Five New Insecticidal Sesquiterpenoids from *Celastrus angulatus*

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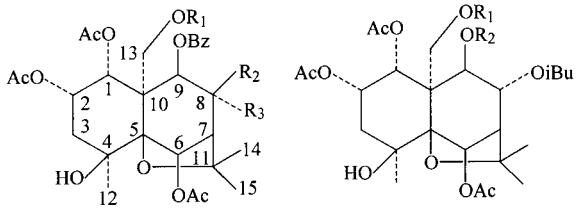
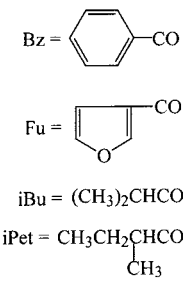
Five new sesquiterpene polyol esters were isolated from the root bark of *Celastrus angulatus* by bioassay-guided fractionation. Their structures were determined by spectral data interpretation as 1α,2α,6β,8β,13-pentaacetoxy-9β-benzoyloxy-4β-hydroxy-β-dihydroagarofuran (**1**), 1α,2α,6β-triacetoxy-8α-(β-furancarbonyloxy)-9β-benzoyloxy-13-isobutanoyloxy-4β-hydroxy-β-dihydroagarofuran (**2**), 1α,2α,6β-triacetoxy-8β-isobutanoyloxy-9β-(β-furancarbonyloxy)-13-(α-methyl)butanoyloxy-4β-hydroxy-β-dihydroagarofuran (**3**), 1α,2α,6β-triacetoxy-8α,13-diisobutanoyloxy-9β-benzoyloxy-4β-hydroxy-β-dihydroagarofuran (**4**), and 1α,2α,6β-triacetoxy-8α-isobutanoyloxy-9β-benzoyloxy-13-(α-methyl)butanoyloxy-4β-hydroxy-β-dihydroagarofuran (**5**). Compounds **1**−**5** exhibited insecticidal activity against the larval of *Mythimna separata*.

Plants of the family Celastraceae produce various β-dihydroagarofuran sesquiterpene polyol esters and alkaloids, of which some exhibit insect antifeedant, insecticidal, and antitumor activity. The Chinese bittersweet, *Celastrus angulatus* Max. (Celastraceae), is a traditional insecticidal plant widely distributed and used in the People's Republic of China.[1] Extracts of this plant have exhibited antifeedant, narcotic, and insecticidal activity against several insect species.[2] In a previous study, several antifeedant and insecticidal components (celangulins I−IV) were isolated from the root bark of *C. angulatus*.[3,4] Continued activity-guided fractionation has led to isolation of five new sesquiterpene polyol esters (**1**−**5**) based on the β-dihydroagarofuran skeleton from *C. angulatus*. All five new compounds showed insecticidal activity against the armyworm [*Mythimna separata* (Walker)]. In this paper, we present the isolation, structure elucidation, and bioassay data for compounds **1**−**5**.



1 R_1 = Ac, R_2 = OAc, R_3 = H
2 R_1 = iBu, R_2 = H, R_3 = OFu
3 R_1 = iPet, R_2 = Fu
4 R_1 = iBu, R_2 = Bz
5 R_1 = iPet, R_2 = Bz



Compound **1** analyzed for $C_{32}H_{40}O_{14}$ by HRFABMS. Its IR spectrum revealed a characteristic ester absorption band at 1748 cm^{-1} and a free hydroxyl absorption band at 3419 cm^{-1}. The NMR spectra suggested the presence of five acetate esters [^{1}H NMR δ 1.61 s, 1.89 s, 2.08, 2.11, and 2.35 s (5 × 3H); ^{13}C NMR δ 20.3, 20.7, 21.1, 21.2, 21.4, 169.1, 169.3, 169.6, 169.9, and 170.6 (5 × Ac)], one benzoate ester [^{1}H NMR δ 8.05 d (2H, J = 7.2 Hz), 7.61 d (1H, J = 7.5 Hz), and 7.48 dd (2H, J = 7.2, 7.5 Hz); ^{13}C NMR δ 128.4, 128.7, 130.3. 133.7, 165.5], and one free hydroxyl group [^{1}H NMR δ 3.81 s (1H, disappeared on exchange with D_2O)].

