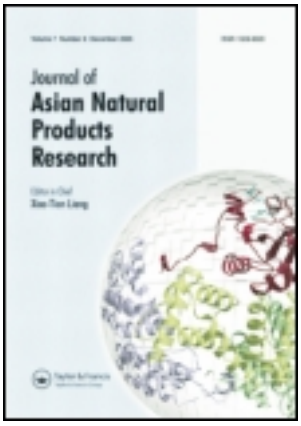

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Two new sesquiterpene polyol esters from the root barks of *Celastrus angulatus*

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Two new sesquiterpene polyol esters from the root barks of *Celastrus angulatus*

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Angulatin F (**1**) and angulatin I (**2**), two new sesquiterpene polyol esters, were isolated from the root barks of *Celastrus angulatus*, together with six known compounds 1β,2β-diacetoxy-4α,6α-dihydroxy-8α-isobutanoyloxy-9β-benzoyloxy-15-(α-methyl) butanoyloxy-β-dihydroagrofuran (**3**), angulatin A (**4**), angulatin B (**5**), celangulatin E (**6**), 1β,2β,15-triacetoxy-4α,6α-dihydroxy-8α-isobutanoyloxy-9β-benzoyloxy-β-dihydroagrofuran (**7**), and celangulin I (**8**). The structures of **1** and **2** were elucidated as 1β,2β,6α,15-tetraacetoxy-4α-hydroxy-8β,9α-difuroyloxy-β-dihydroagrofuran and 1β,2β,6α,8β,15-pentaacetoxy-4α-hydroxy-9β-furoyloxy-β-dihydroagrofuran by spectroscopic means.

Keywords: *Celastrus angulatus*; Celastraceae; sesquiterpene polyol ester; angulatin F; angulatin I

1. Introduction

Celastrus angulatus (Celastraceae) is a perennial shrub widely distributed in the mountain areas of Changjiang and Huang He river basin of China. As a Chinese folk medicine, its root barks and leaves have long been used to kill harmful insects and also to treat furuncles and remove heat [1]. Constituents of the root barks of *C. angulatus* have been reported as sesquiterpenes, alkaloids, triterpenes, and flavonoids [2–19]. In this paper, we report the isolation and structural elucidation of two new sesquiterpene polyol esters named angulatin F (**1**) and angulatin I (**2**), together with six known compounds 1β,2β-diacetoxy-4α,6α-dihydroxy-8α-isobutanoyloxy-9β-benzoyloxy-15-(α-methyl) butanoyloxy-β-dihydroagrofuran (**3**) [9], angulatin A (**4**) [4,5], angulatin B (**5**) [5,6], celangulatin E (**6**) [15], 1β,2β,15-triacetoxy-4α,6α-dihydroxy-8α-isobutanoyloxy-9β-benzoyloxy-β-dihydroagrofuran (**7**) [13] and celangulin I (**8**) [2] (Figure 1).

2. Results and discussion

An 80% CH_3OH-soluble fraction of the C_6H_6 extract of the root barks of *C. angulatus* was repeatedly chromatographed on silica gel column to give compounds **1**–**8**.

The molecular formula of compound **1** was shown as $C_{33}H_{38}O_{16}$ by the pseudo-molecular ion in HR-ESI-MS at *m/z* 713.2057 $[M + Na]^+$. Its IR spectrum showed the absorption bands of hydroxyl at 3438 cm^{-1} and carbonyl at 1743 cm^{-1}. The ^{13}C NMR and DEPT spectra indicated the presence of a β-dihydroagarofuran unit including three methy1 (δ_C 24.3, 25.6, and 29.5), two methylene (δ_C 41.9 and 65.6),

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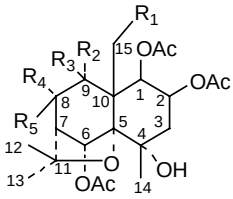
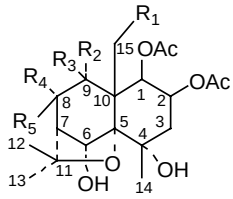




