Two New Sesquiterpenoids from the Seeds of *Celastrus angulatus*

Yanhong Wang,*,† Li Yang,‡ Yongqiang Tu,‡ Kun Zhang,‡ Yaozu Chen,*,‡ and Jinsong Fan§

School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, 510275, People's Republic of China, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China, and Guangzhou Institute of Chemistry, The Chinese Academy of Sciences, Guangzhou, 510600, People's Republic of China

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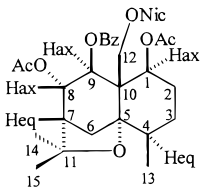
An investigation of seeds of *Celastrus angulatus* led to the isolation of two new sesquiterpenoids (**1** and **2**) with a β-dihydroagarofuran skeleton. Their structures were elucidated on the basis of spectroscopic methods.

In our previous papers, several species in the Celastraceae have been studied, and a series of β-dihydroagarofuran sesquiterpenoids have been reported.[1−3] *Celastrus angulatus* Max. is widely distributed in China, and extracts have shown antifeedant and insecticidal activity.[4,5] In a continued study of this plant, two new β-dihydroagarofuran sesquiterpene polyol esters (**1** and **2)** were isolated from the seeds of *C. angulatus*. The structure elucidation of these new compounds is the subject of this paper.



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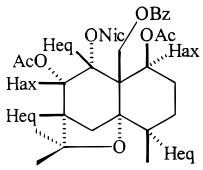

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Compound **1** analyzed for $C_{32}H_{37}NO_9$ by FABMS and elemental analysis. The IR spectrum revealed absorptions for ester groups at 1737 and 1720 cm^{-1} and phenyl groups at 1589 and 1453 cm^{-1}. The FABMS exhibited peaks consistent with losses of benzoic acid (*m/z* 458 [M + 1 − $PhCO_2H$]$^+$) and acetic acid (*m/z* 398 [458 − HOAc]$^+$) units. Moreover, the ^{1}H and ^{13}C NMR spectra of **1** suggested the presence of two acetate esters [^{1}H NMR δ 1.86 and 1.56 (each 3H, s); ^{13}C NMR δ 20.8 and 20.9 (2 × Me), 169.9 and 170.4 (2 × $-CO_2-$)], one β-nicotinate ester [^{1}H NMR δ 9.44 (1H, s), 8.85 (1H, d), 8.51 (1H, dt), and 7.51 (1H, m); ^{13}C NMR δ 153.9, 151.0, 137.0 and 123.6 (each CH), 125.6 (quaternary carbon), and 165.3 ($-CO_2-$)], and one benzoate ester [^{1}H NMR δ 7.34−7.86 (5H, m); ^{13}C NMR δ 128.5 and 129.3 (each 2 × CH), 133.1 (CH), 129.6 (quaternary carbon), and 165.4 ($-CO_2-$)]. In addition, the ^{13}C NMR and DEPT spectra indicated that **1** contained a skeleton based on 15 carbons: three methyl carbons (δ 17.0, 24.4, and 30.6), four methylene carbons (δ 22.7, 26.4, 36.4, and 62.9), five methine carbons (δ 39.7, 47.1, 75.4, 76.0, and 78.2), and three quaternary carbons (δ 50.0, 81.7, and 88.0). These data were suggestive of the presence of a 1,8,9,12-tetrasubstituted β-dihydroagarofuran skeleton.[6,7]

In the ^{1}H NMR spectrum of **1**, the quartet at δ 5.43 (1H, dd, J = 4.1, 11.8 Hz) was assigned to H_{ax}-1, and this quartet resulted from coupling with the methylene hydrogen at C-2. The sole upfield doublet at δ 1.17 (3H, d, J = 8.3 Hz) was assigned to the axial Me-13, and this doublet was caused by the presence of the methine hydrogen at C-4. Generally, H-1 and H-4 have axial and equatorial stereochemistry in this class of compound, respectively.[6,8] On the basis of the $J_{8,9}$ coupling constant, the doublet at δ 6.07 (1H, d, J = 9.8 Hz) and the AB quartet at δ 5.68 (1H, dd, J = 3.3, 9.8 Hz) were assigned to H_{ax}-9 and H_{ax}-8, respectively, because the dihedral angle between H-8 and H-9 was near 180°.[6,9] The AB doublets at δ 4.99 and 4.95 (each d, J = 12.9 Hz) were assigned to Ha-12 and Hb-12, respectively, and the doublets were due to geminal coupling of the methylene hydrogens at C-12.

