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SESQUITERPENOIDS FROM *CELASTRUS PANICULATUS*

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**ABSTRACT.**—Four new  $\beta$ -dihydroagarofuran sesquiterpenoids were isolated from the seed oil of *Celastrus paniculatus*. Their structures have been established, on the basis of uv, ir, mass,  $^1\text{H}$ -nmr,  $^{13}\text{C}$ -nmr, and 2D nmr spectrometry, as 1 $\beta$ ,6 $\alpha$ -diacetoxy-9 $\beta$ -benzoyloxy-8 $\beta$ -hydroxy- $\beta$ -dihydroagarofuran [1], 1 $\beta$ ,8 $\alpha$ -diacetoxy-6 $\alpha$ ,9 $\alpha$ -dibenzoyloxy- $\beta$ -dihydroagarofuran [2], 1 $\beta$ -acetoxy-6 $\alpha$ ,9 $\beta$ -dibenzoyloxy-8 $\beta$ -cinnamoyloxy-4 $\alpha$ -hydroxy- $\beta$ -dihydroagarofuran [3], and 1 $\beta$ -acetoxy-9 $\beta$ -benzoyloxy-8 $\beta$ -cinnamoyloxy-6 $\alpha$ ( $\beta$ -furancarboxyloxy)-4 $\alpha$ -hydroxy- $\beta$ -dihydroagarofuran [4].

The Celastraceae plants are widely distributed in China. Some species, such as *Celastrus angulatus*, have been used traditionally in China as natural insecticides (1). In our previous study on the chemical constituents of *Celastrus paniculatus* (Willd.) we reported several major components (2,3). Continued study has led to isolation of four new minor components that all belong to the  $\beta$ -dihydroagarofuran sesquiterpenoid series.

## RESULTS AND DISCUSSION

Compound **1** analyzed for  $\text{C}_{26}\text{H}_{34}\text{O}_8$  by hrms. Its ir spectrum revealed characteristic absorptions of hydroxyl ( $\nu$  3465  $\text{cm}^{-1}$ ), ester ( $\nu$  1742 and 1717  $\text{cm}^{-1}$ ), and phenyl groups ( $\nu$  1602, 1476, and 1452  $\text{cm}^{-1}$ ). The eims exhibited peaks

due to the losses of acetyl ( $m/z$  43, 52%) and benzoyl ( $m/z$  105, 100%). The nmr indicated the presence of two acetate ( $^1\text{H}$  nmr  $\delta$  1.41 and 2.08,  $2 \times 3\text{H}$ ,  $2 \times s$ ;  $^{13}\text{C}$  nmr  $\delta$  20.8 and 21.3,  $2 \times \text{Me}$ ,  $\delta$  170.5 and 170.8,  $2 \times -\text{CO}_2-$ ) and one benzoate ester ( $^1\text{H}$  nmr  $\delta$  7.46–8.08, 5H, m;  $^{13}\text{C}$  nmr  $\delta$  130.5, C-1', 129.6,  $2 \times \text{C}-2'$ , 128.5,  $2 \times \text{C}-3'$ , 133.3, C-4', 165.5,  $-\text{CO}_2-$ ). Furthermore, the  $^{13}\text{C}$ -nmr (Table 1) and DEPT spectra indicated that the parent consisted of fifteen carbons: four methyls ( $\delta$  12.2, 16.8, 24.0, and 30.6), two methylenes ( $\delta$  21.9 and 26.5), six methines ( $\delta$  33.8, 54.2, 69.9, 74.7, 76.7, and 79.2), and three quaternary carbons ( $\delta$  48.6, 81.3 and 91.6). These  $^{13}\text{C}$ -nmr data were very similar to those assigned to the 1,6,8,9-

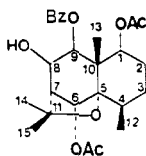
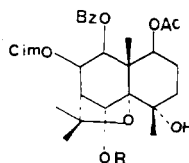
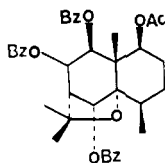
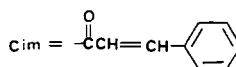
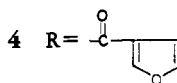
**1****3** R=Bz**2**

TABLE 1.  $^{13}\text{C}$ -nmr Chemical Shifts of 1-4 (400 MHz,  $\text{CDCl}_3$ , TMS).<sup>a</sup>

