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SESQUITERPENES FROM *CELASTRUS PANICULATUS* SUBSP. *PANICULATUS*

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Key Word Index—*Celastrus paniculatus* subsp. *paniculatus*; Celastraceae; sesquiterpenes; isolation; CO_2 supercritical fluid.

Abstract—Two new β-dihydroagarofuran sesquiterpene polyol esters were isolated from *Celastrus paniculatus* subsp. *paniculatus*. Their structures were deduced on the basis of spectral analysis including 2D NMR.

INTRODUCTION

The plants of the Celastraceae are widely distributed in China. Many species have traditionally been used as insecticides [1]. Previous studies on chemical constitutions of Celastraceae plants have disclosed the presence of various β-dihydroagarofuran sesquiterpene polyol esters [2]. Some compounds with a β-dihydroagarofuran sesquiterpene polyol ester skeleton have been isolated from *Celastrus paniculatus* [3–6]. In the present paper, we report two new β-dihydroagarofuran sesquiterpene polyol esters from *Celastrus paniculatus* subsp. *paniculatus*. They were identified as 1β,9α-dibenzoyloxy-4α-hydroxy-6α-acetoxy-β-dihydroagarofuran and 1β,6α,9α-tribenzoyloxy-4α-hydroxy-β-dihydroagarofuran. Several compounds with a similar structure have been found from some species of Celastraceae [7, 8].

RESULTS AND DISCUSSION

Compound **1** analyzed for $C_{31}H_{36}O_8$ by the spectral data. In its IR spectrum the absorption at 1719 cm^{-1} showed the existence of ester groups. In the ^{13}C NMR spectrum peaks at δ 170.5 (—COO—) and 21.6 and the ^1H NMR spectrum at δ 2.15 (Me)—and the presence of cross-peaks between δ 170.5 (—COO—) and δ 2.15 (Me) in COLOC suggested the presence of one acetate ester. ^1H NMR spectral peaks at δ 7.23–7.79 (10H), ^{13}C NMR peaks at δ 127.9–132.9 (C_6H_5), 165.3, 165.4 (—COO—) and the presence of cross-peaks between δ 165.3, 165.4 (—COO—) and δ 7.23–7.79 (10H) in COLOC suggested the presence of two benzoate esters. The 3450 cm^{-1} absorption in the IR spectrum and a ^1H NMR peak at δ 2.94 (1H) suggested the presence of one hydroxyl group. In addition, the ^{13}C NMR and DEPT spectra indicated that compound **1** consisted of four methyl carbons (δ 20.0, 24.1, 25.8, 29.6); three methylene carbons (δ 38.6, 23.5, 31.9); four methine carbons (δ 73.4, 73.4, 49.1, 79.8); and four quaternary carbons (δ 70.5, 84.4, 91.6, 51.8). This parent was identified as β-dihydroagarofuran with four substituents at three methine carbons (δ 73.4, 73.4, 79.8) and one quaternary carbon (δ 70.5) [2].

In the COLOC of compound **1**, C-5 (δ 91.6) was assigned by its correlation to H-12, H-7; and C-11 (δ 84.4) by its correlation to Me-14, Me-15 and H-6; C-4 (δ 70.5) by its correlation to Me-13, H-3 and H-2; the remaining quaternary carbon C-10 was at δ 51.8. In this kind of compound, the hydroxyl group is usually located at the C-4 position [2].

The presence of cross-peaks between H-1 and the signal at δ 165.3 and the signals at δ 165.3 and δ 7.23–7.79 (protons of the phenyl) allowed the assignment of C_6H_5COO— which connected to C-1. The cross-peaks between H-6 and the signal at δ 170.5 together with the signals at δ 170.5 and 2.15 (protons of OAc) allowed the assignments of CH_3COO— which connected to C-6. The cross-peaks between H-9 and the signal at δ 165.4; and the signals at δ 165.4 and 7.23–7.79 (protons of the phenyl) allowed the assignment of C_6H_5COO— which connected to C-9. Furthermore,

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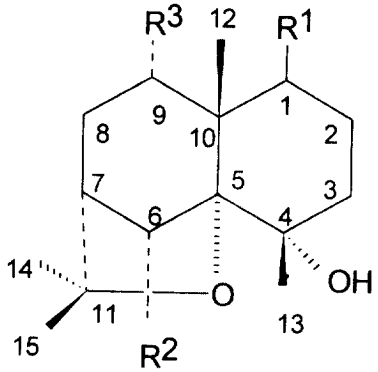

1 R_1= OBz, R_2= OAc, R_3= OBz;

2 R_1= R_2= R_3= OBz;

all the ring-protons were assigned unambiguously by ^{1}H NMR. COLOC and H^1-H^1 COSY. The stereochemistry of the ring-protons was deduced by comparing the coupling constants of protons with those reported in previous reports [9]. Therefore, compound **1** was identified as 1β,9α-dibenzoyloxy-4α-hydroxy-6α-acetoxy-β-dihydroagarofuran. The ^{1}H NMR and ^{13}C NMR spectral data for compound **1** are presented in Tables 1 and 2.

