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A NEW SESQUITERPENE ESTER FROM THE FRUITS OF *CELASTRUS ORBICULATUS*

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From the fruits of *Celastrus orbiculatus* Thunb., a new dihydroagarofuran sesquiterpene ester named 6 α ,13 β -diacetoxy-1 β ,8 β ,9 β -tribenzoyloxy- β -dihydroagarofuran (**1**) has been isolated, along with three known compounds: 1 β ,6 α ,8 β -triacetoxy-9 α -benzoyloxy- β -agarofuran (**2**), 1 β ,6 α -diacetoxy-9 α -benzoyloxy- β -dihydroagarofuran (**3**) and β -sitosterol (**4**). The structure of **1** was elucidated on the basis of spectroscopic methods.

Keywords: *Celastrus orbiculatus*; 6 α ,13 β -Diacetoxy-1 β ,8 β ,9 β -tribenzoyloxy- β -dihydroagarofuran; Sesquiterpene ester

INTRODUCTION

Celastrus orbiculatus is a medicinal plant widely distributed in China, which has activity in tranquilization [1]. Some sesquiterpenes with antitumor and antifeeding activities from the seeds have been reported in the literature [2]. In this paper, we report on the isolation and structural elucidation of a new sesquiterpene ester.

RESULTS AND DISCUSSION

Compound **1** was isolated as white powder, mp 217–219°C. The UV(MeOH) spectrum showed a maximum absorption at 228.2 nm. The peak at m/z 699 $[M + H]^+$ in the ESI-MS spectrum, along with ^1H and ^{13}C NMR data, suggested a molecular formula of $\text{C}_{40}\text{H}_{42}\text{O}_{11}$ for **1**. The proton signals at δ 1.04 (3H, d, $J = 7.2$ Hz, H-12), 1.49 (3H, s, H-14), 1.67 (3H, s, H-15), 2.05 (3H, s), 2.15 (3H, s) in the ^1H NMR spectrum, together with the carbon signals at δ 51.1 (C-10), 53.3 (C-7), 81.2 (C-11), 90.8 (C-5) in the ^{13}C NMR spectrum, indicated in the presence of a β dihydroagarofuran sesquiterpene-type skeleton [3–5].

The ^{13}C NMR spectrum gave five carbon signals, at δ 61.1 (C-13), 71.3 (C-8), 72.9 (C-9), 74.9 (C-6), 79.8 (C-1), which indicated the presence of five oxygenated carbons.

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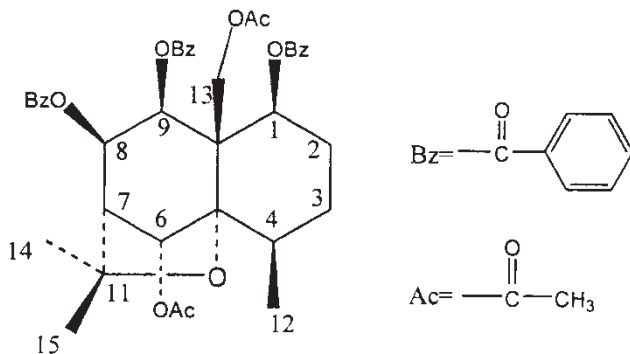


FIGURE 1 Structure of compound 1.

By comparison of the ^{13}C NMR spectral data with known compounds [3–5], the signals at δ 171.0, 169.8 in the indicated that compound **1** contained two acetoxy groups; the aromatic carbon signals at δ 133.1–127.6, with the three carbonyl carbon signals at δ 166.1, 165.4, 164.6 and the proton signals at δ 6.87–8.01, showed the presence of three benzoyloxy groups.

In the HMQC spectrum we observed correlations of signals at δ_{H} 5.75 (1H, dd, $J = 9.6/4.2$ Hz, H-1) with δ_{C} 79.8 (C-1), δ_{H} 6.84 (1H, s, H-6), with δ_{C} 74.9 (C-6), δ_{H} 2.66 (1H, d, $J = 3.9$ Hz, H-7) with δ_{C} 53.3 (C-7), δ_{H} 5.77 (1H, dd, $J = 5.7/3.9$ Hz H-8) with δ_{C} 71.3 (C-8), δ_{H} 5.88 (1H, d, $J = 5.7$ Hz, H-9), with δ_{C} 72.9 (C-9) and δ_{H} 4.95, 4.87 (each 1H, d, $J = 13.2$ Hz, H-13) with δ_{C} 61.1 (C-13), all of which confirmed further the above conclusion.

