11
7	43.4	2.05 (1H, m)	C-6, C-5, C-8, C-9, C-11
8	33.8	2.27 (2H, m)	C-6, C-7, C-10, C-9, C-11
9 <sup>a</sup>	69.2	5.19 (1H, d, <i>J</i> = 6.6 Hz)	C-8, C-7, C-10, C-13, C-1, C-5
10	50.4		
11	81.9		
12	18.5	1.27 (3H, d, <i>J</i> = 8.7 Hz)	C-5, C-3, C-4
13 <sup>b</sup>	65.2	4.82 (1H, d, <i>J</i> = 12.6 Hz) 4.44 (1H, d, <i>J</i> = 12.6 Hz)	C-1, C-10, C-9, C-5
14	24.0	139 (3H, s)	C-15, C-11, C-7
15	30.0	1.27 (3H, s)	C-14, C-11, C-7

All signals assigned by 1D and 2D NMR. <sup>a</sup>Signals of H-1, H-2, H-9 and H-13 were also correlated with carbonyl carbon signals at δ 169.5, 169.8, 165.8, 170.3 respectively.

which was then subjected to HPLC using MeOH–H<sub>2</sub>O (75:25) as eluent to yield compounds **2** (10 mg, 40 min) and **3** (11 mg, 57 min).

Compound **1**: a white powder (EtOAc), mp 207–209°C;  $[\alpha]_D = +75.0$  ( $c = 0.075$  MeOH). UV  $\lambda_{\max}$  (MeOH): 279.6 nm. <sup>1</sup>H NMR (300 MHz, in CDCl<sub>3</sub>) see table 1, acetate:  $\delta$  (ppm): 1.80 (3H, s), 2.10 (3H, s), 2.17 (3H, s); cinnamoyloxy:  $\delta$  7.68, 6.38 (each 1H, d,  $J = 15.9$  Hz), 7.37–7.55 overlapped. <sup>13</sup>C NMR (75 MHz, in CDCl<sub>3</sub>) see table 1, acetate:  $\delta$  (ppm): 20.5, 21.1, 21.2, 169.5, 169.8, 170.3; cinnamoyloxy:  $\delta$  165.8, 117.9, 145.2, 134.2, 130.2, 128.7, 128.1. EIMS  $m/z$  (rel. int. %): 542 [M]<sup>+</sup> (2) 411 (57) 351 (25) 291 (20) 231 (12) 131 (100) 103 (28) 43 (25); HRMS:  $m/z$  542.2520 [M]<sup>+</sup> (calcd for C<sub>30</sub>H<sub>38</sub>O<sub>9</sub>, 542.2516).

<sup>1</sup>H and <sup>13</sup>C NMR data of compounds **2** and **3** are in accordance with the known compounds 6 $\alpha$ -acetoxo-1 $\beta$ ,9 $\beta$ -dibenzoyloxy-8 $\beta$ -hydroxy- $\beta$ -dihydroagarofuran [5] and 1 $\beta$ ,6 $\alpha$ -diacetoxo-9 $\beta$ -benzoyloxy-8 $\beta$ -hydroxy- $\beta$ -dihydroagarofuran [7] respectively.

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