Carbon	Compound			
	1	2	3	4
C-1 <sup>b</sup>	69.9	69.2	70.9	70.6
C-2	21.9	21.4	24.3	23.9
C-3	26.5	26.8	38.6	38.3
C-4	33.8	34.4	70.5	70.1
C-5	91.6	89.9	92.5	92.1
C-6 <sup>b</sup>	74.7	72.7	74.2	73.8
C-7	54.2	53.8	53.0	52.4
C-8 <sup>b</sup>	76.7	73.3	76.0	75.0
C-9 <sup>b</sup>	79.2	78.1	77.8	77.4
C-10	48.6	48.9	49.9	49.4
C-11	81.3	82.9	83.3	82.9
Me-12	16.8	17.3	23.4	23.1
Me-13	12.2	18.7	12.9	12.6
Me-14	24.0	26.5	23.9	23.6
Me-15	30.6	31.5	29.5	29.2

<sup>a</sup>The assignments of chemical shifts were made with the aid of DEPT spectra.

<sup>b</sup>Data in the same column may be exchangeable.

tetrasubstitued  $\beta$ -dihydroagarofuran skeleton (2). In addition, the molecular composition suggested the presence of one free hydroxy group. Thus, **1** had three ester groups and one hydroxy group at C-1, C-6, C-8, and C-9.

In this class of compounds H-1 and H-6 generally have axial stereochemistry (4,5). In a qualitative nOe difference experiment, irradiation of H-14 ( $\delta$  1.50) caused enhancements of H-8 ( $\delta$  4.39) and H-9 ( $\delta$  5.43), suggesting that H-8 had equatorial stereochemistry and that H-9 was axial. The ester distribution was determined on the basis of  $^1\text{H}$ - $^{13}\text{C}$  long-range COSY (COLOC) analysis (3). The COLOC spectrum showed cross peaks between H-1 and H-6 and the carbonyls of two acetate esters, and between H-9 and the carbonyl of a benzoate ester. This indicated that the two acetate esters were located at C-1 and C-6, and that the benzoate ester was at C-9. Thus, the hydroxyl group was at C-8 and the structure of **1** was elucidated as  $1\beta,6\alpha$ -diacetoxy- $9\beta$ -benzoyloxy- $8\beta$ -hydroxy- $\beta$ -dihydroagarofuran.

Compound **2** analyzed for  $\text{C}_{33}\text{H}_{38}\text{O}_9$  by hrms. Its spectral data suggested the presence of two acetate esters, two benzoate esters, and the 1,6,8,9-tetra-substitued  $\beta$ -dihydroagarofuran parent. In a qualitative nOe difference experiment, irradiation of H-13 ( $\delta$  1.43) caused enhancements of H-12 ( $\delta$  0.99), H-6 ( $\delta$  5.54), H-8 ( $\delta$  5.65), and H-9 ( $\delta$  5.31), suggesting that H-8 had axial stereochemistry and that H-9 was equatorial. The ester distribution was determined from a COLOC spectrum, which showed cross peaks between H-1 and H-8 and the carbonyls of two acetate esters, and between H-6 and H-9 and the carbonyls of two benzoate esters. This indicated that two acetate esters were located at C-1 and C-8, and that two benzoate esters were at C-6 and C-9. Therefore, the structure of **2** was elucidated as  $1\beta,8\alpha$ -diacetoxy- $6\alpha,9\alpha$ -dibenzoyloxy- $\beta$ -dihydroagarofuran.

Compound **3** analyzed for  $\text{C}_{40}\text{H}_{42}\text{O}_{10}$  by hrms. The spectral data suggested the presence of one acetate ester, two benzoate esters, one cinnamoate ester, one hydroxy group, and the 1,4,6,8,9-pentasubstitued  $\beta$ -dihydroagarofuran parent (4). The nOe difference experiment suggested that H-8 was equatorial and that H-9 was axial. In the COLOC spectrum there only were two cross peaks between H-6 and H-9 and the carbonyls of two benzoate esters, suggesting that the two benzoate esters were located at C-6 and C-9. The acetate ester was located at C-1, as the acetate methyl showed an upfield  $^1\text{H}$ -nmr chemical shift 1.40 ppm more than the normal (5). This assignment of the acetate methyl was confirmed by the cross peak between acetate methyl hydrogens and the carbonyl in the COLOC spectrum. Furthermore, the free hydroxy group was located at C-4, as in all compounds of this class the tertiary free hydroxy group at C-4 is not always esterified (4,5). Therefore, the remaining cinnamoate ester was located at C-8, and the structure of **3** was elucidated as  $1\beta$ -acetoxy- $6\alpha,9\beta$ -dibenzoyloxy- $8\beta$ -

cinnamoyloxy-4 $\alpha$ -hydroxy- $\beta$ -dihydroagarofuran.

