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STRUCTURE OF SESQUITERPENOIDS FROM *CELASTRUS ANGULATUS*

YONG Q. TU* and YUN J. HU,

Department of Chemistry, Lanzhou University, Lanzhou, Gansu Province, People's Republic of China

ABSTRACT.—Three new β -dihydroagarofuran sesquiterpene polyol esters were isolated from the seed oil of *Celastrus angulatus*. Their structures have been elucidated, on the basis of uv, ir, mass, and 1D and 2D nmr spectroscopy, as 6 α -acetoxy-1 β ,8 β ,9 β -tribenzoyloxy- β -dihydroagarofuran [1], 1 β ,8 β ,13-triacetoxy-9 β -benzoyloxy- β -dihydroagarofuran [2], and 1 β ,8 α ,13-triacetoxy-9 β -benzoyloxy- β -dihydroagarofuran [3].

Celastrus angulatus Max. (Celastraceae) is widely distributed in China, where its root bark and leaves are used traditionally as natural insecticides (1). An insecticidal β -dihydroagarofuran polyol ester of the root bark has been isolated (2) which is similar in structure to those isolated from other species of Celastraceae plants (3,4). However, recent investigation showed that the seed oil of *C. angulatus* also contained constituents of this kind, and this paper presents the structure elucidation of three major components.

RESULTS AND DISCUSSION

Compound 1 analyzed for $C_{38}H_{40}O_9$ by hrms. The ir spectrum revealed characteristic absorptions of ester at ν 1726 cm^{-1} and phenyl at ν 1605 and 1451 cm^{-1} . The eims exhibited peaks characteristic of acetyl (m/z 43, 41%) and benzoyl (m/z 105, 100%) groups. In agreement with these data, the 1H -nmr and ^{13}C -nmr spectra suggested the presence of one acetate ester group [1H nmr δ

2.13 (3H, s); ^{13}C nmr δ 21.2 (Me) and 169.9 (-CO₂-)] and three benzoate ester groups [1H nmr δ 6.83–7.58 (15H, m); ^{13}C nmr δ 127.4–133.0 (m, Ph), 164.8, 165.3, and 165.4 (3 \times -CO₂-)]. In addition, the ^{13}C -nmr and DEPT spectra indicated that the remaining moiety contained fifteen carbons: four methyls (δ 12.4, 16.7, 24.1, and 30.5), two methylenes (δ 22.2 and 26.5), six methines (δ 33.8, 52.8, 71.6, 74.3, 74.9, and 79.0) and three quaternary carbons (δ 49.0, 81.7, and 91.1). These ^{13}C -nmr data (Table 1) together with the 1H -nmr coupling patterns and coupling constants (Table 2) were very close to those assigned to the 1,6,8,9-tetra-substituted β -dihydroagarofuran skeleton (5). Therefore, 1 had ester groups at C-1, C-6, C-8, and C-9.

In the 1H -nmr spectrum, the double doublet at δ 5.56 (1H, $J = 4.5, 12$ Hz) and the singlet at δ 6.25 (1H) were assigned to H_{ax}-1 and H_{ax}-6, respectively, since in all compounds of this class

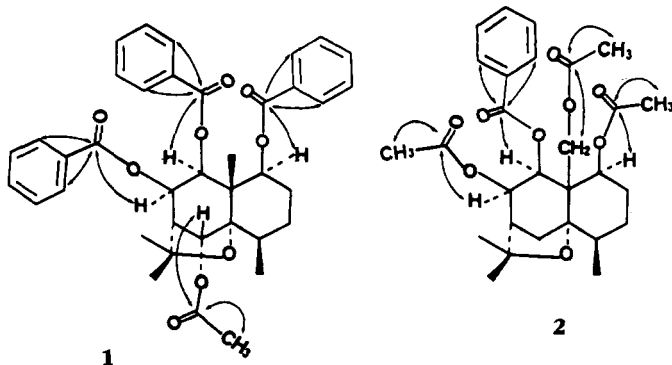
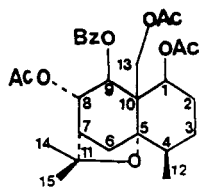


FIGURE 1. COLOC of Compounds 1 and 2.