The ^{1}H NMR spectrum of compound **1** showed the presence of three tertiary methyl groups at δ 1.50, 1.58, and 1.67 s. The signals observed at δ 5.58 d (J = 3.4 Hz), 5.50 m, 5.84 dd (J = 6.4, 3.1 Hz), 5.62 d (J = 6.4 Hz), and 6.08 s were assigned to five protons attached to carbon atoms bearing secondary ester groups, while signals at δ 4.45 and 4.83 d (J = 13.1 Hz) were assigned to the two protons attached to carbon atoms bearing primary ester groups. The ^{13}C NMR spectrum of the parent skeleton of **1** showed three methyls, one methylene, one methylene attached to an oxygen function, one methine, five methines attached to an oxygen function, one quaternary carbon, and three quaternary carbons attached to an oxygen function, whose chemical shifts were very similar to those of other 1,2,4,6,8,9,13-heptasubstituted β-dihydroagarofurans.[5−7] It was determined that compound **1** was esterified at C-1, C-2, C-4, C-6, C-8, C-9, and C-13.

From the ^{1}H−^{1}H COSY spectrum of compound **1**, the cross-peaks of the protons at δ 4.45 and 4.83, δ 5.58 and 5.50, and δ 5.84 and 5.62 permitted their assignment to H-13, H-1, H-2, H-8, and H-9, respectively. The singlet peak at δ 6.08 was assigned to H-6 because the dihedral angles of H-6 and H-7 were near 90°, as observed for similar compounds containing an ester group at C-6.[3−8] The remaining ^{1}H NMR signals were assigned as shown in Table 1. The ^{13}C NMR signals were assigned on the basis of ^{13}C−^{1}H COSY data and are given in Table 2. Generally, H-1, H-2, and H-6 in this class of compounds have axial, equatorial, and axial stereochemistry,[3−5] respectively. The coupling constant ($J_{8,9}$ = 6.4 Hz) between H-8 and H-9 suggested that H-8 and H-9 have a different orientation. The stereochemistry for H-8 and H-9 was determined from the NOESY spectrum, which showed cross-peaks between H-8 and H-6, H-8 and H-9, and H-9 and H-13, suggesting that H-8 is axial and H-9 is equatorial, respectively, in **1**.

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Table 1. ^{1}H NMR Chemical Shifts of Compounds **1**−**5** in $CDCl_3$[a]

position	1	2	3	4	5
1	5.58 d (3.4)	5.61 d (3.6)	5.57 d (3.7)	5.62 d (3.6)	5.64 d (3.6)
2	5.50 m	5.58 m	5.54 m	5.56 m	5.59 m
3	2.03 m	2.02 m	1.98 dd (15.2, 2.7)	1.98 dd (15.0, 2.7)	1.98 dd (15.0, 2.7)
	2.35 m	2.25 m	2.20 dd (15.2, 3.8)	2.25 dd (15.0, 4.1)	2.27 dd (15.0, 4.0)
6	6.08 s	6.41 s	6.19 s	6.27 s	6.27 s
7	2.44 d (3.1)	2.50 d (3.0)	2.38 d (3.0)	2.38 d (2.8)	2.44 d (3.0)
8	5.84 dd (6.4, 3.1)	5.49 d (3.0)	5.26 d (3.0)	5.30 d (2.8)	5.32 d (3.0)
9	5.62 d (6.4)	5.88 s	5.58 s	5.71 s	5.73 s
12	1.50 s	1.51 s	1.48 s	1.50 s	1.53 s
13	4.45 d, 4.83 d (13.1)	4.30 d, 5.01 d (12.6)	4.79 d, 4.87 d (12.7)	4.80 d, 4.91 d (12.7)	4.87 d, 4.90 d (12.8)
14	1.58 s	1.62 s	1.61 s	1.65 s	1.69 s
15	1.67 s	1.72 s	1.56 s	1.58 s	1.61 s
OH-4	2.79 s	2.78 s	2.72 s	2.78 s	2.79 s

[a] Spectra obtained for **1** and **2** at 300 MHz and for **3**−**5** at 600 MHz.