Compound **4** analyzed for C<sub>38</sub>H<sub>40</sub>O<sub>11</sub> by hrms. The spectral data suggested the presence of one acetate ester, one benzoate ester, one cinnamate ester, one  $\beta$ -furancarboxylate ester, one free hydroxy group, and the 1,4,6,8,9-pentasubstituted  $\beta$ -dihydroagarofuran. Comparison of compound **3** and **4** demonstrated that the parent moieties for both compounds had very similar <sup>1</sup>H-nmr (Table 2) and <sup>13</sup>C-nmr (Table 1) spectra, and that only H-6 had somewhat different chemical shifts ( $\Delta \delta = 0.12$  ppm). This suggested that the stereochemistry at all of the parent carbons and the ester distribution at C-1, C-8, and C-9 were the same as those of **3**. However, the ester group at C-6 was a  $\beta$ -furancarboxylate rather than benzoate. This small difference of <sup>1</sup>H-nmr chemical shifts caused by different esters (benzoate and  $\beta$ -furancarboxylate) was found in our previous study (6). As a result, the structure of compound **4** was elucidated as 1 $\beta$ -acetoxy-9 $\beta$ -benzoyloxy-8 $\beta$ -cinnamoyloxy-6 $\alpha$ -( $\beta$ -furancarboxylate)-4 $\alpha$ -hydroxy- $\beta$ -dihydroagarofuran.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—<sup>1</sup>H-nmr, <sup>13</sup>C-nmr, DEPT, nOe, and 2D nmr

spectra were obtained on a Bruker AM-400 nmr spectrometer with CDCl<sub>3</sub> as solvent and TMS as internal standard. The data matrix for COLOC spectra of compounds **1–3** was 512  $\times$  2K, NS = 128, NE = 128. Uv spectra in MeOH were obtained on a UV-210A spectrophotometer. Ir spectra were obtained on an FT Nicolet-5DX instrument with KBr disc. Eims and hrms were obtained on a VG ZAB-HS mass spectrometer operating at 70 eV ionizing energy. Rotation data were recorded on a J-20C instrument. Liquid chromatography was carried out on a Si gel (200–300 mesh) column with petroleum ether-Me<sub>2</sub>CO (9:1 $\rightarrow$ 1:9) as eluent. Reversed-phase liquid chromatography was carried out on a Merck RP-8 short column with MeOH-H<sub>2</sub>O (1:4) as the eluent. Preparative tlc was carried out on Merck RP-18 plates with MeOH-H<sub>2</sub>O (4:1) as eluent. Plant material was collected from Yunnan Province, China. Voucher specimens (No. 39869) are deposited at the Botanical Garden of Kunming Institute of Botany, The Academy of Science of China.

EXTRACTION AND ISOLATION.—After the major components were isolated by the literature procedure (2,3), the remaining mixture containing minor components was combined and successively chromatographed on preparative RP-18 plates using MeOH-H<sub>2</sub>O (4:1) as eluent to yield compounds **1–4**.

*Compound 1*.—Compound **1**: amorphous white powder;  $[\alpha]_D^{23} -78.7$  ( $c = 0.525$ , CHCl<sub>3</sub>); uv  $\lambda$  max nm (log  $\epsilon$ ) 232 (4.283), 281 (2.186), 273 (2.415), 239.5 (4.186), 211 (3.910); ir  $\nu$  max cm<sup>-1</sup> (KBr) 3465 (OH), 3296, 2973, 2933, 1742 and 1717 (C=O), 1602, 1476, and 1452 (Ph), 1368, 1284, 1232, 1095, 1071, 1026, 963, 874, 821, 714; eims  $m/z$  (rel. int.)