The locations of the ester functions in **1** were determined on the basis of an HMBC NMR experiment. The cross signals between δ 165.3 and 4.99 and δ 165.4 and 6.07 indicated that the β-nicotinate and benzoate esters occurred at C-12 and C-9, respectively. The two acetate esters were affixed to C-1 and C-8, from the cross-peaks between δ 169.9 and 5.43 and δ 170.4 and 5.68, respectively. On the basis of the above evidence, compound **1** was elucidated as 1β,8α-diacetoxy-9β-(benzoyloxy)-12-(β-nicotinoyloxy)-β-dihydroagarofuran.

Compound **2** possessed a molecular formula of $C_{32}H_{37}NO_9$ as determined by FABMS and elemental analysis. Its characteristic IR absorptions at 1740 and 1723 cm^{-1} suggested the presence of several ester functions. The NMR spectral data showed the presence of one β-nicotinate ester [^{1}H NMR δ 9.32 (1H, s), 8.76 (1H, d), 8.37 (1H, dt), and 7.46 (1H, m); ^{13}C NMR δ 153.5, 151.0, 137.1 and 123.3 (each CH), 126.1 (quaternary carbon), and 164.8 ($-CO_2-$)], one benzoate ester [^{1}H NMR δ 7.30−7.96 (5H, m); ^{13}C NMR δ 128.3 and 129.4 (each 2 × CH), 133.1 (CH), 129.5 (quaternary carbon), and 165.2 ($-CO_2-$)], and two acetate esters [^{1}H NMR δ 1.83 and 1.54 (each 3H, s); ^{13}C NMR δ 20.8 and 20.9 (2 × Me), 169.7 and 170.1 (2 × $-CO_2-$)]. On comparison of the NMR data of **2** with those of compound **1**, it was concluded that both compounds possessed the same substituted β-dihydroagarofuran skeleton.

The same molecular formula and substituted functions and the different locations of the ester functions

* To whom correspondence should be addressed.
† Zhongshan University.
‡ Lanzhou University.
§ Guangzhou Institute of Chemistry.

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Table 1. ^{1}H NMR Spectral Data for Compounds **1** and **2**[a]

proton	1	2
H-1	5.43 (dd, 4.1, 11.8)	5.47 (dd, 4.6, 11.5)
H_2−2	1.86, 2.24 (overlap)	1.99, 2.27 (overlap)
H_{ax}−6	1.58 (overlap)	1.58 (overlap)
H_{eq}−7	2.40 (overlap)	2.31 (overlap)
H-8	5.68 (dd, 3.3, 9.8)	5.57 (br.t, 4.1)
H-9	6.07 (d, 9.8)	5.70 (d, 5.2)
Ha-12	4.99 (d, 12.9)	5.16 (d, 12.9)
Hb-12	4.95 (d, 12.9)	5.11 (d, 12.9)
Me-13	1.17 (d, 8.3)	1.21 (d, 8.9)
Me-14	1.58 (s)	1.47 (s)
Me-15	1.21 (s)	1.23 (s)
OAc	1.86, 1.56 (each 3H, s)	1.83, 1.54 (each 3H, s)
OBz	7.34−7.86 (5H, m)	7.30−7.96 (5H, m)
ONic	9.44 (1H, s) 8.85 (1H, d), 8.51 (1H, dt), 7.51 (1H, m)	9.32 (1H, s), 8.76 (1H, d), 8.37 (1H, dt), 7.46 (1H, m)

[a] Obtained in $CDCl_3$. *J* values are shown in parentheses.

Table 2. ^{13}C NMR Spectral Data for Compounds **1** and **2**[a]

carbon	1	2
C-1	75.4 (d)	73.8 (d)
C-2	22.7 (t)	23.4 (t)
C-3	26.4 (t)	27.0 (t)
C-4	39.7 (d)	39.8 (d)
C-5	88.0 (s)	88.1 (s)
C-6	36.4 (t)	32.2 (t)
C-7	47.1 (d)	47.7 (d)
C-8	76.0 (d)	69.9 (d)
C-9	78.2 (d)	79.1 (d)
C-10	50.0 (s)	49.8 (s)
C-11	81.7 (s)	80.9 (s)
C-12	62.9 (t)	62.3 (t)
C-13	17.0 (q)	16.9 (q)
C-14	24.4 (q)	22.9 (q)
C-15	30.6 (q)	29.8 (q)
OAc	20.8 (q), 20.9 (q), 170.4 (s), 169.9 (s)	20.8 (q), 20.9 (q), 170.1 (s), 169.7 (s)
OBz	128.5, 129.3 (each 2 × CH), 133.1 (CH), 129.6 (quaternary carbon), 165.4 (−CO_2−)	128.3, 129.4 (each 2 × CH), 133.1 (CH), 129.5 (quaternary carbon), 165.2 (−CO_2−)
ONic	153.9, 151.0, 137.0, 123.6 (each CH), 125.6 (quaternary carbon), 165.3 (−CO_2−)	153.5, 151.0, 137.1, 123.3 (each CH), 126.1 (quaternary carbon), 164.8 (−CO_2−)