Table 2. ^{13}C NMR Chemical Shifts of Compounds **1**−**5** in $CDCl_3$[a]

position	1	2	3	4	5
1	70.2 (d)	70.8 (d)	70.9 (d)	70.9 (d)	70.9 (d)
2	68.1 (d)	67.3 (d)	68.3 (d)	68.0 (d)	68.1 (d)
3	42.1 (t)	42.0 (t)	42.3 (t)	42.1 (t)	42.1 (t)
4	69.8 (s)	69.9 (s)	70.1 (s)	69.9 (s)	69.9 (s)
5	91.0 (s)	91.3 (s)	91.6 (s)	91.4 (s)	91.4 (s)
6	76.2 (d)	75.6 (d)	75.7 (d)	76.2 (d)	76.2 (d)
7	53.9 (d)	53.5 (d)	53.1 (d)	53.1 (d)	53.0 (d)
8	70.1 (d)	76.2 (d)	76.3 (d)	75.5 (d)	75.6 (d)
9	68.2 (d)	70.9 (d)	71.7 (d)	72.0 (d)	72.0 (d)
10	53.9 (s)	54.5 (s)	53.2 (s)	54.1 (s)	54.1 (s)
11	85.0 (s)	83.4 (s)	83.7 (s)	83.5 (s)	83.5 (s)
12	25.1 (q)	24.3 (q)	24.8 (q)	24.5 (q)	24.5 (q)
13	64.5 (t)	65.2 (t)	65.8 (t)	65.5 (t)	65.6 (t)
14	26.4 (q)	25.6 (q)	25.7 (q)	25.6 (q)	25.6 (q)
15	30.0 (q)	29.6 (q)	29.8 (q)	29.6 (q)	29.6 (q)

[a] Spectra obtained for **1** and **2** at 75 MHz, and for **3**−**5** at 150 MHz.

The free hydroxyl group of **1** was assumed to be at C-4 because in all other known compounds of this class, the tertiary OH-4 is not esterified and has an equatorial orientation.[3−8] In the ^{1}H−^{13}C long-range correlation (COLOC) spectrum,[9] the cross-peak between H-9 at δ 5.62 and the carbonyl at δ 165.5 of a benzoate ester suggested that the ester group at C-9 is a benzoate. The remaining five acetate esters were placed at C-1, C-2, C-6, C-8, and C-13. Therefore, structure of **1** was elucidated as 1α,2α,6β,8β,13-pentaacetoxy-9β-benzoyloxy-4β-hydroxy-β-dihydroagarofuran.

Compound **2** analyzed for $C_{37}H_{44}O_{15}$ by HRFABMS. The spectral data of **2** suggested the presence of three acetate esters, one isobutanoate ester, one benzoate ester, one β-furancarboxylate ester, and one free hydroxyl group. The ^{1}H NMR and ^{13}C NMR data for the parent ring system were very similar to those of **1**, suggesting that **2** also contains the 1,2,4,6,8,9,13-heptasubstituted β-dihydroagarofuran skeleton and that **2** has the same stereochemistry for H-1, H-2, and H-6 as **1**. The weak coupling ($J_{8,9} = 0$ Hz) between H-8 and H-9 suggested that both H-8 and H-9 have an equatorial orientation, with the angle between H-8 and H-9 near 90°.[3,5−7] As with **1**, the free hydroxyl group was at C-4 with equatorial orientation, and the ester group distribution was determined from the COLOC spectrum, which showed cross-peaks between H-9 and the carbonyl at δ 164.2 of the benzoate ester, H-8 and the carbonyl at δ 161.3 of the β-furancarboxylate ester, and H-1, H-2, and H-6 and the carbonyls at δ 169.6, 169.7, and 169.4 of three acetate esters, respectively. These observations suggested three acetate esters were at C-1, C-2, and C-6, one benzoate ester was at C-9, and one β-furancarboxylate ester was at C-8. The remaining isobutanoate ester was located at C-13. Thus, **2** was elucidated as 1α,2α,6β-triacetoxy-8α-(β-furancarbonyloxy)-9β-benzoyloxy-13-isobutanoyloxy-4β-hydroxy-β-dihydroagarofuran.

