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SESQUITERPENE POLYOL ESTERS FROM *CELASTRUS PANICULATUS*

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ABSTRACT.—From the MeOH extract of the seed oil of *Celastrus paniculatus*, a known sesquiterpene, 1 β ,6 α ,8 β -triacetoxo-9 α -(β -furancarboxyloxy)- β -dihydroagarofuran [**1**], and a new sesquiterpene, 1 β ,6 α -diacetoxo-9 β -benzoyloxy-8 β -cinnamoyloxy- β -dihydroagarofuran [**2**], were isolated. Their structures were elucidated on the basis of spectral analysis.

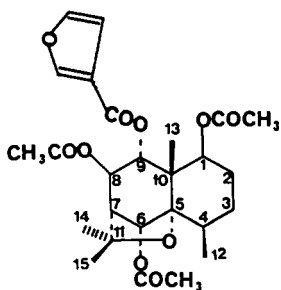
In previous papers, we have reported several sesquiterpene polyol esters with a β -dihydroagarofuran skeleton from the seeds of *Euonymus bungeanus* Loes. (Celastraceae) (1,2), some of which exhibit insect antifeedant effects. During further studies of chemical constituents of the Celastraceae, we have isolated two sesquiterpene polyol esters **1** and **2** from the seed oil of *Celastrus paniculatus* Willd. Several polyalcohols and alkaloids with the β -dihydroagarofuran skeleton have been isolated previously from this species (3–7). The structure elucidation of compounds **1** and **2** is the subject of this paper.

RESULTS AND DISCUSSION

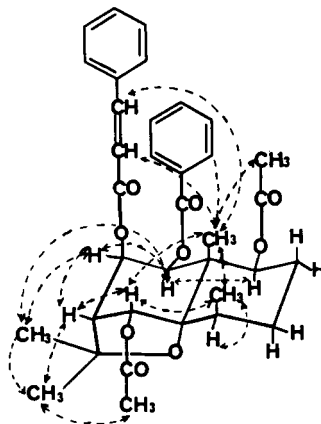
Compound **1** had the molecular formula $C_{26}H_{34}O_{10}$, determined by exact mass measurement of its high resolution mass spectrum. Its structure was identified as 1 β ,6 α ,8 β -triacetoxo-9 α -(β -fu-

rancarboxyloxy)- β -dihydroagarofuran, mainly based on the similarity of its nmr, ir, uv, and mass spectral data to those of the known compound (8).

Compound **2** had the molecular formula $C_{35}H_{40}O_9$, also determined by hrms. Its ir revealed the absorption of an ester group at 1725 cm^{-1} , a phenyl group at 1600 and 1450 cm^{-1} , and a carbon-carbon double bond at 1630 cm^{-1} . The eims showed the presence of an acetate ester at m/z 544 [$M - \text{HOAc}$] $^+$ and 43 [Ac] $^+$, benzoate ester at m/z 440 [$M - \text{C}_6\text{H}_5\text{COOH}$] $^+$ and 105 [$\text{C}_6\text{H}_5\text{CO}$] $^+$, and cinnamate at m/z 473 [$M - \text{C}_6\text{H}_5 = \text{CHCO}$] $^+$. Moreover, the nmr suggested the presence of two acetate esters [^1H nmr δ 2.13 and 1.43 ($2 \times 3\text{H}$, $2 \times \text{s}$); ^{13}C nmr δ 21.3 and 20.8 ($2 \times \text{Me}$), δ 170.1 and 169.8 ($2 \times \text{COO-}$)], one benzoate ester [^1H nmr δ 7.36–8.01 (5H, m); ^{13}C nmr δ 133.0 (CH), δ 128.3 and 129.5 (each $2 \times \text{CH}$),



