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Chemical constituents from the stems of *Celastrus orbiculatus*

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[ABSTRACT] AIM: To investigate the chemical constituents from the stems of *Celastrus orbiculatus* Thunb.. **METHODS:** The chemical constituents were isolated and purified by silica gel, Sephadex LH-20 and ODS column chromatography. Their structures were elucidated on the basis of physical characteristics and spectral data. **RESULTS:** Eleven compounds were obtained and their structures were identified as 3*β*-hydroxy-2-oxoolean-12-ene-22, 29-lactone (**1**), 2, 6-dimethoxybenzoquinone (**2**), 3-oxoolean-12-en-28-oic acid (**3**), 3-oxo-24-norolean-12-en-28-oic acid (**4**), 23-hydroxybetulonic acid (**5**), vanillic acid (**6**), 23-hydroxy-3-oxoolean-12-en-28-oic acid (**7**), syringic acid (**8**), oleanolic acid (**9**), *β*-sitosterol (**10**), *β*-daucosterol (**11**). **CONCLUSION:** Compound **1** is a new triterpene; compounds **2**−**5** and **7** were isolated from this genus for the first time and compounds **8** and **9** were firstly isolated from this plant.
[KEY WORDS] *Celastrus orbiculatus* Thunb.; Triterpenes; Chemical constituents

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1 Introduction

Celastrus orbiculatus Thunb.(Celastraceae), widely distributed in China, has been used as folk remedy for rheumatoid arthritis, low back pain, muscles pain, toothache, amenorrhea, dysentery, bruises, snake bites, sores and carbuncle furuncle[1]. In the past years, a lot of sesquiterpenes, flavonoids, triterpenes and alkaloids have been isolated from the seeds, fruit and roots of *C. orbiculatus*[2]. However, the chemical constituents of the stems of *C. orbiculatus* have rarely been studied. It was reported recently that ethanol extract of the stems of *C. orbiculatus* had significant anti-tumor activities *in vivo* and *in vitro*[3]. And the total terpenes in *C. orbiculatus* could improve lipoprotein level and morphological structure of liver steatosis[4]. The pharmacological importance of *C. orbiculatus* prompted us to investigate its chemical constituents. As a result, eleven compounds were isolated, including six triterpenes (**1**, **3**, **4**, **5**, **7** and **9**), two phenolics (**6** and **8**), two steroids (**10** and **11**) and a benzoquinone (**2**). The structures of these compounds were identified as 3*β*-hydroxy -2-oxoolean-12-ene-22, 29-lactone (**1**), 2, 6-dimethoxybenzoquinone (**2**), 3-oxoolean-12-en-28-oic acid (**3**), 3-oxo-24-norolean-12-en-28-oic acid (**4**), 23-hydroxybetulonic acid (**5**), vanillic acid (**6**), 23-hydroxy-3-oxoolean-12-en-28-acid (**7**), syringic acid (**8**), oleanolic acid (**9**), *β*-sitosterol (**10**), *β*-daucosterol (**11**). Compound **1** is a new triterpene, compounds **2**-**5** and **7** were isolated from this genus for the first time and compounds **8** and **9** were firstly isolated from this plant.

2 Result and Discussion

Compound 1 $[\alpha]_D^{28}$ + 93.8° (*c* 0.123, $CHCl_3$), was obtained as white powder, and was positive for the Liebermann-Burehard reaction. The molecular formula was determined as $C_{30}H_{44}O_4$ by HRESI-MS *m/z* : 491.313 1 $[M + Na]^+$ (Calcd. 491.313 7). The IR spectrum showed absorption bands at 3 475, 1 766 and 1 707 cm^{-1}, suggesting the presence of a hydroxy group and two carbonyl groups. ^1H NMR spectrum of compound **1** showed the presence of seven tertiary methyl groups [δ_H 0.71, 0.87, 0.91, 0.93, 1.12, 1.20, 1.21 (each 3H, s)], two methine protons [δ_H 3.90 (1H, s), 4.15 (1H, d, *J* = 5.5 Hz)] attached to oxygen functionalities and one olefinic proton [δ_H 5.31(1H, t, *J* = 3.5 Hz)]. Its ^{13}C NMR spectrum revealed that its C-skeleton contains 30 carbons, including two carbonyl carbons (δ_C 211.1, 182.5), two car-

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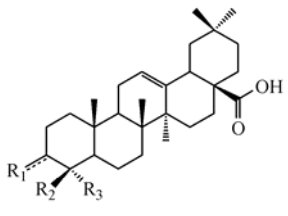
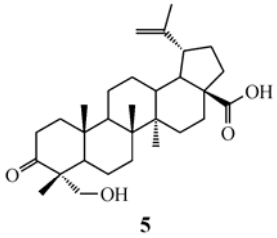
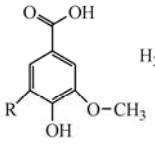
bons (δ_C 140.7, 124.1) attached to a double bond, two methine carbons (δ_C 83.1, 83.2) attached to oxygen functionalities and seven methyl carbons (δ_C 16.7, 16.8, 16.9, 21.2, 24.3, 25.2, 29.6). From the carbon number (C30) and the presence of seven tertiary methyl groups and one double bone compound **1** was deduced to be an oleanane-type triterpene.