Compound **3** analyzed for $C_{35}H_{48}O_{15}$ by HRFABMS. The spectral data also suggested the presence of three acetate esters, one isobutanoate ester, one β-furancarboxylate ester, one α-methylbutanoate ester, one free hydroxyl group, and the same 1,2,4,6,8,9,13-heptasubstituted β-dihydroagarofuran skeleton as **1** and **2**. On careful comparison with the ^{1}H NMR spectrum of **2**, **3** had the same stereochemistry for H-1, H-2, H-6, H-8, and H-9 because of the similar coupling constants and cross-peaks in the NOESY spectrum. The ester group distribution was determined from the HMBC spectrum,[10] which showed cross-peaks between H-13 and the carbonyl at δ 176.1 of the α-methylbutanoate ester, between H-8 and the carbonyl at δ 175.9 of the isobutanoate ester, between H-9 and the carbonyl at δ 161.1 of the β-furancarboxylate ester, and between H-1, H-2, and H-6 and the carbonyls at δ 169.9, 169.9, and 170.0 of three acetate esters. These observations indicated that three acetate esters were at C-1, C-2, and C-6, one isobutanoate ester was at C-8, one β-furancarboxylate ester was at C-9, and one α-methylbutanoate ester was at C-13. As with **1** and **2**, the free hydroxyl group was at C-4 and had equatorial orientation. Therefore, the structure of **3** was elucidated as 1α,2α,6β-triacetoxy-8α-isobutanoyloxy-9β-(β-furancarbonyloxy)-13-(α-methyl)-butanoyloxy-4β-hydroxy-β-dihydroagarofuran.

Compound **4** analyzed for $C_{36}H_{48}O_{14}$ by HRFABMS. The spectral data indicated the presence of three acetate esters, two isobutanoate esters, one benzoate ester, and one free hydroxyl group, all based on a 1,2,4,6,8,9,13-heptasubstituted β-dihydroagarofuran skeleton. On comparison of the coupling constants with **2** and **3**, **4** had the same sterochemistry for H-1, H-2, H-6, H-8, H-9, and OH-4 as **2** and **3**. In the HMBC spectrum, the two carbonyls at δ 175.6 and 175.7 of two isobutanoate esters showed long-range correlations with H-8 and H-13, the three carbonyls of three acetate esters at δ 169.3, 169.4, and 169.6 showed long-range correlations with H-1, H-2, and H-6, and the carbonyl at δ 164.5 of the benzoate ester showed a long-range correlation with H-9. These results clearly indicated that the three acetate esters were located at C-1, C-2, and C-6, the two isobutanoate esters were located at C-8 and C-13, and the benzoate ester was located at C-9. As with **1**−**3**, the free hydroxyl group was at C-4 with an equatorial orientation. Thus, the structure of **4** was assigned as 1α,2α,6β-triacetoxy-8α,13-diisobutanoyloxy-9β-benzoyloxy-4β-hydroxy-β-hydroagarofuran.

Compound **5** analyzed for $C_{37}H_{50}O_{14}$ by HRFABMS. The spectral data suggested the presence of three acetate esters, one isobutanoate ester, one α-methylbutanoate ester, one

benzoate ester, and one free hydroxy group, and once again a 1,2,4,6,8,9,13-heptasubstituted β-dihydroagarofuran skeleton. By a careful comparison of **5** with **2**−**4**, it could be seen that these compounds exhibited very similar ^{1}H NMR, ^{13}C NMR, COSY, HMQC, and HMBC spectra, which indicated that the esters at C-1, C-2, C-6, C-8, and C-9 in **5** were the same as those of **4**, and the ester at C-13 was an α-methylbutanoate ester. Thus, **5** was established as 1α,2α,6β-triacetoxy-8α-isobutanoyloxy-9β-benzoyloxy-13-(α-methyl)butanoyloxy-4β-hydroxy-β-hydroagarofuran.

Using a previously published protocol,[4] the KD_{50} values (the dose required to knock down 50% of the population of *M. separata*) determined for compounds **1**−**5** were 159.8, 58.9, 91.4, 271.5, and 168.8 μg/g, respectively. On comparison of the insecticidal activities of **1**−**5**, **2** and **3** showed stronger activity than **1**, **4**, and **5**, which may be due to the presence of a β-furancarbonyloxy group. It is interesting to note that the insects treated with compounds **1** and **2** were immobilized without convulsive symptoms, while the insects treated with compounds **3**−**5** lost fluid with slight convulsive symptoms. Compounds **1**−**5** may have a different mode of action compared with insecticidal compounds isolated from other plants.