In the HMBC spectrum, the proton signal of H-1 at δ 5.75 showed long-range correlations with the carbon signals at δ 51.1 (C-10), 90.7 (C-5), 23.2 (C-2), 26.4 (C-3), 61.1 (C-13), 166.1. Long range correlations of signals at δ_{H} 5.77 (1H, dd, $J = 5.7/3.9$ Hz, H-8) with δ_{C} 53.3 (C-7), 72.9 (C-9), 74.9 (C-6), 51.1 (C-10), 81.2 (C-11), 165.4 and δ_{H} 5.88 (1H, d, $J = 5.7$ Hz, H-9) with δ_{C} 51.1 (C-10), 71.3 (C-8), 79.8 (C-1), 90.7 (C-5), 53.3 (C-7), 61.1 (C-13), 164.6 were observed in the HMBC spectrum; hence the three benzoyloxy groups are situated C-1, C-8 and C-9 respectively. The signal at δ_{H} 6.84 (1H, s, H-6) showed long-range correlations with the carbon signals at δ_{C} 90.7 (C-5), 53.3 (C-7), 33.4 (C-4), 71.3 (C-8), 51.1 (C-10), 81.2 (C-21), 169.8, and the signals at δ_{H} 4.95, 4.87 (each 1H, d, $J = 13.2$ Hz, H-13) with signals at δ_{C} 51.1 (C-10), 53.3 (C-7), 72.9 (C-9), 79.8 (C-1), 90.7 (C-5), 171.0 showing that two acetoxy groups are linked at C-6, C-13 respectively.

The configurations of substituted groups of the dihydroagarofuran skeleton were determined by the coupling constants in the ^1H NMR spectrum [3,6]. Thus, compound **1** was identified as 6 α ,13 β -diacetoxy-1 β ,8 β ,9 β -tribenzoyloxy- β -dihydroagarofuran (Fig. 1) by comparison with known compound [3].

EXPERIMENTAL

General Experiment Procedures

Melting points were measured on a Yamaco hot-stage and are uncorrected. All NMR spectra were recorded a Bruker-ARX-300 spectrometer, using TMS 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 Qingdao Ocean Chemical Group Co. of China.

Plant Material

The plant material was collected in Shenyang city, Liaoning province, and was identified by Professor Guo Yunzheng (Shenyang Pharmaceutical University).

Extraction and Isolation

Dried fruits of *Celastrus orbiculatus* were extracted with 95% ethanol. The extract was concentrated, and then extracted successively with light petroleum, EtOAc and *n*-BuOH. The light petroleum extract was subjected to column chromatography on silica gel eluted with light petroleum–acetone (100:2) to yield compound **4**; and light petroleum–acetone (100:3) provided fraction 1, which was subjected to column chromatography on silica gel to yield compounds **2** (20 mg) and **3** (15 mg) using light petroleum–EtOAc (20:1) as eluent; and light petroleum–acetone (100:5) yielded compound **1** (10 mg).

Compound **1**: white powder (EtOAc), mp 217–219°C. UV λ_{\max} (MeOH): 228.2 nm, ESI-MS: 699 $[M + H]^+$ $[\alpha]_D = -2$ (MeOH, *c* 0.01). ^1H NMR (300 MHz, in CDCl_3) see Table I, acetate at C-6: δ_{H} 2.15 (3H, s); acetate at C-13: δ_{H} 2.05 (3H, s), benzoate: δ_{H} 6.87–8.01 overlapped. ^{13}C NMR (75 MHz in CDCl_3) see Table I acetate at C-6: δ_{C} 21.4, 169.8; acetate at C-13: δ_{C} 21.3, 171.0; benzoate: 166.1, 165.4, 164.6, 133.1, 132.6, 132.4, 130.2, 129.8, 129.3, 129.2, 129.2, 128.3, 127.9, 127.6.

Compound **2**: white powder $[\alpha]_D = +39.0$ (MeOH, *c* 0.1), UV λ_{\max} (MeOH): 232 nm. ESI-MS: 516 $[M]^+$. ^1H NMR (300 MHz, in CDCl_3) see Table II, acetate: δ_{H} 1.60, 2.10, 2.21 (each 3H, s); benzoate: δ_{H} 7.44 (2H, t, *J* = 7.2 Hz), 7.56 (1H, t, *J* = 7.2 Hz), 8.04 (2H, d, *J* = 7.2 Hz). ^{13}C NMR (75 MHz in CDCl_3) see Table II acetate: δ_{C} 20.8, 21.1, 21.1, 169.4, 170.0, 170.0, benzoate: δ_{C} 128.4, 128.4, 129.0, 129.0, 120.1, 133.5, 164.9. All spectral data were accordance with the known compound 1 β ,6 α ,8 β -triacetoxy-9 α -benzoyloxy- β -dihydroagarofuran [3].

