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TWO NEW SESQUITERPENOIDS FROM *CELASTRUS ROSTHORNIANUS*

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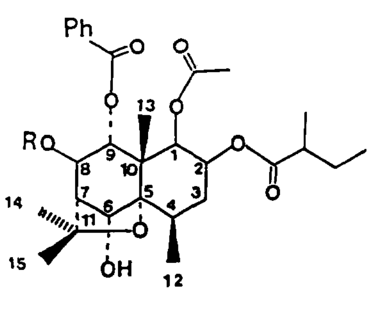
ABSTRACT.—Two new minor sesquiterpenoids have been isolated from the root bark of *Celastrus rosthornianus*. Their structures were elucidated, on the basis of spectral analysis including 2D nmr, as 1β-acetoxy-8β,9α-dibenzoyloxy-6α-hydroxy-2β(α-methylbutanoyloxy)-β-dihydroagarofuran [**1**] and 1β-acetoxy-9α-benzoyloxy-8β(β-furancarbonyloxy)-6α-hydroxy-2β(α-methylbutanoyloxy)-β-dihydroagarofuran [**2**].

Plants of the Celastraceae are distributed in all parts of China. Some species, such as *Tripterygium wilfordii* Hook. fil. var. *regelii* Makino, are used in China as drugs for the treatment of cancer or as insecticides (1). The chemical constituents isolated from this family of plants are mainly sesquiterpene polyol esters, alkaloids, and lactones with the β-dihydroagarofuran skeleton (2–4). Previous studies on the chemical constituents from *Euonymus bungeanus* resulted in the isolation of several bioactive sesquiterpene polyol esters (5). Recently, a continued study resulted in isolation of two new minor sesquiterpene polyol esters **1** and **2** from *Celastrus rosthornianus* Loes. This paper deals with the structure elucidation of compounds **1** and **2**.

RESULTS AND DISCUSSION

Compound **1** analyzed for $C_{36}H_{44}O_{10}$ by eims and elementary analysis. Its ^{1}H-nmr, ^{13}C-nmr, and ms data suggested the presence of four esters: one acetate ester, two benzoate esters and one α-methylbutanoate ester. The ^{13}C-nmr and DEPT spectra indicated that the parent skeleton consisted of fifteen carbons whose ^{13}C-nmr chemical shifts, together with the ^{1}H-nmr coupling patterns and constants (see Experimental), suggested that this parent was a 1,2,6,8,9-oxygen-substituted β-dihydroagarofuran skeleton (3–5, 7).



1 R=Bz
2 R=

In addition, the molecular composition suggested the presence of one hydroxyl group. Therefore, compound **1** had four ester groups at C-1, C-2, C-6, and C-8, and one free hydroxy group at C-9 of β-dihydroagarofuran. The stereochemistry of H-1 is generally axial in this class of compound (2,7); thus the coupling constant ($J_{1,2}$ = 4 Hz) suggested that H-2 was equatorial. Irradiation of the signal at 1.73 (3H, s), Me-13, caused enhancement of signals at δ 5.11 (1H, s) for H-9 and 4.99 (1H, brs) for H-6, suggesting that H-9 had equatorial and H-6 had axial stereochemistry. Irradiation of the H-8 signal at δ 5.55 (1H, d, J = 3 Hz) caused enhancement of the Me-14 signal at δ 1.54 (3H, s), suggesting that H-8 was equatorial. Weak couplings between H_{ax}-6 and H_{eq}-7 and between H_{eq}-8 and H_{eq}-9 are found in previous reports (2,5,8).

Generally, the H-6 in this class of compounds has a ^{1}H-nmr δ value near or greater than 6 ppm when OH-6 is esterified (2). Therefore, the ^{1}H-nmr δ value 4.99 for H-6 suggested that the free hydroxy group was located at C-6. In addition, the ^{1}H–^{13}C long-range correlation (COLOC) spectrum showed cross peaks between H-8 and the carbonyl of one benzoate ester and between H-9 and the carbonyl of the second benzoate ester. This indicated that the two benzoate esters were located at C-8 and C-9, respectively (6). Furthermore, the upfield ^{1}H-nmr singlet at δ 1.57 (3H) for acetate methyl suggested that the acetate ester was located at C-1 (7). The α-methylbutanoate ester was thus located at C-2. Therefore, structure **1** was elucidated as 1β-acetoxy-8β,9α-dibenzoyloxy-6α-hydroxy-2β(α-methylbutanoyloxy)-β-dihydroagarofuran.