1



2

δ 130.0 (quaternary carbon), δ 165.0 (-COO-) (12) and one cinnamate ester [^1H nmr δ 7.36–7.56 (5H, m), δ 7.72 and 6.48 ($2 \times 1\text{H}$, ABq, $J = 16$ Hz); ^{13}C nmr δ 130.4 (CH), δ 128.2 and 129.6 (each $2 \times \text{CH}$), δ 134.4 (quaternary carbon), δ 145.8 and 117.6 ($2 \times \text{CH}$), δ 165.5 (-COO-)] (9, 10). In addition, the ^{13}C -nmr and DEPT spectra indicated that **2** contained a skeleton including fifteen carbons: four methyls (δ 12.2, 16.8, 24.4, and 30.6), two methylene carbons (δ 22.1 and 26.6), six methine carbons (δ 33.8, 52.9, 71.2, 74.5, 74.9, and 78.9) and three quaternary carbons (δ 48.8, 81.6, and 91.5). These data were suggestive of a 1,6,8,9-tetra-substituted- β -dihydroagarofuran skeleton (4,8).

In ^1H -nmr and NOESY spectra, the doublet at δ 5.25 (1H, dd, $J = 5, 11$ Hz) was assigned to $\text{H}_{\text{ax}}-1$ because in this class of compound H-1 had generally axial stereochemistry (11). The sole upfield doublet at δ 1.07 (3H, $J = 7.4$ Hz) was assigned to axial Me-12, this doublet was caused by the methine hydrogen at C-4. The singlet at δ 6.13 (1H) was assigned to $\text{H}_{\text{ax}}-6$ because of the weak coupling between $\text{H}_{\text{ax}}-6$ and $\text{H}_{\text{eq}}-7$ in all compounds of this class (11) and the nOe cross peak between the axial Me-12 and H-6 observed in the NOESY spectrum. The cross signal between the signal of Me-12 and that at δ 1.55 (3H, s) assigned the signal axial at δ 1.55 to axial Me-13. The cross signal between the signal of $\text{H}_{\text{ax}}-1$ and that at 5.62 (1H, d, $J = 5$ Hz) assigned the signal at δ 5.62 to $\text{H}_{\text{ax}}-9$. The cross signal between the signal at δ 5.72 (1H, dd, $J = 4.3, 5$ Hz) and that at δ 1.61 (3H, s) assigned the signal at δ 5.72 to $\text{H}_{\text{eq}}-8$, and that at δ 1.61 to Me-14. The cross signal between the signal at δ 2.53 (1H, d, $J = 4.3$ Hz) and that at δ 1.45 (3H, s) assigned the signal at δ 2.53 to $\text{H}_{\text{eq}}-7$ and that at 1.45 to Me-15. Other cross signals such as those between $\text{H}_{\text{ax}}-9$ and $\text{H}_{\text{eq}}-8$, between Me-12 and $\text{H}_{\text{eq}}-4$, between Me-14 and Me-15, between $\text{H}_{\text{ax}}-9$ and Me-

14, between $\text{H}_{\text{eq}}-8$ and $\text{H}_{\text{eq}}-7$, between $\text{H}_{\text{ax}}-6$ and Me-13, and between $\text{H}_{\text{ax}}-6$ and $\text{H}_{\text{eq}}-7$ could be found, which were in good agreement with the stereochemistry elucidations and chemical shift assignments above.

The ester group situation was based on the NOESY and high resolution mass spectra. By careful examination of the NOESY spectrum, it could be deduced that the signal at 2.13 (3H, s) for an acetate methyl and that for Me-15 had a cross signal; the signal at 1.43 (3H, s) for the second acetate methyl and that for Me-13 had a cross signal; the signal at δ 8.01 for two protons of benzoate and that for Me-13 had a cross signal; and the signals at δ 6.48 and 7.72 for the two vinyl protons of cinnamate and that for Me-13 had a cross signal. These observations located one acetate at C-6 and the remaining three esters at C-1, C-8, and C-9.

Generally, if an aromatic acid ester and an aliphatic acid ester, such as an acetate ester, are situated at C-1 and C-9 (or conversely C-9 and C-1), the aliphatic ester signal of ^1H nmr will be shifted upfield from its normal value (1.9–2.7 ppm) (12). Thus, the upfield chemical shift (δ 1.43 ppm) for the second acetate methyl suggested that this acetate ester and the benzoate ester were situated at C-1 and C-9, or vice versa, and the cinnamate ester was at C-8.