1: R_1 = OAc, R_2 = R_5 = OFu, R_3 = R_4 = H

2: R_1 = R_5 = OAc, R_3 = OFu, R_2 = R_4 = H

3: R_1 = OiPet, R_3 = OBz, R_4 = OiBu, R_2 = R_5 = H

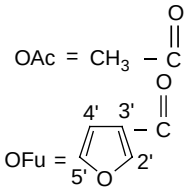
4: R_1 = R_4 = OiBu, R_3 = OBz, R_2 = R_5 = H

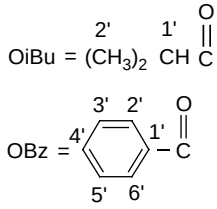
5: R_1 = R_5 = OiBu, R_2 = OFu, R_3 = R_4 = H

6: R_1 = OAc, R_2 = OFu, R_5 = OiBu, R_3 = R_4 = H

7: R_1 = OAc, R_3 = OBz, R_4 = OiBu, R_2 = R_5 = H

8: R_1 = R_5 = OAc, R_3 = OBz, R_2 = R_4 = H





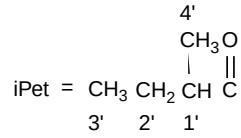
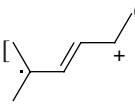


Figure 1. Structures of compounds **1**–**8**.

six methine (δ_C 53.8, 67.8, 70.5, 71.6, 75.3, and 76.5), and four quaternary (δ_C 54.3, 69.9, 83.1, and 91.3) carbons, whose chemical shifts were closely similar to those of angulatin B (**5**) and celangulatin E (**6**). Its ^{1}H NMR spectrum exhibited signals assignable to protons on the methines carrying five secondary ester groups at δ_H 5.52 (1H, s), 5.52 (1H, m), 6.56 (1H, s), 5.42 (1H, d, J = 2.9 Hz), and 5.66 (1H, s), and on the methylene bearing ester group at δ_H 4.69 (1H, d, J = 12.9 Hz) and 5.02 (1H, d, J = 12.9 Hz), and one hydroxyl group at δ_H 2.72 (1H, s). The NMR spectra suggested the presence of four acetate esters [δ_C 169.5 (CO), 169.8 (CO), 169.9 (CO), 170.5 (CO), 20.5 (CH_3), 21.1 (CH_3), 21.1 (CH_3), 21.5 (CH_3); δ_H 1.66 (3H, s), 2.09 (3H, s), 2.10 (3H, s), 2.14 (3H, s)] and two furoate esters [δ_C 161.6 (CO), 148.9 (CH), 118.8 (C), 110.0 (CH), 144.0 (CH); 160.5 (CO), 148.7 (CH), 109.8 (CH), 118.0 (C), 144.0 (CH); δ_H 8.22 (1H, br d, J = 1.0 Hz), 6.87 (1H, br d, J = 1.5 Hz), 7.47 (1H, dd, J = 1.0, 1.5 Hz), 8.02 (1H, br d, J = 1.0 Hz), 6.74 (1H, br d, J = 1.5 Hz), 7.44 (1H, dd, J = 1.0, 1.5 Hz)]. The characteristic fragments in its EI-MS at *m/z* 43 [$CH_3C \equiv O^+$], 95 [], and 192 [] further confirmed the above results.

According to the ^{1}H–^{1}H COSY spectrum of compound **1**, the protons at δ 4.69 and 5.02, 1.98 and 2.21, 5.52, 2.43, 5.42 were assigned to H-15, H-3, H-2, H-7, H-8, respectively. In addition, the HSQC experiment revealed the correlations between the proton signals at δ_H 5.42 (H-8), 2.43 (H-7), 6.56, 5.66 and the corresponding carbon signals at δ_C 76.5 (C-8), 53.8 (C-7), 75.3, 71.6, respectively, as well as between the proton signals at δ_H 5.52 and the carbon signals at δ_C 70.5 and 67.8. Moreover, after a detailed inspection of the HMBC spectrum, the long-range correlations between H-7 at δ_H 2.43 and

the carbon signals at δ_C 75.3, 76.5 (C-8), and 71.6, the proton signals at δ_H 4.69 (H-15a), 5.02 (H-15b) and the carbon signal at δ_C 71.6, and the proton signal at δ_H 1.98 (H-3a) and the carbon signals at δ_C 70.5 and 67.8, led to the assignment of the other methine protons and carbons of the unit, i.e. H-1/2 at δ_H 5.52, H-6 at δ_H 6.56, H-9 at δ_H 5.66, and C-9 at δ_C 71.6, C-6 at δ_C 75.3, C-1 or C-2 at δ_C 70.5 or 67.8. Furthermore, by comparing with the ^{13}C NMR spectral data of celangulatin E [15], the chemical shifts of C-1 and C-2 were distinguished at δ_C 70.5 and 67.8, respectively.