Compound **2** analyzed for $C_{34}H_{42}O_{11}$. Its ^{1}H-nmr, ^{13}C-nmr, and mass spectral data (see Experimental) suggested the presence of one acetate ester, one benzoate ester, one β-furancarboxylate ester, one α-methylbutanoate ester, and the 1,2,6,8,9-pentasubstituted β-dihydroagarofuran skeleton (5,6). In addition, the molecular composition suggested the presence of one free hydroxyl. As with compound **1**, the smaller ^{1}H-nmr δ value (4.93) for H-6 suggested this free hydroxyl was at C-6. Irradiation of H-13 and H-14 caused enhancement of H-9, H-6, and H-8, respectively, suggesting that H-6 had axial and H-8 and H-9 had equatorial stereochemistry. Compound **2** had nearly the same ^{1}H-nmr chemical shifts as **1** for H-1 and H-2, respectively, which indicated that two aliphatic acid esters, namely the acetate and α-methylbutanoate, were located at C-1 and C-2, and two aromatic acid esters were at C-8 and C-9. Moreover, the upfield ^{1}H-nmr singlet at δ 1.57 (3H) suggested acetoxy at C-1. Thus, the α-methylbutanoate ester was located at C-2. The nOe effect between H-14 (δ 1.54) and H-2′ (δ 8.04) of the benzoate ester suggested the location of the benzoyloxy at C-9. The β-furancarboxylate ester thus was located at C-8. Compound **2** was thus elucidated as 1β-acetoxy-9α-benzoyloxy-8β(β-furancarbonyloxy)-6α-hydroxy-2β(α-methylbutanoyloxy)-β-dihydroagarofuran.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp: Kofler apparatus (uncorrected). Elementary analyses: MOD 1106 instrument. Ir: FT-5DX instrument with KBr discs. Uv: DU-7 uv-vis spectrophotometer in MeOH. Ms: VG ZAB-HS instrument, 70 eV. All nmr spectra: Bruker AM-400 spectrometer with solvent $CDCl_3$ and internal standard TMS. Assignments of ^{13}C-nmr chemical shifts were made using DEPT and ^{1}H–^{13}C COSY spectra. Si gel (200–300 mesh), neutral Al_2O_3, Merck Si gel 60 F_{254} preparative plates, and Merck preparative plates were used as chromatographic materials. Voucher specimens are deposited at the Botanical Garden of Kunming Institute of Botany, Academy of Science of China.

EXTRACTION AND ISOLATION.—The air-dried and pulverized root bark (2 kg) of *C. rosthornianus* was extracted with Me_2CO. The residue was chromatographed on an Al_2O_3 column with $CHCl_3$ and then on a Si gel column with Me_2CO-petroleum ether (1:9↦9:1) to give three groups of fractions. The middle polar group was separated on Merck Si gel preparative plates with Me_2CO-C_6H_6 (1:1) and purified on C-18 reversed-phase preparative plates with MeOH-H_2O (8:2) to give compounds **1** (55 mg) and **2** (21 mg).

Compound **1**.—Compound **1** was isolated as crystals, mp 225–226° (from petroleum ether/EtOAc. Found C 67.90, H 6.91, calcd for $C_{36}H_{44}O_{10}$, C 67.92, H 6.92. Uv λ max nm (log ε) 233 (2.833), 274 (1.536), 281 (1.403); ir ν max (KBr) cm^{-1} 3458 (OH), 2966, 2931, 1742 (C=O), 1600 and 1454 (Ph), 1370, 1271, 1096, 963, 709; ^{1}H nmr δ ppm 5.57 (1H, d, J = 4 Hz, H-1), 5.66 (1H, dd, J = 4, 8 Hz, H-2), 1.78 and 2.46 (each 1H, m, H-3), 2.42 (1H, m, H-4), 4.99 (1H, br s, H-6), 2.53 (1H, d, J = 3 Hz, H-7), 5.55 (1H, d, J = 3 Hz, H-8), 5.11 (1H, s, H-9), 1.45 (3H, d, J = 7.3 Hz, H-12), 1.73 (3H, s, H-13), 1.54 (3H, s, H-14), 1.58 (3H, s, H-15), 1.57 (3H, s, AcO), 7.48–8.09 (10H, m, 2 × PhCO), 0.90 (3H, t, J = 7 Hz), 1.14 (3H, d, J = 7 Hz), 1.48 and 1.66 (each 1H, m), and 2.35 (1H, m) (α-methylbutanoyloxy); ^{13}C nmr δ ppm 71.4 (C-1), 69.5 (C-2), 31.3 (C-3), 33.2 (C-4), 91.6 (C-5), 73.2 (C-6), 55.2 (C-7), 77.1 (C-8), 77.0 (C-9), 48.8 (C-10), 82.3 (C-11), 19.1 (C-12), 20.7 (C-13), 26.0 (C-14), 31.3 (C-15), 20.3 and 169.4 (AcCO), 128.5–133.6 and 2 × 164.8 (2 × PhCO), 11.5 (CH_3), 16.7 (CH_3), 26.6 (CH_2), 41.7 (CH), 175.7 (-CO_2-) (α-methylbutanoyloxy); eims m/z (%) [M]$^+$ 636 (41), [M − Me]$^+$ 621 (83), [621 − HOAc]$^+$ 561 (2), [M − α-methylbutanoic acid]$^+$ 534 (13), [M − $PhCO_2$]$^+$ 515 (10), [M − $PhCO_2H$]$^+$ 514 (3), 481 (10), 379 (21), 249 (8), 237 (61), 215

(70), 173 (39), $[PhCO]^+$ 105 (100), [α-methylbutanoyl]$^+$ 85 (43), $[Ph]^+$ 77 (48), $[AcO]^+$ 69 (10), [2-butyl]$^+$ 57 (69), $[Ac]^+$ 43 (35).