TABLE I ^{13}C NMR data for compound **1** in CDCl_3 [δ (ppm)]

No.	δ_{C}	δ_{H}	HMBC
1*	79.8	5.75 (1H, dd, <i>J</i> =9.6/4.2 Hz)	C-2, C-3, C-5, C-10, C-13
2	23.2	1.91 (2H, m)	C-1, C-3, C-4, C-10
3	26.4	2.32 (1H, m)	C-2, C-5, C-1, C-4
		1.61 (1H, m)	
4	33.4	2.32 (1H, m)	C-12, C-2, C-3, C-5, C-10, C-6
5	90.7		
6*	74.9	6.84 (1H, s)	C-4, C-5, C-7, C-8, C-10, C-11
7	53.3	2.66 (1H, d, <i>J</i> =3.9 Hz)	C-6, C-5, C-8, C-9, C-11
8*	71.3	5.77 (1H, dd, <i>J</i> =5.7/3.9 Hz)	C-6, C-7, C-10, C-9, C-11
9*	72.9	5.88 (1H, d, <i>J</i> =5.7 Hz)	C-8, C-7, C-10, C-13, C-1, C-5
10	51.1		
11	81.2		
12	15.1	1.04 (3H, d, <i>J</i> =7.2 Hz)	C-5, C-3, C-4
13*	61.1	4.95 (1H, d, <i>J</i> =13.2 Hz)	C-1, C-10, C-9, C-5
		4.87 (1H, d, <i>J</i> =13.2 Hz)	
14	24.6	1.67 (3H, s)	C-15, C-11, C-7
15	30.4	1.49 (3H, s)	C-14, C-11, C-7

* Signals of H-1, H-6, H-8, H-9, H-13 were also correlated with carbonyl carbon signals at δ 166.1, 169.8, 165.4, 164.6, 171.0 respectively.

All the signals were assigned by ^1H and ^{13}C NMR, HMQC, HMBC.

TABLE II ^1H and ^{13}C NMR data for **2** and **3** in CDCl_3 [δ (ppm)]

No	2		3	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	73.6	5.41 (1H, dd, $J=12.4/4.4$ Hz)	73.7	5.46 (1H, dd, $J=10.7/5.4$ Hz)
2	21.3	1.60 (1H, m)	21.5	1.59 (1H, m)
3	26.7	1.89 (1H, m)	26.8	1.88 (1H, m)
		1.44 (1H, m)		1.45 (1H, m)
4	33.8	2.22 (1H, m)	30.4	2.20 (1H, m)
		2.26 (1H, qui, $J=7.6$ Hz)		2.26 (1H, qui, $J=7.2$ Hz)
5	90.4		89.9	
6	75.8	5.73 (1H, s)	79.6	5.32 (1H, s)
7	53.0	2.48 (1H, d, $J=3.4$ Hz)	48.9	2.21 (1H, m)
8	76.1	5.25 (1H, d, $J=3.4$ Hz)	32.1	2.18 (1H, m)
9	77.2	5.03 (1H, s)	73.4	2.42 (1H, ddd, $J=16.6/6.8$ Hz)
				5.01 (1H, d, $J=6.8$ Hz)
10	50.0		50.6	
11	81.9		82.6	
12	17.3	1.03 (3H, d, $J=7.6$ Hz)	17.4	1.01 (3H, d, $J=7.2$ Hz)
13	18.7	1.46 (3H, s)	18.8	1.33 (3H, s)
14	25.6	1.48 (3H, s)	26.0	1.40 (3H, s)
15	30.9	1.41 (3H, s)	30.8	1.41 (3H, s)

Compound **3**: white powder, EI-MS: 458 $[\text{M}]^+$. ^1H NMR (300 MHz, in CDCl_3) see Table II, acetate: δ_{H} 1.61 (3H, s), 2.11 (3H, s), benzoate: δ_{H} 7.44 (2H, t, $J = 7.8$ Hz), 7.55 (1H, t, $J = 7.8$ Hz), 8.06 (2H, d, $J = 7.8$ Hz). ^{13}C NMR (75 MHz in CDCl_3) see Table II acetate: δ_{C} 20.8, 21.4, 170.0, 170.1, benzoate: δ_{C} 128.2, 129.7, 130.0, 133.2, 165.6. All spectral data were accordance with the known compound 1 β ,6 α -diacetoxyl-9 α -benzoyloxy- β -dihydroagarofuran [3].

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