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H-1 and H-6 generally have axial stereochemistry and H_{ax} -6 and H_{eq} -7 generally show weak coupling ($J_{6,7} = 0$ Hz) (2,6). The double doublet at δ 5.82 (1H, $J = 4, 5$ Hz) and the doublet at δ 5.78 (1H, $J = 5$ Hz) were assigned, in view of their coupling patterns and constants, to H-8 and H-9, respectively (other assignments are summarized in Table 2). The stereochemistry for H-8 and H-9 was determined by a NOESY spectrum, which showed cross peaks between H-14 (δ 1.64) and H-8 (δ 5.82), and between H-14 and H-9 (δ 5.78), suggesting H-8 to be equatorial and H-9 to be axial.

The ester distribution was determined on the basis of a 1H - ^{13}C long-range correlation (COLOC) spectrum

(5,7), which showed cross peaks between H-1 (δ 5.56), H-8 (δ 5.82) and H-9 (5.78) and the carbonyls (δ 165.4, 165.3, and 164.8) of three benzoate esters, respectively, between H-6 (δ 6.25) and the carbonyl (δ 169.9) of the acetate ester, and between the carbonyl (δ 169.9) of the acetate ester and its methyl (δ 2.13) (Figure 1). This indicated that the three benzoate ester groups were located at C-1, C-8, and C-9, respectively, and that the acetate ester was at C-6. Thus, the structure of **1** was elucidated as 6 α -acetoxy-1 β ,8 β ,9 β -tribenzoyloxy- β -dihydroagarofuran.

Compound **2** analyzed for $C_{28}H_{36}O_9$ by hrms. The uv, ir, and mass and nmr spectral data suggested the presence of three acetate esters, one benzoate ester, and the 1,8,9,13-tetrasubstituted β -dihydroagarofuran parent (8). In the 1H -nmr spectrum, the double doublet at δ 5.30 (1H, $J = 4.8, 12$ Hz) was assigned to H_{ax} -1, the double doublet at δ 5.51 (1H, $J = 4, 5.3$ Hz) to H-8, the doublet at δ 5.63 (1H, $J = 5.3$ Hz) to H-9, and the AB quartet at δ 4.75 and 4.82 ($J = 13$ Hz) to H-13 (other assignments

TABLE 1. ^{13}C -nmr Chemical Shifts of **1-3** (400 MHz, $CDCl_3$, TMS).

Carbon	Compound		
	1 ^a	2	3
C-1	79.0 (CH)	79.0 (CH) ^b	75.6 (CH) ^b
C-2	22.2 (CH ₂)	23.4 (CH ₂)	22.7 (CH ₂)
C-3	26.5 (CH ₂)	26.7 (CH ₂)	26.4 (CH ₂)
C-4	33.8 (CH)	39.9 (CH)	39.8 (CH)
C-5	91.1 (C)	88.5 (C)	88.2 (C)
C-6	74.9 (CH)	32.0 (CH ₂)	36.2 (CH ₂)
C-7	52.8 (CH)	48.0 (CH)	47.3 (CH)
C-8	71.6 (CH)	74.3 (CH) ^b	76.0 (CH) ^b
C-9	74.3 (CH)	79.0 (CH) ^b	78.2 (CH) ^b
C-10	49.0 (C)	49.0 (C)	50.1 (C)
C-11	81.7 (C)	80.5 (C)	81.6 (C)
C-12	16.7 (Me)	16.1 (Me)	16.6 (Me)
C-13	12.4 (Me)	61.2 (CH ₂)	61.5 (CH ₂)
C-14	24.1 (Me)	22.9 (Me)	24.3 (Me)
C-15	30.5 (Me)	29.9 (Me)	30.7 (Me)

^aAssignments of ^{13}C -nmr chemical shifts for **1** were based on comparison with data from Sang *et al.* (5).

^bData in the same column may be exchangeable.