[a] Obtained in $CDCl_3$.

at C-9 and C-12 suggested that compound **2** was a positional isomer of **1**. The above conclusion was supported by the following evidence. In the HMBC spectrum of **2**, the cross signals between δ 165.2 and 5.16 and δ 164.8 and 5.70 suggested that the benzoate and β-nicotinate esters were affixed at C-12 and C-9, respectively. The two acetate esters were determined to be present at C-1 and C-8 by the cross-peaks between δ 169.7 and 5.47 and δ 170.1 and 5.57, respectively. In addition, compound **2** had a difference in the C-9 stereochemistry compared with that in **1**. In the NOESY spectrum of **2**, the presence of cross signals between H_{eq}-9 (δ 5.70) and H_{ax}-1 (δ 5.47), H_{eq}-9 and H_{ax}-8 (δ 5.57), Heq-9 and H_2-12 (δ 4.95 and 4.99), and H_{eq}-9 and H_{ax}-6 (δ 1.58) showed that the stereochemistry of the substitued ester group at C-9 was α in compound **2**. Thus, compound **2** was elucidated as 1β,8α-diacetoxy-9α-(β-nicotinoyloxy)-12-(benzoyloxy)-β-dihydroagarofuran.

Experimental Section

General Experimental Procedures. Melting points were determined on a Kofler apparatus. Optical rotations were measured with a J-20C automatic apparatus. UV spectra in MeOH were obtained on a UV-240 spectrophotometer. IR spectra with KBr plates were determined on a FT-170SX spectrometer. ^{1}H NMR, ^{13}C NMR, DEPT, NOESY, and HMBC spectra were recorded on a Bruker AM-400 NMR spectrometer with TMS as internal standard and $CDCl_3$ as solvent. FABMS were obtained on a VG ZAB-HS mass spectrometer. Elemental analysis data were obtained on a Perkin-Elmer 240C instrument. HPLC was carried out on a Merck RP-18 short column.

Plant Material. The seeds of *C. angulatus* were obtained from Zunyi City, Guizhou Province, People's Republic of China, in October 1990. Voucher specimens (no. ZY9010) are deposited at the Department of Chemistry, Lanzhou University.

Extraction and Isolation. The air-dried and pulverized seeds (2 kg) of *C. angulatus* were extracted with petroleum ether to give an oil, which was re-extracted with MeOH to obtain a crude sesquiterpene mixture (22 g). This was chromatographed on a silica gel column (300 g) with petroleum ether−Me_2CO (9:1−3:2) as eluent to give 48 fractions. Fractions 10−26 were combined and purified on a RP-18 short column using MeOH−H_2O (4:1) as eluent to afford compounds **1** (34 mg) and **2** (38 mg).

Compound 1: amorphous powder; $[\alpha]_D$ 48.6° (*c* 0.35, MeOH); UV (MeOH) λ_{max} (log ϵ) 201 (3.24), 224 (3.26), 263 (2.58) nm; IR (KBr) ν_{max} 1737, 1720, 1589, 1453, 1293, 1225, 1095, 1022 cm^{-1}; ^{1}H NMR spectral data, see Table 1; ^{13}C NMR spectral data, see Table 2; FABMS *m/z* 580 $[M + 1]^+$ (100), 519 (12), 458 (16), 398 (14), 275

(56), 215 (73); *anal.* C 66.13%, H 6.47%, N 2.37%, calcd for $C_{32}H_{37}NO_9$, C 66.31%, H 6.43%, N 2.42%.

Compound 2: colorless needles (Me_2CO); mp 168−170 °C; $[\alpha]_D$ 25.4° (*c* 0.52, MeOH); UV (MeOH) λ_{max} (log ϵ) 201 (3.23), 224 (3.28), 263 (2.56) nm; IR (KBr) ν_{max} 1740, 1723, 1590, 1453, 1286, 1231, 1106, 1023 cm^{-1}; ^1H NMR spectral data, see Table 1; ^{13}C NMR spectral data, see Table 2; FABMS *m*/*z* 580 $[M + 1]^+$ (100), 520 (26), 457 (21), 369 (8), 275 (52), 215 (100); *anal.* C 66.23%, H 6.49%, N 2.36%, calcd for $C_{32}H_{37}NO_9$, C 66.31%, H 6.43%, N 2.42%.

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