TABLE 2. <sup>1</sup>H-nmr Spectra Data of **1–4** (400 MHz, CDCl<sub>3</sub>, TMS).<sup>a</sup>

Hydrogen	Compound			
	1	2	3	4
H-1 . . . . .	5.18 dd (4.7, 11.4)	5.48 dd (4.3, 12)	5.17 dd (4.2, 12)	5.14 dd (4, 12)
H-2 . . . . .	1.39–2.47	1.39–2.42	1.35–1.90	1.32–1.88
H-3 . . . . .	1.39–2.47	1.39–2.42	1.35–1.90	1.32–1.88
H-4 . . . . .	1.39–2.47	1.39–2.42		
H-6 . . . . .	6.07 s	5.54 s	6.46 s	6.34 s
H-7 . . . . .	2.46 d (4)	2.61 d (2.8)	2.62 d (4.2)	2.60 d (4.2)
H-8 . . . . .	4.39 dd (4, 4.8)	5.65 dd (2.8, 6.2)	5.75 dd (4.2, 5.2)	5.72 dd (4.2, 5.2)
H-9 . . . . .	5.43 d (4.8)	5.31 d (6.2)	5.68 d (5.2)	5.66 d (5.2)
Me-12 . . . . .	1.02 d (7.4)	0.99 d (7.4)	1.39 s	1.37 s
Me-13 . . . . .	1.47 s	1.43 s	1.62 s	1.60 s
Me-14 . . . . .	1.50 s	1.55 s	1.69 s	1.67 s
Me-15 . . . . .	1.41 s	1.45 s	1.58 s	1.55 s

<sup>a</sup>Coupling constants are in parentheses.

$[M + H - \text{ketene}]^+$  433 (13),  $[M - \text{OAc}]^+$  415 (8),  $[M - \text{OBz}]^+$  353 (21), 310 (11), 250 (12), 192 (14),  $[\text{Bz}]^+$  105 (100),  $[\text{Ac}]^+$  43 (52); hrms  $m/z$  353.1971 (calcd for  $\text{C}_{19}\text{H}_{29}\text{O}_6$ , 353.1956);  $^1\text{H}$  nmr  $\delta$  1.41 and 2.08 ( $2 \times 3\text{H}$ ,  $2 \times \text{s}$ ,  $2 \times \text{Ac}$ ), 7.46–8.08 (5H, m, Ph);  $^{13}\text{C}$ -nmr  $\delta$  20.8, 21.3, 170.5 and 170.8 ( $2 \times \text{OAc}$ ),  $\delta$  128.5–133.3, 165.5 (OBz);  $^1\text{H}$  nmr see Table 2;  $^{13}\text{C}$  nmr see Table 1.

**Compound 2.**—Compound 2 was obtained as amorphous white powder:  $[\alpha]^{23}_{\text{D}} - 8.4$  ( $c = 0.500$ ,  $\text{CDCl}_3$ ); uv  $\lambda$  max nm (log  $\epsilon$ ) 238 (4.489), 275 (3.035); ir  $\nu$  max  $\text{cm}^{-1}$  (KBr) 2992, 1747, and 1722 (C=O), 1455 (Ph), 1369, 1276, 1229, 1096, 1023, 711; eims  $m/z$  (rel. int.)  $[M + 1]^+$  579 (13),  $[M - \text{HOAc}]^+$  518 (4),  $[M - 2 \times \text{HOAc}]^+$  458 (10), 399 (8), 339 (7), 244 (12), 203 (14),  $[\text{Bz}]^+$  105 (100),  $[\text{Ph}]^+$  77 (11); hrms  $m/z$  579.2565 (calcd for  $\text{C}_{33}\text{H}_{39}\text{O}_9$ , 579.2583);  $^1\text{H}$  nmr  $\delta$  1.62 and 1.87 ( $2 \times 3\text{H}$ ,  $2 \times \text{s}$ ,  $2 \times \text{Ac}$ ), 7.23–8.09 (10H, m,  $2 \times \text{ph}$ );  $^{13}\text{C}$  nmr  $\delta$   $2 \times 20.7$ , 169.3 and 169.9 ( $2 \times \text{OAc}$ ),  $\delta$  128.3–133.5, 165.3 and 165.7 ( $2 \times \text{OBz}$ );  $^1\text{H}$  nmr see Table 2;  $^{13}\text{C}$  nmr see Table 1.