In the ^{1}H NMR spectrum, no obvious coupling ($J_{9,8} = 0$ Hz) between H-9 (s) and H-8 suggested that both H-9 and H-8 have an equatorial orientation, with the dihedral angle between H-8 and H-9 near 90°. The NOESY correlations (Figure 2) between H-15, H-6 and H-9, H-1 and H-3ax, H-8 and H-13, H-7 and H-12 indicated the β-orientation of H-6 and H-9 and the α-orientation of H-1 and H-8. The baseline width of H-2 was less than 10, which indicated that H-2 was equatorial and at the α-orientation. The configurations of C-10 and C-5 were determined by the NOESY correlations between H-15 and H-9, H-6, H-14.

The location of the six ester groups was determined by the correlations in the HMBC spectrum between H-1, 2 at δ_H 5.52 and the carbon signals at δ_C 169.5 and 169.8, H-6 and the carbon at δ_C 169.9, H-15 and the carbon at δ_C 170.5, H-8 and the carbon at δ_C 161.6, H-9 and the carbon at δ_C 160.5.

Thus, the structure of **1** was elucidated to be 1β,2β,6α,15-tetraacetoxy-4α-hydroxy-8β,9α-difuroyloxy-β-dihydroagrofuran. A complete assignment of ^{1}H and ^{13}C NMR spectral data is given in Table 1.

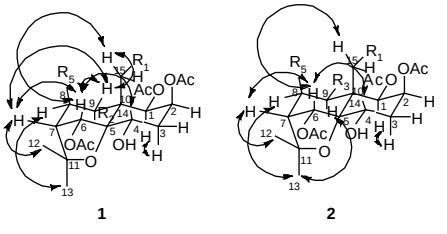


Figure 2. Major NOESY correlations in **1** and **2**.

The molecular formula of compound **2** was shown as $C_{30}H_{38}O_{15}$ by the pseudo-molecular ion in HR-ESI-MS at *m/z* 661.2105 $[M + Na]^+$. Its IR spectrum showed the absorption bands of hydroxyls at 3448 cm^{-1} and carbonyls at 1744 cm^{-1}. Its ^{1}H and ^{13}C NMR (DEPT) spectral data suggested the presence of a β-dihydroagarofuran sesquiterpene substituted with five acetate esters and one furoate ester (Table 2). The characteristic fragments in its EI-MS at *m/z* 43, 95, and 192 further confirmed the above results.

From the ^{1}H NMR and COSY spectra of compound **2**, the doublets at δ_H 4.88 ($J = 13.4$ Hz) and 4.98 ($J = 13.4$ Hz), the doublet at δ 5.43 ($J = 3.9$ Hz), the multiplet at δ 5.35, the double doublets at δ 1.93 ($J = 2.5$, 15.2 Hz) and 2.16 ($J = 4.3$, 15.2 Hz), the doublets at δ 2.35 ($J = 2.9$ Hz) and 5.52 ($J = 2.9$ Hz) were assigned to H-15, H-1, H-2, H-3, H-7, and H-8, respectively. In an investigation of the HSQC spectrum of **2**, the methine carbon signals at δ_C 71.1 and 69.8 correlated with the proton signal at δ_H 5.52 (2H), the methine carbon signal at δ_C 75.0 with the proton signal at δ_H 6.94, the carbon signal at δ_C 53.2 with H-7 at δ_H 2.35, and the methyl carbon signals at δ_C 24.1, 24.4, 29.3 with the proton signals at δ_H 1.49, 1.60, 1.54, respectively. The HMBC correlations of H-7 with the methine carbon signals at δ_C 71.1, 69.8, 75.0, H-1 and H-15 with the methine carbon signal at δ_C 71.1, the methine proton signal at δ_H 6.94 (s) with the methine carbon signal at δ_C 69.8, H-8 with the methine carbon signal at δ_C 75.0, and H-3a with the methyl carbon signal at δ_C 24.1, resulted in the assignment of H-6 at δ_H 6.94, H-8/9 at δ_H 5.52, H-14 at δ_H 1.49, and C-9 at δ_C 71.1,C-6 at δ_C 75.0, C-8 at δ_C 69.8, C-14 at δ_C 24.1. Additionally, by comparing the ^{13}C NMR spectral data of **2** with other 1,2,4,6,8,9,15-heptasubstituted β-dihydroagarofurans [4,11–13], the