The mass spectrum gave a fragment ion m/z 202 (15%), which analyzed for $\text{C}_{13}\text{H}_{14}\text{O}_2$ by hrms. A reasonable fragmentation path for this peak suggested that the benzoate ester was situated at C-9 (12). Based on the evidence above, the structure of **2** was elucidated as 1 β ,6 α -diacetoxy-9 β -benzoyloxy-8 β -cinnamoyloxy- β -dihydroagarofuran.

EXPERIMENTAL

GENERAL PROCEDURES.—Melting point was determined on a Kofler apparatus. ^1H -nmr, ^{13}C -nmr, ^1H , ^{13}C -COSY, and NOESY spectra were recorded on a Bruker AM-400 nmr spectrometer with TMS as internal standard and CDCl_3 as solvent. Experimental data of HC-COSY spectrum:

spectral widths, $SW_1 = 1515.152$ Hz, $SW_2 = 15151.515$ Hz; digitization, F_1 , Hz/PT = 5.919 Hz, F_2 , Hz/PT = 14.796 Hz; total experimental time, 7 h and 24 min. Assignments of ^{13}C -nmr chemical shifts were made with the aid of DEPT and HC-COSY spectra (13). Uv spectra in MeOH were obtained on a UV-240 spectrophotometer. Eims were obtained on VG ZAB-HS mass spectrometer, operating at 70 eV ionizing energy; with Software Peak Matching method, $R_p > 5000$; Valley definition, 10%. Ir spectra

TABLE 1. ^{13}C -nmr (400 MHz) Data for the Sesquiterpene Skeletons of **1** and **2** in CDCl_3 .^a

Carbon	1	1 ^b	2
C-1	73.3	73.3	78.9
C-2	26.5	26.6	26.6
C-3	21.4	21.3	22.1
C-4	33.7	33.7	33.8
C-5	91.7	90.3	91.5
C-6	76.4	76.4	74.9
C-7	52.9	52.9	52.9
C-8	75.9	76.0	71.2
C-9	75.6	75.7	74.5
C-10	49.7	49.7	48.8
C-11	81.7	81.7	81.6
C-12	17.2	17.3	16.8
C-13	18.6	18.6	12.2
C-14	25.3	25.4	24.4
C-15	30.8	30.8	30.6

^aThe data of **1** were assigned based on comparison with the literature data, and those of **2** on the HC-COSY and DEPT spectra.

^bData in this column are from Becerra *et al.* (8).

with KBr plates were determined on NICOLET-5DX spectrometer. Lc was carried out on a Si gel (200–300 mesh) column. Hplc was carried out on a Merck RP-8 short column. Detection of components was with a uv lamp. Voucher specimens are deposited at the Botanical Garden of Kunming Institute of Botany (Academy of Science of China).

EXTRACTION AND ISOLATION.—The air-dried seeds (2 kg) of *C. paniculatus* were extracted with petroleum ether at room temperature for a week. Removal of the solvent under reduced pressure afforded a brown oil. The oil was re-extracted with MeOH-H₂O (8:2) solution three times. Removal of the solution under reduced pressure afforded a yellowish solid (75 g). A portion (10 g) of the crude extract was chromatographed on a Si gel column using petroleum ether-Me₂CO (8:2→2:8) as eluent to give 43 fractions. The middle polar fractions were combined and purified on an RP-8 short column using MeOH-H₂O (8:2) as eluent to give the trace compounds **1** (39 mg) and **2** (30 mg).