**Compound 3.**—Compound 3: amorphous white powder;  $[\alpha]^{23}_{\text{D}} - 27.3$  ( $c = 0.505$ ,  $\text{CHCl}_3$ ); uv  $\lambda$  max nm (log  $\epsilon$ ) 232 (5.065), 279.5 (3.953); ir  $\nu$  max  $\text{cm}^{-1}$  (KBr) 3509 (OH), 2923, 1745 and 1718 (C=O), 1655, 1600, 1579 and 1450 (Ph), 1262, 1165, 1087, 1023, 804, 768, 713; eims  $m/z$  (rel. int.)  $[M - \text{Bz}]^+$  577 (29),  $[M - \text{Me} - \text{ketene} - \text{PhCH} = \text{CHCO}_2\text{H}]^+$  477 (10),  $[M - \text{Bz} - \text{PhCH} = \text{CHCO}_2\text{H}]^+$  429 (13), 404 (50), 291 (80), 179 (79), 167 (26),  $[\text{PhCH} = \text{CHCO}_2 + \text{H}]^+$  149 (100),  $[\text{Bz}]^+$  105 (10); hrms  $m/z$  577.2430 (calcd for  $\text{C}_{33}\text{H}_{37}\text{O}_9$ , 577.2427);  $^1\text{H}$  nmr  $\delta$  1.40 (3H, s, Ac), 7.36–8.21 (15H, m,  $3 \times \text{Ph}$ ), 6.50 and 7.80 ( $2 \times 1\text{H}$ , ABq,  $J = 16$  Hz,  $-\text{CH} = \text{CH}-$ ),  $^{13}\text{C}$  nmr  $\delta$  20.8 and 170.1 (OAc), 128.3–134.4, 117.5, 145.9, 164.9, 165.6 and 166.0 ( $2 \times \text{OBz}$  and  $\text{PhCH} = \text{CHCO}_2$ );  $^1\text{H}$  nmr see Table 2;  $^{13}\text{C}$  nmr see Table 1.

**Compound 4.**—Compound 4: amorphous white powder; uv  $\lambda$  max nm (log  $\epsilon$ ) 281 (4.013), 239 (4.164), 234.5 (4.283), 200 (3.160); ir  $\nu$  max  $\text{cm}^{-1}$  (KBr) 3510 (OH), 2931, 1745 and 1716 (C=O), 1655, 1600, 1570 and 1450 (Ph), 1365, 1317, 1263, 1166, 1086, 1024, 805, 767, 714; eims  $m/z$  (rel. int.)  $[M]^+$  672 (3),  $[M - \text{Me}]^+$  657 (3),  $[M - \text{OAc}]^+$  613 (2),  $[M - \text{furancarboxyloxy}]^+$  561 (4),  $[M - \text{PhCH} = \text{CHCO}_2\text{H}]^+$  524 (85),  $[524 - \text{HOBz} - \text{HOAc}]^+$  342 (5), 270 (15), 260 (14), 248 (15), 230 (18), 202 (10), 173 (11),  $[\text{PhCH} = \text{CHCO}_2\text{H}]^+$  148 (68),  $[\text{PhCH} = \text{CHCO}]^+$  131 (81),  $[\text{Ph}]^+$  77 (25),  $[\text{Ac}]^+$  43 (18); hrms  $m/z$  524.2031 (calcd for  $\text{C}_{29}\text{H}_{32}\text{O}_9$ , 524.2037);  $^1\text{H}$  nmr  $\delta$  1.39 (3H, s, Ac), 7.34–7.98 (10H, m,  $2 \times \text{Ph}$ ), 6.48 and 7.74 ( $2 \times 1\text{H}$ , ABq,  $J = 16$  Hz,  $-\text{CH} = \text{CH}-$ ), 6.80, 7.38, and 8.15 ( $3 \times 1\text{H}$ ,  $3 \times$  brs,  $\beta$ -furancarboxyl);  $^{13}\text{C}$  nmr  $\delta$  20.4 and 169.8 (OAc), 128.0–134.0, 117.1, 145.6, 164.0, and 165.2 (OBz and  $\text{PhCH} = \text{CHCO}_2$ ), 109.4, 118.9, 143.7, 148.7, and 161.9 ( $\beta$ -furancarboxyloxy),  $^1\text{H}$  nmr see Table 2;  $^{13}\text{C}$  nmr see Table 1.

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