Table 1. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **1** in $CDCl_3$.

No.		δ_H (J, Hz)	δ_C (DEPT)	HMBC (δ_H/δ_C)
1		5.52, s	70.5 (CH)	C-9, C-10, C-15, OAC-1 (C=O)
2		5.52, m	67.8 (CH)	C-1, C-4, C-10, OAC-2 (C=O)
3	Heq	1.98, dd (2.0, 14.1)	41.9 (CH_2)	C-1, C-2, C-4, C-5, C-14
	Hax	2.21, dd (3.2, 14.1)		C-4, C-14
4			69.9 (C)	
5			91.3 (C)	
6		6.56, s	75.3 (CH)	C-5, C-7, C-8, C-10, C-11, OAC-6 (C=O)
7		2.43, d (2.9)	53.8 (CH)	C-5, C-8, C-9, C-13
8		5.42, d (2.9)	76.5 (CH)	C-6, C-9, C-10, OFu-8 (C=O)
9		5.66, s	71.6 (CH)	C-5, C-7, C-10, C-15, OFu-9 (C=O)
10			54.3 (C)	
11			83.1 (C)	
12		1.60, s	29.5 (CH_3)	C-7, C-11, C-13
13		1.68, s	25.6 (CH_3)	C-7, C-11, C-12
14		1.48, s	24.3 (CH_3)	C-3, C-4, C-5
15	Ha	4.69, d (12.9)	65.6 (CH_2)	C-5, C-9, C-10, OAC-15 (C=O)
	Hb	5.02, d (12.9)		C-5, C-9, C-10, OAC-15 (C=O)
OAC-1	C=O		169.5 (C)	
		1.66, s	20.5 (CH_3)	OAC-1 (C=O)
OAC-2	C=O		169.8 (C)	
		2.10, s	21.13 (CH_3)	OAC-2 (C=O)
OAC-6	C=O		169.9 (C)	
		2.14, s	21.5 (CH_3)	OAC-6 (C=O)
OAC-15	C=O		170.5 (C)	
		2.09, s	21.11 (CH_3)	OAC-15 (C=O)
OFu-8	C=O		161.6 (C)	
	2′	8.22, br d (1.0)	148.7 (CH)	OFu-8 (C-3′), OFu-8 (C-4′), OFu-8 (C-5′)
	3′		118.8 (C)	
	4′	6.87, br d (1.5)	110.0 (CH)	OFu-8 (C=O), OFu-8 (C-2′), OFu-8 (C-3′), OFu-8 (C-5′)
	5′	7.47, dd (1.0, 1.5)	144.0 (CH)	OFu-8 (2′), OFu-8 (C-3′), OFu-8 (C-4′)
OFu-9	C=O		160.5 (C)	
	2′	8.02, br d (1.0)	148.9 (CH)	OFu-9 (C-3′), OFu-9 (C-4′), OFu-9 (C-5′)

Table 1 – *continued*

No.	δ_H (J, Hz)	δ_C (DEPT)	HMBC (δ_H/δ_C)
3′		118.0 (C)	
4′	6.74, br d (1.5)	109.8 (CH)	OFu-9 (C=O), OFu-9 (C-2′), OFu-9 (C-3′), OFu-9 (C-5′)
5′	7.44, dd (1.0, 1.5)	144.0 (CH)	OFu-9 (2′), OFu-9 (C-3′), OFu-9 (C-4′)
OH-4	2.72, s		C-3, C-4, C-5, C-14

chemical shifts of C-12 and C-13 were distinguished at δ_C 29.3 and 24.4, respectively.