Experimental Section

General Experimental Procedures. Melting points were measured on a X_4 apparatus and are uncorrected. Optical rotations were measured on a Jasco 500C polarimeter. UV spectra were obtained on UV 756MC spectrophotometer. IR spectra were determined on an Equinox 55 instrument (KBr plate). ^{1}H NMR, ^{13}C NMR, COSY, ^{13}C−^{1}H COSY, HMQC, NOESY, COLOC, and HMBC spectra were recorded on a Bruker Avance DPX 300 or DMX 600 NMR spectrometer with $CDCl_3$ as solvent and TMS as internal standard, respectively. EIMS and HRFABMS were obtained on a VG ZAB-HS mass spectrometer operating at 70 eV with a direct insert system or a Bruker Apex II mass spectrometer using nitrobenzoyl alcohol and sodium chloride as matrix.

Plant Material. The root bark of *C. angulatus* was collected in Mazhao village, Zhouzhi county, Shaanxi Province, People's Republic of China, in October 1995, and authenticated by Prof. Yang Jinqiang of the Department of Plant Protection (Northwestern Agricultural University). A voucher specimen (sample no. NWAU95-C06) was deposited at the Department of Plant Protection.

Extraction and Isolation. The dried and pulverized root bark (6.6 kg) of *C. angulatus* was extracted with petroleum ether under reflux for 3 h. The extracted material was re-extracted with petroleum ether twice. The extracts obtained were combined and concentrated to give a yellow semisolid residue (260 g). This crude extract was chromatographed on a Si gel (200−300 mesh) column using EtOAc−petroleum ether (2:8→8:2) as eluent to give 180 fractions (each 500 mL). Fractions 46−75 were combined (40 g) and rechromatographed on a Si gel (200−300 mesh) column using EtOAc−petroleum ether (4:6) to give 23 fractions (each 500 mL). Fractions 17−22 (8 g) were subjected to low-pressure liquid chromatography (RP-18, MeOH−H_2O, 65:35) to give 110 fractions (each 100 mL). Subfractions 3−9, 10−16, and 21−22 were combined, respectively, and subjected to HPLC (RP-18, MeOH−H_2O−CH_3CN, 62:35:3) to afford compounds **1** (35 mg), **2** (32 mg), and **3** (65 mg). Subfractions 40−48 were combined and subjected to HPLC to afford compounds **4** (21 mg) and **5** (28 mg).

Compound 1: amorphous white powder; mp 117−118 °C; $[\alpha]^{24}_D$ −23.2° (*c* 0.46, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 243 (3.61) nm; IR (KBr) ν_{max} 3419, 1748, 1371, 1234, 1153, 1096, 1040, 955, 712 cm^{-1}; ^{1}H NMR δ 1.61 s, 1.89 s, 2.08, 2.11, and 2.35 s (each 3H, 5 × Ac), 8.05 d (2H, J = 7.2 Hz), 7.61 d (1H, J = 7.5 Hz), 7.48 dd (2H, J = 7.2, 7.5 Hz), C_6H_5CO; ^{13}C NMR δ 20.3, 20.7, 21.1, 21.2, 21.4, 169.1, 169.3, 169.6, 169.9, 170.6 (5 × Ac), 128.4, 128.7, 130.3, 133.7, 165.5 (C_6H_5CO); ^{1}H NMR and ^{13}C NMR (sesquiterpenoid portion), see Tables 1 and 2; FABMS *m/z* 649 $[M + H]^+$, 631 $[M + H - H_2O]^+$, 589 $[M + H - HOAc]^+$, 547 $[M + H - HOAc - Ac]^+$, 529 $[M + H - 2 \times HOAc]^+$; EIMS *m/z* 633 $[M - CH_3]^+$, 605 $[M - Ac]^+$, 588 $[M\text{-}HOAc]^+$, 528 $[M - 2 \times HOAc]^+$, 511 $[M - CH_3 - C_6H_5\text{-}CO_2H]^+$, 307, 289, 262, 202, 105, 43; HRFABMS *m/z* 671.2315 $[M + Na]^+$ (calcd for $C_{32}H_{40}O_{14}Na$, 671.2310), 649.2471 $[M + H]^+$ (calcd for $C_{32}H_{41}O_{14}$, 649.2491).