Compound **2**, $C_{36}H_{38}O_8$ was very similar to compound **1**. The IR spectrum of **2** showed absorption at 1714 cm^{-1} revealing the existence of ester groups. ^{1}H NMR peaks at δ 7.25–8.16 (15H) and ^{13}C NMR peaks at δ 128.0–133.3 (3 × C_6H_5)—and δ 165.3, 165.4, 165.5 (3 × —COO—) suggested the presence of three benzoate esters. The presence of cross-peaks between H-1 and the signal at δ 165.3, and the signals at δ 165.3 and δ 7.25–8.16 (protons of the phenyl) allowed the assignments of C_6H_5COO— which connected to C-1. The cross-peaks between H-6 and the signal at δ 165.4 and the signals at δ 165.4 and δ 7.25–8.16 (protons of the phenyl) allowed the assignment of the second C_6H_5COO— which connected to C-6. The cross-peaks between H-9 and the signal at δ 165.5, and the signals at δ 165.5 and δ 7.25–8.16 (protons of the phenyl) allowed the assignment of the third C_6H_5COO— which connected to C-9. The other spectral data of compound **2** were almost the same as those of compound **1**. Thus compound **2** was identified as 1β,6α,9α-tribenzoyloxy-4α-hydroxyl-β-dihydroagarofuran. The ^{1}H NMR and ^{13}C NMR spectral data for compound **2** are presented in Table 2.

EXPERIMENTAL

General experimental procedures

Mps were determined on a Kolfer apparatus. Optical rotation was determined on Perkin-Elmer 241 apparatus. ^{1}H NMR, ^{13}C NMR, DEPT, COSY and COLOC spectra were recorded on a Bruker AM-400 NMR spectrometer with TMS as internal standard. UV spectra in EtOH were on a UV-210A spectrophotometer. FAB-MS were obtained on VG ZHB-HS mass spectrometer. IR spectra were determined on a NICOLET FT-IR spectrophotometer. SFE was carried out on a modified ISCO-100D supercritical fluid extraction system.

Plant material

The seeds of *Celastrus paniculatus* subsp. *paniculatus* were collected from Xishuang Banna, Yunan province, China, in September and identified by Mr Cheng Biqiang, a senior researcher of the Tropical Botanical Garden of Xishuang Banna, Chinese Acad-

Table 1. ^{1}H NMR spectral data for compounds **1** and **2** (400 MHz, $CDCl_3$)

Proton	1	2
1	5.59 (*dd*, 3.96, 11.93)	5.65 (*dd*, 3.68, 11.85)
2	1.74, 2.00 (each 1 H, *m*)	1.80, 2.06 (each 1 H, *m*)
3	1.61, 2.07 (each 1 H, *m*)	1.65, 2.11 (each 1 H, *m*)
6	5.55 (*s*)	5.71 (*s*)
7	2.50 (*m*)	2.52 (*m*)
8	2.18, 2.23 (each 1 H, *m*)	2.30, 2.38 (each 1 H, *m*)
9	5.10 (*d*, 6.82)	5.16 (*d*, 6.98)
Me-12	1.55 (*s*)	1.59 (*s*)
Me-13	1.38 (*s*)	1.26 (*s*)
Me-14	1.50 (*s*)	1.54 (*s*)
Me-15	1.54 (*s*)	1.56 (*s*)
OH	2.94	3.15
OAc	2.15 (*s*)	
OBz	7.23–7.80 (*m*, 10 H)	7.25–8.16 (*m*, 15 H)

Table 2. ^{13}C NMR spectral data for compounds **1** and **2** (400 MHz, $CDCl_3$)