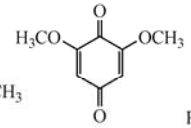




5

	R_1	R_2	R_3
3	O	CH_3	CH_3
4	O	H	CH_3
7	O	CH_3	CH_2OH
9	β-OH	CH_3	CH_3





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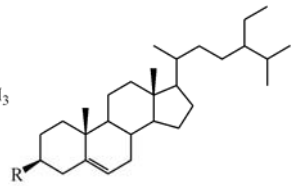

R	
6	H
8	OCH_3

R	
10	OH
11	OGlc

The structure of compound **1** was determined by a detailed analysis of the HSQC, HMBC and ROESY spectral data as well as the ^{1}H and ^{13}C NMR spectral data. ^{13}C NMR spectral data of compound **1** were similar to those of wilforlide A[5] and wilforlide B[6], except for ring A. These data suggested that the *B-E* ring systems of compound **1** were the same as in wilforlides A and B. In the HMBC spectrum of **1**, the methine proton signal at δ_H 3.90 was correlated with the carbon signals at δ_C 45.9 (C-4), 29.6 (C-23) and 16.8 (C-24), suggesting that the hydroxy group was located at C-3. The proton signal at δ_H 2.48 (H_β-1) was correlated with the carbon signals at δ_C 83.1 (C-3), 43.8 (C-10), 54.8 (C-5) and the ketone carbon signal at δ_C 211.1, and the proton signal at δ_H 3.90 (H-3) was correlated with the ketone carbon signal at δ_C 211.1. Thus, the ketone group was located at C-2. Furthermore, the β-configuration of the hydroxy group was confirmed from the ROESY spectrum, which showed significant through-space correlation between H-23 (δ_H 1.20) and H-5 (δ_H 1.46, Hα), H-23 (δ_H 1.20) and H-3 (δ_H 3.90). Based upon the above information, the structure of compound **1** was unambiguously established as 3β-hydroxy-2-oxoolean-12 -ene-22, 29-lactone. The full assignments of the ^{1}H and ^{13}C NMR data of **1** (Table 1) were achieved in combination with HMBC, HSQC and ROESY experiments (the structure of compound **1** and some key HMBC and ROESY correlations are shown in Figs. 1 and 2, respectively).

Table 1 ^{1}H and ^{13}C NMR spectral data for compound 1 in $CDCl_3$ (500 MHz for H, 125 MHz for C)[a]

Proton	δ_H	Carbon	δ_C
1α	2.08 (d, 12.5)	**1**	53.5
1β	2.48 (d, 12.5)	**2**	211.1
3α	3.90 (s)	**3**	83.1
5	1.46 (m)	**4**	45.9
6	1.45 (m)	**5**	54.8
	1.68 (m)	**6**	18.8
7	1.48 (m)	**7**	33.0
	1.62 (m)	**8**	40.1
9	1.86 (m)	**9**	47.7
11	1.87 (m)	**10**	43.8
	1.94 (m)	**11**	23.7
12	5.31 (t, 3.5)	**12**	124.1
15	1.10 (m)	**13**	140.7
	1.74 (m)	**14**	42.9
16	0.89 (m)	**15**	24.5
	1.92 (m)	**16**	25.4
18	2.16 (m)	**17**	35.5
19	1.51 (m)	**18**	43.6
	1.92 (m)	**19**	40.0
21α	1.94 (m)	**20**	39.7
21β	2.26 (d, 11.5)	**21**	34.0
22	4.15 (d, 5.5)	**22**	83.2
23	1.20 (s)	**23**	29.6
24	0.71 (s)	**24**	16.8
25	0.91 (s)	**25**	16.7
26	0.93 (s)	**26**	16.9
27	1.12 (s)	**27**	24.3
28	0.87 (s)	**28**	25.2
30	1.21 (s)	**29**	182.5
		30	21.2

[a] Data were recorded on a Bruker AV-500 spectrometer, assignments were confirmed by HSQC and HMBC.

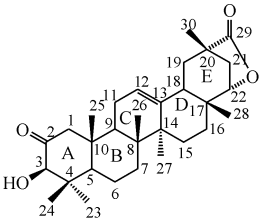

Fig. 1 Structure of compound 1

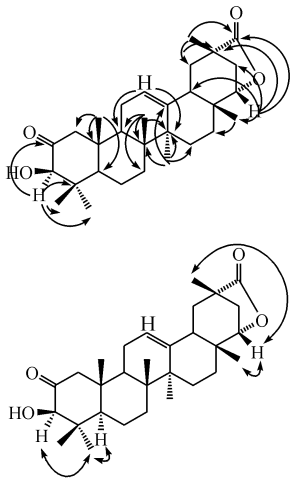

Fig. 2 Key HMBC (H→C) and ROESY (↔) correlations of compound 1