After a detailed examination of the HMBC spectrum, the long-range correlations between H-1, H-2 and the carbon signal at δ_C 169.5, H-6 and the carbon signal at δ_C 169.7, H-8 and the carbon signal at δ_C 169.9, H-9 and the carbon signal at δ_C 161.0, as well as H-15 and the carbon signal at δ_C 170.3, suggested that the position of six ester groups would be at C-1, C-2, C-6, C-8, C-9, and C-15, respectively.

The stereochemical assignment of **2** was based on the NOESY spectrum as well as on ^{1}H NMR analysis (Figure 2). In the NOESY spectrum, the correlations between H-15 and H-6, H-1 and H-3ax, H-14 and H-6, H-8, 9 and H-13 suggested the α-configuration for H-1, H-3ax, H-8, H-9, and OH-4. The baseline width of H-2 was less than 20, which indicated that H-2 was equatorial and at the α-orientation. The configurations of C-10 and C-5 were determined by the NOESY correlations between H-15 and H-6, H-14.

Therefore, the structure of **2** was determined to be 1β,2β,6α,8β,15-pentaacetoxy-4α-hydroxy-9β-furoyloxy-β-dihydroagrofuran. A complete assignment of ^{1}H and ^{13}C NMR spectral data is given in Table 2.

3. Experimental

3.1 General experimental procedures

Optical rotations were taken on a Perkin-Elmer 341 Polarimeter. IR spectra were obtained on a Testscan Shimadzu FT-IR 8000 series HYPER infrared spectrometer. NMR spectra were recorded on a Bruker DPX400 spectrometer. The ESI-MS spectra were recorded on a Q-Tof Micro™ instrument (Waters Micromass Corp., Leederville, WA, USA), and EI-MS on a Autospec-Ultima ETOF spectrometer. Silica gel for TLC and column chromatography was obtained from Qingdao Marine Chemical Inc., Qingdao, China.

Table 2. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectral data of **2** in $CDCl_3$.

No.		δ_H (J, Hz)	δ_C (DEPT)	HMBC (δ_H/δ_C)
1		5.43, d (3.9)	75.9 (CH)	C-9, C-10, C-15, OAC-1 (C═O)
2		5.35, m	67.8 (CH)	OAC-2 (C═O)
3	Heq	1.93, dd (2.5, 15.2)	41.9 (CH_2)	C-1, C-2, C-4, C-5, C-14
	Hax	2.16, dd (4.3, 15.2)		
4			69.7 (C)	
5			91.7 (C)	
6		6.94, s	75.0 (CH)	C-4, C-5, C-7, C-8, C-10, C-11, OAC-6 (C═O)
7		2.35, d (2.9)	53.2 (CH)	C-5, C-6, C-8, C-9
8		5.52, d (2.9)	69.8 (CH)	C-6, C-7, C-10, OAC-8 (C═O)
9		5.52, s	71.1 (CH)	C-1, C-7, C-10, C-15, OFu-9 (C═O)
10			53.0 (C)	
11			82.5 (C)	
12		1.54, s	29.3 (CH_3)	C-7, C-11, C-13
13		1.60, s	24.4 (CH_3)	C-7, C-11, C-12
14		1.49, s	24.1 (CH_3)	C-3, C-4, C-5
15	Ha	4.88, d (13.4)	59.8 (CH_2)	C-5, C-9, C-10, OAC-15 (C═O)
	Hb	4.98, d (13.4)		C-5, C-9, C-10, OAC-15 (C═O)
OAC-1	C═O		169.5** (C)	
		1.63, s	20.3 (CH_3)	OAC-1 (C═O)
OAC-2	C═O		169.5** (C)	
		2.06*, s	21.0*** (CH_3)	OAC-2 (C═O)
OAC-6	C═O		169.7** (C)	
		2.08*, s	21.2*** (CH_3)	OAC-6 (C═O)
OAC-8	C═O		169.9** (C)	
		2.13*, s	21.5*** (CH_3)	OAC-8 (C═O)
OAC-15	C═O		170.3 (C)	
		2.31, s	21.6 (CH_3)	OAC-15 (C═O)
OFu	C═O		161.0 (C)	
	2′	8.11, br d (1.0)	148.4 (CH)	OFu-9 (C-3′), OFu-9 (C-4′), OFu-9 (C-5′)
	3′		118.4 (C)	