Compound **2**.—Compound **2** was isolated as an amorphous powder. Found C 65.16, H 6.69; calcd for $C_{34}H_{42}O_{11}$, C 65.18, H 6.71. Uv λ max nm (log ε) 232 (3.226), 275 (3.051), 282 (2.964); ir ν max (KBr) cm^{-1} 3520 (OH), 2930, 1730 (C=O), 1600 and 1454 (Ph), 1385, 1365, 1076; ^{1}H-nmr δ ppm 5.56 (1H, d, J = 4 Hz, H-1), 5.66 (1H, dd, J = 4, 8 Hz, H-2), 1.79 and 2.46 (each 1H, m, H-3), 2.42 (1H, m, H-4), 4.93 (1H, br s, H-6), 2.47 (1H, d, J = 4 Hz, H-7), 5.47 (1H, d, J = 4 Hz, H-8), 5.03 (1H, s, H-9), 1.45 (3H, d, J = 7.2 Hz, H-12), 1.66 (3H, s, H-13), 1.53 (3H, s, H-14), 1.58 (3H, s, H-15), 1.57 (3H, s, AcO), 7.44–8.04 (5H, m, PhCO), 6.78, 7.48, and 8.08 (each 1H, br s, β-furancarbonyloxy), 0.90 (3H, t, J = 7 Hz), 1.14 (3H, d, J = 7 Hz), 1.48, 1.66, and 2.35 (each 1H, m) (α-methylbutanoyloxy); ^{13}C nmr δ ppm 71.2 (C-1), 69.4 (C-2), 31.3 (C-3), 33.2 (C-4), 91.5 (C-5), 73.2 (C-6), 55.2 (C-7), 76.4 (C-8), 77.0 (C-9), 48.9 (C-10), 82.3 (C-11), 19.1 (C-12), 20.7 (C-13), 26.0 (C-14), 31.3 (C-15), 20.4 and 169.4 (AcO), 128.7–133.6 and 164.9 (PhCO), 109.8 (CH), 119.1 (quaternary carbon), 144.0 (CH), 148.0 (CH), and 161.1 ($-CO_2-$) (β-furancarbonyloxy), 11.6 (CH_3), 16.7 (CH_3), 26.6 (CH_2), 41.7 (CH) and 175.8 ($-CO_2-$) (α-methylbutanoyloxy); eims m/z (%) $[M]^+$ 626 (62), $[M-Me]^+$ 611 (81), $[611-HOAc]^+$ 551 (2), [M − α-methylbutanoic acid]$^+$ 524 (13), [611 − PhCO + H]$^+$ 507 (11), $[M-PhCO_2H]^+$ 504 (3), 481 (10), 379 (19), 249 (10), 237 (42), 215 (63), 173 (35), $[PhCO]^+$ 105 (100), [β-furancarbonyl]$^+$ 95 (88), [α-methylbutanoyl]$^+$ 85 (67), $[Ph]^+$ 77 (23), [2-butyl]$^+$ 57 (67), $[Ac]^+$ 43 (38).

LITERATURE CITED

1. G. Jiling, Y. Shixing, W. Xichum, X. Shixi, and L. Deda, *Chin. Med. J., Beijing, Engl. Ed.*, **94**, 405 (1981).
2. R. Bruning and H. Wagner, *Phytochemistry*, **17**, 1821 (1978).
3. Z. Rozsa, A. Perjesi, I. Pelczer, G. Argay, and A. Kalman, *J. Chem. Soc., Perkin Trans. 1*, 1079 (1989).
4. Z. Rozsa and I. Pelczer, *J. Chem. Soc., Perkin Trans. 1*, 1089 (1989).
5. Y.Q. Tu, D.G. Wu, J. Zhou, Y.Z. Chen, and X.F. Pan, *J. Nat. Prod.*, **53**, 603 (1990).
6. Y. Takaishi, K. Ujita, H. Noguchi, K. Nakano, T. Tomimatsu, S. Kadota, K. Tsubono, and T. Kikuchi, *Chem. Pharm. Bull.*, **35**, 3534 (1987).
7. N. Wakabayashi, W.J. Wu, R.M. Waters, R.E. Redfern, J.G.D. Mills, B.A. DeMilo, W.R. Lusby, and D. Andrzejewski, *J. Nat. Prod.*, **51**, 537 (1988).
8. J. Becerra, L. Gaete, M. Silva, F. Bohlmann, and J. Jakupovic, *Phytochemistry*, **26**, 3073 (1987).

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