TABLE 2. ¹H-nmr Spectra of 1-3 (400 MHz, CDCl₃, TMS).^a

Proton	Compound		
	1	2	3
H-1	5.56 dd(4.5, 12)	5.30 dd(4.8, 12)	5.30 dd(4, 12)
H-2	1.40-2.32	1.66-2.80	1.37-2.72
H-3	1.40-2.32	1.66-2.80	1.37-2.72
H-4	1.40-2.32	1.66-2.80	1.37-2.72
H-6	6.25 s	1.66-2.80	1.37-2.72
H-7	2.60 dd(4)	1.66-2.80	1.37-2.72
H-8	5.82 dd(4, 5)	5.51 dd(4, 5.3)	5.47 dd(3.2, 9.7)
H-9	5.78 d(5)	5.63 d(5.3)	5.97 d(9.7)
H-12	1.12 d(8)	1.11 d(7.8)	1.09 d(7.6)
H-13	1.67 s	4.75, 4.82 (ABq)(13)	4.39, 4.86 ABq(13)
H-14	1.64 s	1.50 s	1.54 s
H-15	1.47 s	1.18 s	1.17 s

^aCoupling constants are in parentheses.

are summarized in Table 2). The stereochemistry for H-8 and H-9 was determined from the NOESY spectrum, which showed the cross peaks between H-14 (δ 1.50) and H-8 (δ 5.51) and between H-14 and H-9 (δ 5.63), suggesting that H-8 has equatorial stereochemistry and that H-9 is axial. The ester distribution was also determined from a COLOC spectrum (Figure 1), which showed the cross peaks between H-1 (δ 5.30), H-8 (δ 5.51), and H-13 (4.75 and 4.82) and the carbonyls (δ 170.5, 169.8, and 170.8) of three acetate esters, respectively, and between H-9 (δ 5.63) and the carbonyl (δ 165.3) of the benzoate ester. These data indicated that three acetate esters were located at C-1, C-8, and C-13, respectively, and that the benzoate ester was at C-9. Thus, the structure of **2** was elucidated as 1 β ,8 β ,13-triacetoxy-9 β -benzoyloxy- β -dihydroagarofuran.

Compound **3** analyzed for C₂₈H₃₆O₉ by hrms. As with compound **2**, the uv, ir, mass, and nmr spectral data suggested that **3** also contained three acetate esters, one benzoate ester, and the 1,8,9,13-tetra-substituted β -dihydroagarofuran skeleton. In the ¹H-nmr spectrum, the coupling constant ($J_{8,9} = 9.7$ Hz) between H-8 and H-9 suggested that both H-8 and

H-9 had axial stereochemistry. In addition, the upfield sharp singlet at δ 1.50 (3H) for one acetate methyl suggested that this acetate ester and the benzoate ester were located at C-1 and C-9 (or at C-9 and C-1), respectively (**2**). By careful comparison of **3** with **2**, it was found that both compounds had the same ¹H-nmr chemical shifts (5.30 ppm) for H-1, suggesting that the ester at C-1 in **3** also was acetate, and that the benzoate ester was located at C-9. Thus the structure of **3** was elucidated as 1 β ,8 α ,13-triacetoxy-9 β -benzoyloxy- β -dihydroagarofuran.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—¹H-nmr, ¹³C-nmr, DEPT, NOESY, and COLOC spectra were obtained on a Bruker AM-400 nmr spectrometer with CDCl₃ as solvent and TMS as internal standard. Uv spectra (MeOH) were obtained on a uv-210A spectrophotometer. Ir spectra were obtained on an FT Nicolet-5DX instrument (KBr). Eims and hrms were obtained on a VG ZAB-HS mass spectrometer operating at 70 eV. Rotation data were recorded on a J-20C instrument. Liquid chromatography was carried out on Si gel (200-300 mesh) with petroleum ether-Me₂CO (9:1→1:9) as eluent. Reversed-phase liquid chromatography was carried out on a Merck RP-18 B(310-25) column using MeOH-H₂O (4:1). Plant material was collected in Guizhou Province, China. Voucher specimens (No. 087603) were deposited at the Biology De-

partment of Lanzhou University and assigned by Prof. Zhang Guoliang.

EXTRACTION AND ISOLATION.—The air-dried and pulverized seed of *C. angulatus* was extracted with petroleum ether at room temperature. Removal of the solvent under reduced pressure left a reddish-brown oil that was re-extracted with MeOH-petroleum ether (1:1). After removal of the solvent from the MeOH layer under reduced pressure, the residue was subjected to cc on Si gel using petroleum ether-Me₂CO (9:1→1:9) as the eluent. The major fractions were successively purified on a Merck RP-18 B(310-25) column using MeOH-H₂O (4:1) to give compounds **1** (193 mg, 0.013%), **2** (215 mg, 0.014%), and **3** (86 mg, 0.0057%).