Table 2 – *continued*

No.	δ_H (*J*, Hz)	δ_C (DEPT)	HMBC (δ_H/δ_C)
4′	6.73, br d (1.7)	109.5 (CH)	OFu-9 (C-2′), OFu-9 (C-3′), OFu-9 (C-5′)
5′	7.43, dd (1.0, 1.7)	144.2 (CH)	OFu-9 (2′), OFu-9 (C-3′), OFu-9 (C-4′)
OH-4	2.70, br		

Note: *, **, ***, the assignments of these signals may be interchangeable.

3.2 Plant material

Root barks of *C. angulatus* were collected in Nanyan county, Henan province, China, in May 2007, and identified by Professor C.S. Zhu, Henan Agricultural University. A voucher specimen (CA06) is deposited at the Key Laboratory of Natural Products, Henan Academy of Science, China.

3.3 Extraction and isolation

Dried root barks (1 kg) of *C. angulatus* were extracted with benzene (6 liters × 3) under reflux and filtered. The filtrate was concentrated to give a yellow semi-solid residue (31.2 g). The residue was dissolved in 80% methanol and extracted with petroleum ether. The 80% MeOH extract (27.5 g) was chromatographed on a silica gel (200–300 mesh) column eluting with a gradient system of petroleum ether–EtOAc (10:1, 9:1, 7:1, 6:1, 5:1, 4:1, 7:3, 6:4, 4:6) to give 80 fractions (each 250 ml). Fractions 69–70 (350 mg) were combined and subjected to preparative HPLC (RP-18, MeOH–H_2O, 65:35) to afford compound **1** (40 mg). Fraction 76 (210 mg) was subjected to preparative HPLC (RP-18, MeOH–H_2O, 65:35) to afford compounds **2** (45 mg) and **8** (95 mg). Compound **3** (18 mg) was obtained from fraction 38 (90 mg) and purified by preparative HPLC (RP-18, MeOH–H_2O, 65:35). Compound **4** (60 mg) was obtained from fractions 42–43 (300 mg) and purified by crystallization. Compounds **5** (25 mg) and **6** (40 mg) were obtained from fraction 54 (120 mg) and purification through preparative HPLC (RP-18, MeOH–H_2O, 65:35). Compound **7** (95 mg) was obtained from fraction 61 (310 mg) by purification via crystallization.

3.3.1 Angulatin F (*1*)

$C_{33}H_{38}O_{16}$. Pale solid. $[\alpha]_D^{25}$ −21.2 (MeOH, $c = 0.20$). IR ν_{max} cm^{-1}: 3439, 2927, 1743, 1631, 1432, 1370, 1311, 1232, 1160, 1079, 1048, 874, 760, 603; The ^1H and ^{13}C NMR spectral data see Table 1.

EI-MS *m/z*: 192 (49.1%), 95 (100%), 43 (44.7%); HR-ESI-MS *m/z*: 713.2057 $[M + Na]^+$ (calcd for $C_{33}H_{38}O_{16}Na$, 713.2056).

3.3.2 Angulatin I (2)

$C_{30}H_{38}O_{15}$. Pale solid. $[\alpha]_D^{25}$ −18.5 (MeOH, $c = 0.20$). IR ν_{max} cm^{-1}: 3447, 2980, 1744, 1636, 1576, 1508, 1431, 1371, 1305, 1235, 1157, 1080, 1047; The ^1H and ^{13}C NMR spectral data see Table 2. EI-MS *m/z*: 192 (40.1%), 95 (100%), 43 (45.6%); HR-ESI-MS *m/z*: 661.2105 $[M + Na]^+$ (calcd for $C_{30}H_{38}O_{15}Na$, 661.2106).

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