COMPOUND **1**.—Compound **1** was obtained as amorphous white powder: uv λ max nm (log ϵ) 207 (2.357), 233 (2.363); ir ν max cm^{-1} (KBr) 3136, 2966, 2931, 1736, 1581, 1518, 1377, 1236, 871, 758; eims m/z $[\text{M}]^+$ 506 (15), $[\text{M} - \text{Me}]^+$ 491 (22), $[\text{M} - \text{ketene}]^+$ 464 (100), $[\text{M} - \text{AcO}]^+$ 447 (10), $[\text{M} - \text{HOAc}]^+$ 446 (5), $[\text{M} - \beta - \text{furan-carbonyloxy}]^+$ 395 (19), $[\beta - \text{furan-carbonyl}]^+$ 95 (100); hrms m/z 506.2168 (calcd for $\text{C}_{26}\text{H}_{34}\text{O}_{10}$, 506.2175); ^{13}C nmr see Table 1; ^1H nmr see Table 2.

COMPOUND **2**.—Compound **2** was obtained as colorless crystals: mp 219–220° from petroleum ether/EtOAc; $[\alpha]^{19}_D -92$ ($c = 0.655$,

TABLE 2. ^1H -nmr (400 MHz) Data for Compounds **1** and **2** in CDCl_3 .

Proton	1 ^a	2 ^b
H-1	5.33, ddd, $J = 4, 9$ Hz	5.25, dd, $J = 5, 11$ Hz
H-2	1.3–2.4, m	1.45, 2.15, $2 \times$ m
H-3	1.3–2.4, m	1.38, m
H-4	2.25, m	2.25, m
H-6	5.69, s	6.13, s
H-7	2.46, d, $J = 3.2$ Hz	2.53, d, $J = 4.3$ Hz
H-8	5.21, d, $J = 3.2$ Hz	5.72, dd, $J = 4.3, 5$ Hz
H-9	4.91, s	5.62, d, $J = 5$ Hz
H-12	1.01, d, $J = 7.2$ Hz	1.07, d, $J = 7.4$ Hz
H-13	1.46, s	1.55, s
H-14	1.44, s	1.61, s
H-15	1.38, s	1.45, s
Acetates	1.73, 2.09, 2.18, $3 \times$ s	1.43, 2.13, $2 \times$ s

^a**1**: β -furan-carboxylate: δ 6.74, 7.42 and 8.03 ($3 \times$ 1H, $3 \times$ brs).

^b**2**: benzoate: δ 7.36–8.01 (5H, m); cinnamate: δ 7.36–7.56 (5H, m), δ 6.48 and 7.72 ($2 \times$ 1H, ABq, $J = 16$ Hz).

MeOH); uv λ max nm (log ϵ) 281 (2.561), 231 (2.351), 224 (2.548), 218 (2.575), 200 (2.727); iv ν max cm^{-1} (KBr) 2970, 2910, 1725, 1630, 1600, 1450, 1245, 1225; eims m/z $[\text{M}]^+$ 604 (8), $[\text{M} - \text{Me}]^+$ 589 (3), $[\text{M} - \text{ketene}]^+$ 562 (30), $[\text{M} - \text{HOAc}]^+$ 544 (8), $[\text{M} - \text{AcOH}]^+$ 502 (21), $[\text{M} - \text{C}_6\text{H}_5\text{CH} = \text{CHCO}]^+$ 473 (25), $[\text{M} - \text{C}_6\text{H}_5\text{COOH}]^+$ 440 (17), $[\text{M} - \text{AcO}]^+$ 414 (19), $[\text{M} - \text{C}_6\text{H}_5\text{COO}]^+$ 381 (20), $[\text{M} - \text{C}_6\text{H}_5\text{CH} = \text{CHCO}]^+$ 371 (18), $[\text{C}_{13}\text{H}_{14}\text{O}_2]^+$ 202 (15), $[\text{C}_6\text{H}_5\text{CH} = \text{CHCO}]^+$ 131 (87), $[\text{C}_6\text{H}_5\text{CO}]^+$ 105 (100), $[\text{C}_6\text{H}_5]^+$ 77 (20), $[\text{Ac}]^+$ 43 (41); hrms m/z 604.2638 (calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$, 604.2661), m/z 202.0963 (calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$, 202.0990); ^{13}C nmr see Table 1; ^1H nmr see Table 2.

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