Compound 1.—Compound **1** was obtained as an amorphous white powder; $[\alpha]^{23}_D -30.8$ ($c = 0.520$, CHCl₃), uv λ max nm (log ϵ), 233.5 (4.496), 274 (2.490), 214.5 (4.1654); ir ν max cm⁻¹ (KBr) 2970, 2952, 1726 (C=O), 1605 and 1451 (Ph), 1320, 1284, 1115, 1092, 1026, 959, 706; eims m/z (rel. int.) [M + H]⁺ 641 (13), [M + H - ketene]⁺ 599 (19), [M - PhCO₂H]⁺ 518 (6), [599 - PhCO₂H]⁺ 477 (23), [M - ketene - 2 × PhCO₂H]⁺ 354 (10), 296 (12), 175 (10), [PhCO]⁺ 105 (100), [Ph]⁺ 77 (43), [Ac]⁺ 43 (41); hrms m/z 614.2751 (calcd for C₃₈H₄₁O₉, 641.2739); ¹H nmr δ 2.13 (3H, s, Ac), 6.83–7.58 (15H, m, 3 × Ph); ¹³C nmr δ 21.2 and 169.9 (OAc), 127.4–133.0, 164.8, 165.3, and 165.4 (3 × PhCO₂). ¹H- and ¹³C-nmr data for the sesquiterpene parent are tabulated in Tables 2 and 1, respectively.

Compound 2.—Compound **2** was obtained as an amorphous white powder; $[\alpha]^{23}_D -77.6$ ($c = 0.515$, CHCl₃); uv λ max nm (log ϵ) 215.5 (4.058), 218 (2.228), 274.5 (2.417), 238.5 (4.349); ir ν max cm⁻¹ (KBr) 2971, 2947, 1747, and 1730 (C=O), 1603 and 1463 (Ph), 1404, 1369, 1279, 1229, 1096, 1072, 1027, 882, 860, 716; eims m/z (rel. int.) [M + H]⁺ 517 (21), [M - OAc]⁺ 457 (10), [M - 2 × HOAc]⁺ 396 (25), 215 (8), 137 (34), 124 (21), [PhCO]⁺ 105 (100), [Ph]⁺ 77 (30), [Ac]⁺ 43 (95); hrms m/z 517.2453 (calcd for C₂₈H₃₇O₉, 517.2427); ¹H nmr δ 1.40, 1.99 and 2.10 (3 × 3H, 3 × s, 3 × Ac), 7.38–8.02 (5H, m, Ph); ¹³C nmr δ

20.7, 20.9, 21.5, 169.8, 170.5, and 170.8 (3 × OAc), 128.4–133.1 and 165.3 (PhCO₂). ¹H- and ¹³C-nmr data for the sesquiterpene parent are tabulated in Tables 2 and 1, respectively.

Compound 3.—Compound **3** was obtained as an amorphous white powder; $[\alpha]^{23}_D -9.24$ ($c = 0.530$, CHCl₃); uv λ max nm (log ϵ) 232 (4.801), 206 (3.701); ir ν max cm⁻¹ (KBr) 3966, 2946, 1741 (C=O), 1605, 1461, and 1451 (Ph), 1369, 1277, 1227, 1117, 1032, 937, 887, 862, 714; eims m/z (rel. int.) [M + H]⁺ 517 (28), [M - OAc]⁺ 457 (10), [M - 2 × HOAc]⁺ 396 (28), 215 (8), 137 (41), 124 (30), [PhCO]⁺ 105 (100), [Ph]⁺ 77 (27), [Ac]⁺ 43 (88); hrms m/z 517.2433 (calcd for C₂₈H₃₇O₉, 517.2427); ¹H nmr δ 1.50, 1.85, and 2.27 (3 × 3H, 3 × s, 3 × Ac), 7.38–7.89 (5H, m, Ph); ¹³C nmr δ 20.8, 20.9, 21.4, 169.8, 170.4, and 170.5 (3 × OAc), 128.6–133.0 and 165.6 (PhCO₂). ¹H- and ¹³C-nmr data for the sesquiterpene parent are tabulated in Tables 2 and 1, respectively.

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