Compound 2: amorphous white powder; mp 109−110 °C; $[\alpha]^{24}_D$ −25.9°(*c* 0.58, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 243 (3.61) nm; IR (KBr) ν_{max} 3555, 2979, 1744, 1372, 1233, 1154, 1033, 871, 757, 711 cm^{-1}; ^{1}H NMR δ 1.51, 2.08, and 2.25 s (each 3H, 3 × Ac), 1.09 and 1.17 d (each 3H, J = 7.1 Hz), 2.62 m (1H, isobutanoyl), 8.05 d (2H, J = 7.2 Hz), 7.60 d (1H, J = 7.5 Hz), 7.47 m (2H, C_6H_5CO), 6.87 d (1H, J = 1.8 Hz), 7.47 m (1H), 8.24 d (1H, J = 0.5 Hz, β-furancarbonyl); ^{13}C NMR δ 20.3, 21.0, 21.4, 169.6, 169.7 (3 × Ac), 18.8, 18.9, 33.9, 176.8 (isobutanoyl), 128.4, 129.6, 130.2, 133.7, 164.2 (C_6H_5CO), 109.8, 118.7, 143.9, 148.6, 161.3 (β-furancarbonyl); ^{1}H NMR and ^{13}C NMR (sesquiterpenoid portion), see Tables 1 and 2; FABMS *m/z* 711 $[M - OH]^+$, 603 $[MH - CH_3 - FuOH]^+$; EIMS *m/z* 713 $[M - CH_3]^+$, 686 $[M + H - Ac]^+$, 668 $[M - HOAc]^+$, 653 $[M - CH_3 - HOAc]^+$, 616 $[M - FuOH]^+$, 608 $[M - 2 \times HOAc]^+$, 244, 202, 105, 95, 71, 43; HRFABMS *m/z* 751.2560 $[M + Na]^+$ (calcd for $C_{37}H_{44}O_{15}Na$, 751.2572).

Compound 3: amorphous white powder; mp 78−79 °C; $[\alpha]^{24}_D$ −25.8°(*c* 0.60, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 217 (3.18), 245 (3.36) nm; IR (KBr) ν_{max} 3430, 2975, 1742, 1371, 1233, 1151, 876, 758 cm^{-1}; ^{1}H NMR δ 1.64, 2.08, and 2.10 s (each 3H, 3 × Ac), 1.24 and 1.25 d (each 3H, J = 7.2 Hz), 2.66 m (1H, isobutanoyl), 0.96 t (3H, J = 6.9 Hz), 1.23 d (3H, J = 7.1 Hz), 1.54, 1.79, and 2.57 m (each 1H, α-methylbutanoyl), 6.72 d (J = 1.8 Hz), 7.43 d (J = 1.8 Hz) and 8.00 d (J = 0.5 Hz) (each 1H, β-furancarbonyl); ^{13}C NMR δ 21.3, 21.6, 20.8, 3 × 169.9 (3 × Ac), 2 × 19.0, 34.2, 175.9 (isobutanoyl), 11.9, 16.8, 26.8, 41.4, 176.1 (α-methylbutanoyl), 109.9, 118.0, 144.2, 149.2, 161.1 (β-furancarbonyl); ^{1}H NMR and ^{13}C NMR (sesquiterpenoid portion), see Tables 1 and 2; FABMS *m/z* 709 $[M + H]^+$, 603 $[M - OH - (CH_3)_2CHCOOH]^+$, 577 $[M - FuOH - H_2O]^+$; EIMS *m/z* 693 $[M - CH_3]^+$, 691 $[M - OH]^+$, 666 $[M + H - Ac]^+$, 648 $[M - HOAc]^+$, 633 $[M - CH_3 - HOAc]^+$, 631 $[M - OH - HOAc]^+$, 244, 95, 85, 71, 43; HRFABMS *m/z* 731.2876 $[M + Na]^+$ (calcd for $C_{35}H_{48}O_{15}Na$, 731.2885), 691.2917 $[M - OH]^+$ (calcd for $C_{35}H_{47}O_{14}$, 691.2910).