Carbon	**1**	**2**
1	73.4 *d*	73.4 *d*
2	38.6 *t*	39.0 *t*
3	23.5 *t*	23.5 *t*
4	70.5 *s*	70.8 *s*
5	91.6 *s*	91.6 *s*
6	73.4 *d*	73.4 *d*
7	49.1 *d*	49.1 *d*
8	31.9 *t*	31.9 *t*
9	79.8 *d*	80.6 *d*
10	51.8 *s*	51.8 *s*
11	84.4 *s*	84.5 *s*
12	20.0 *q*	20.1 *q*
13	24.1 *q*	24.0 *q*
14	25.8 *q*	25.9 *q*
15	29.6 *q*	29.7 *q*
OAc	170.5, 21.6	
OBz	165.4, 165.3 (2 × —CO_2—)	165.5, 165.4, 165.3 (3 × —CO_2—)
	132.9 *d*, 132.6 *d*,	133.3 *d*, 132.9 *d*, 132.6 *d*
	130.0 *s*, 129.8 (2 × *d*)	130.2 (2 × *d*), 130.0 *s*
	129.3 *s*, 129.0 (2 × *d*)	129.8 *s*, 129.8 (2 × *d*)
	128.0 (2 × *d*), 127.9 (2 × *d*)	129.3 *s*, 129.1 (2 × *d*)
		128.6 (2 × *d*), 128.0 (4 × *d*)

emy of Sciences. Voucher specimens are deposited at the Tropical Botanical Garden of Xishuang Banna.

Extraction and isolation

Air-dried and pulverized seeds (1.5 kg) of *Celastrus paniculatus* subsp. *paniculatus* were extracted with CO_2 supercritical fluid at 500 bar and 45°C for 2 h, A brown oil was obtained (180 g). Silica gel was used to absorb the oil. After air drying, the silica gel carrying the oil was eluted with CO_2 supercritical fluid at 100, 150, 200, 250, 300, 350, 400 and 450 bar at 45°C. Eight fractions were collected; the last three fractions were combined to give a yellowish extract (1.43 g). The extract was chromatographed on a silica gel (80 g) column with a gradient mixture of petrol and Me_2CO (9:1, 8:2, 7:3 ...) as eluent. compound **1** (108 mg) and compound **2** (144 mg) can be obtained from 8:2 and 7:3 fractions, respectively.

Compound **1**. Colourless crystals (petrol/Me_2CO); mp 197–198°C; $[\alpha]_D^{25} = +80.4°$ (CH_3Cl, *c* 0.26). UV λ_{max}^{MeOH} nm: 273.6, 230.8, 201.0. IR ν_{max}^{KBr} cm^{-1}: 3450, 2952, 2934, 1719, 1602, 1584, 1490, 1387, 1367, 1283, 1244, 1097. ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (400 MHz, $CDCl_3$) see Tables 1 and 2; FAB-MS *m/z* (rel. int.) 537 ($[M+1, 23]^+$ (2), 520 (82), 478 (15), 415 (100), 397 (11), 355 (14), 337 (15), 293 (64), 233 (73).

Compound **2**. Colourless crystals (petrol/Me_2CO) mp 281–282°C; $[\alpha]_D^{25} = +78°$ (CH_3Cl, *c* 0.27). UV λ_{max}^{MeOH} nm: 274.2, 231.4, 201.6. IR ν_{max}^{KBr} cm^{-1}: 3532, 2985, 2961, 1714, 1600, 1584, 1488, 1389, 1337, 1280, 1262, 1114, 1097. FAB-MS *m/z* (rel. int.): 599 ($[M+1]^+$ 26), 582 (59), 563 (14), 477 (79), 460 (28), 354 (50), 233 (100). ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (400 MHz, $CDCl_3$) see Tables 1 and 2.

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REFERENCES

1. Wakabaysshi, N., Wu, W. J., Water, R. M., Redfern, R. E., Mills Jr., G. D., DeMilo, A. B., Lusby, W. R. and Andrzejewski, D., *J. Nat. Prod.*, 1988, **51**, 537.
2. Bruning, R. and Wagner, H., *Phytochemistry*, 1978, **17**, 1821.
3. den Hertog Jr., H. H., Kruk, C., Nanavati, D. D. and Sukh Dev., *Tetrahedron Lett.*, 1974, 2219.
4. Wagner, H., Heckel, E. and Sonnenbichler, J., *Tetrahedron*, 1975, **31**, 1949.
5. Tu, Y. Q., Tong, X., Wu, X., Chen, Y. Z. and Zi Zh. Li, *J. Nat. Prod.*, 1991, **54**, 1383.
6. Hong Sang, Hanqing Wang, Tu, Y. Q. and Chen, Y. Z., *Phytochemistry*, 1991, **30**, 1547.
7. Liu, J. and Jia, Z., *Chin. Sci. Bull.*, 1989, **34**(9), 1639.
8. Liu, J. and Wu, D., *Planta Med.*, 1991, **57**, 475.
9. Takaishi, Y., Ujita, K., Nakano, K. and Tomimatsu, T., *Phytochemistry*, 1987, **26**, 2325.