Compound 4: amorphous white powder; mp 94−95 °C; $[\alpha]^{24}_D$ −34.3°(*c* 0.35, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 243 (3.69) nm; IR (KBr) ν_{max} 3554, 2979, 1744, 1373, 1233, 1151, 712 cm^{-1}; ^{1}H NMR δ 2.07 s, 2.11 s, 1.47 s (each 3H, 3 × Ac), 1.26 d (2 × 3H, J = 7.2 Hz), 1.27 d (2 × 3H, J = 7.2 Hz), 2.68 m (2 × 1H, 2 × isobutanoyl), 8.01 d (2H, J = 7.1 Hz), 7.59 d (1H, J = 7.5 Hz), 7.45 dd (2H, J = 7.1, 7.5 Hz, C_6H_5CO); ^{13}C NMR δ 20.3, 21.0, 21.4, 169.3, 169.4, 169.6 (3 × Ac), 18.7, 18.9, 19.0, 19.1, 34.0, 34.1, 175.7, 175.8 (2 × isobutanoyl), 128.4, 130.0, 130.1, 133.8, 164.5 (C_6H_5CO); ^{1}H NMR and ^{13}C NMR (sesquiterpenoid portion), see Tables 1 and 2; FABMS *m/z* 705 $[M + H]^+$, 687 $[M - OH]^+$, 599 $[M - C_6H_5CO]^+$, 539 $[M - C_6H_5CO - HOAc]^+$; EIMS *m/z* 689 $[M - CH_3]^+$, 662 $[M + H - Ac]^+$, 644 $[M - HOAc]^+$, 629 $[M - CH_3 - HOAc]^+$, 616 $[M - (CH_3)_2\text{-}CHCOOH]^+$, 244, 202, 105, 71, 43; HRFABMS *m/z* 727.2936 $[M + Na]^+$ (calcd for $C_{36}H_{48}O_{14}Na$, 727.2936), 687.3020 $[M - OH]^+$ (calcd for $C_{36}H_{47}O_{13}$, 687.3011).

Compound 5: amorphous white powder; mp 95−96 °C; $[\alpha]^{24}_D$ −17.9° (*c* 0.60, $CHCl_3$); UV (MeOH) λ_{max} (log ϵ) 246 (3.43), 275 (3.11) nm; IR (KBr) ν_{max} 3559, 2977, 1744, 1372, 1233, 1149, 1095, 713 cm^{-1}; ^{1}H NMR δ 1.51 s, 2.10 s, 2.14 s (each 3H, 3 × Ac), 1.28 and 1.29 d (each 3H, J = 7.2 Hz), 2.71 m (1H, isobutanoyl), 1.01 t (3H, J = 7.1 Hz), 1.27 d (3H, J = 6.9 Hz), 1.54 m, 2.72 m, 1.80 m (each 1H, α-methylbutanoyl), 8.05 d (2H, J = 7.2 Hz), 7.63 d (1H, J = 7.5 Hz), 7.49 dd (2H, J = 7.2, 7.5 Hz, C_6H_5CO); ^{13}C NMR δ 20.3, 21.1, 21.4, 169.3, 169.4, 169.6 (3 × Ac), 18.8, 19.0, 34.0, 175.7 (isobutanoyl), 11.6, 16.5, 24.5, 47.2, 176.5 (α-methylbutanoyl), 128.4, 129.9, 130.2, 133.8, 164.5 (C_6H_5CO); ^{1}H NMR and ^{13}C NMR (sesquiterpenoid portion), see Tables 1 and 2; FABMS *m/z* 719 $[M + H]^+$, 701

$[M - OH]^+$, 641 $[M - OH - Ac]^+$, 613 $[M - OH - (CH_3)_2CHCOOH]^+$; EIMS *m/z* 703 $[M - CH_3]^+$, 676 $[M + H - Ac]^+$, 658 $[M - HOAc]^+$, 643 $[M - CH_3 - HOAc]^+$, 613 $[M + H - (CH_3)_2CHCOOH]^+$, 244, 202, 105, 85, 71, 43; HRFABMS *m/z* 741.3071 $[M + Na]^+$ (calcd for $C_{37}H_{50}O_{14}Na$, 741.3092), 701.3043 $[M - OH]^+$ (calcd for $C_{37}H_{49}O_{13}$, 701.3167).

References and Notes

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