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ENT-KAURANOID DITERPENES FROM *ARTEMISIA SACRORUM*

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ABSTRACT.—A new *ent*-kauranoid diterpene diglycoside has been isolated from *Artemisia sacrorum* along with two known *ent*-kauranoid diterpenes. Their structures are elucidated by means of nmr analysis (DEPT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, and ^{1}H-^{1}H decoupling).

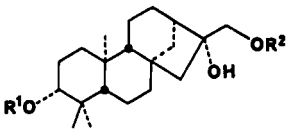
Artemisia sacrorum Ledeb. (Compositae), distributed in the Northeast District of China, is known as a Chinese folk medicine in the treatment of hepatitis. Our investigations have led to the isolation of three compounds, including two glycosides. Compounds **1** and **2** were a known diterpene and glycoside, respectively. Compound **3** was a new diterpene diglycoside. Their structures have been established by means of high-resolution nmr (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) spectroscopy.

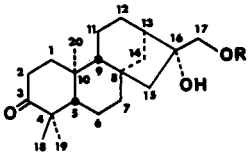
Aerial parts of the plant afforded compounds **1–3** on extraction with hot H_2O followed by the chromatographic separation of the extracts. Their characterization was made by nmr analysis (DEPT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY, and ^{1}H-^{1}H decoupling). It was found that several proton resonances overlapped. However, thorough examination of the 2D-nmr spectra led to unambiguous assignments. The ^{1}H- and ^{13}C-nmr data obtained for **1** and **2** are given in the Experimental section. The 2D-nmr data for **3** are listed in Table 1. Because nmr analysis could not distinguish between C-7 and C-15, between C-11 and C-12, and between C-18 and C-19 in all compounds, their assignments were made by well-known empirical rules. The long-range correlations of H_3-18 and H_3-19 to C-4 and C-5, and H_3-20 to C-1, C-9, and C-10 in **2** and **3** distinguished C-20 from C-18 and C-19. However, C-20 in **1** was empirically assigned.

Compound **1**, $C_{20}H_{34}O_3$, was obtained as colorless needles, mp 220–222°, $[\alpha]^{28}D$ −38.89° (pyridine). The ^{1}H-nmr and DEPT spectra showed the presence of three methyls, nine methylenes, four methines, four quaternary carbons, and three hydroxyls. The hydroxyls were determined to be a primary OH (δ_H 6.030, t, J = 4.5 Hz), *sec*-OH (δ_H 5.667, d, J = 5.5 Hz) and *tert*-OH (δ_H 5.095, s). Thus, nmr analysis suggested **1** to be a tetracyclic diterpene with three hydroxyls. The comparisons of the carbon resonances with those of related *ent*-kauranoid diterpenes (1–3) suggested **1** to be *ent*-kaurane-3β,16β,17-triol, previously isolated from *Croton lacciferus* (4–6).

Compound **2**, $C_{26}H_{42}O_8$, was obtained as colorless needles, mp 216–218°, $[\alpha]^{28}D$ −61.64° (pyridine), and exhibited a positive Molisch color reaction. Nmr analysis showed the presence of seven protons belonging to one methylene and five methines in the δ 5.0–3.8 region, each of which arises from a glucose unit. This was supported by the nmr data obtained for methyl β-D-glucopyranoside [**4**] by 2D-nmr spectroscopy. Nmr analysis of the remaining protons and carbons showed the aglycone ($3 \times C^3$, $9 \times C^2$, $3 \times C^1$, $5 \times C^0$) to be a tetracyclic diterpene with three oxygen functions (δ_C 216.871, s; δ_C 80.924, s; δ_C 75.731, t). Comparison of the carbon resonances with those of abbeokutone 17-*O*-acetate [**5**] (6) led to **2** being identified as abbeokutone 17-*O*-β-D-glucopyranoside (sugeroside), previously isolated from *Ilex sugerokii* Maxim. var. *brevipedunculata* and var. *longipedunculata* (7).

Acidic methanolysis of **2** afforded *ent*-16ξ-kaurane-3,17-dione [**6**] (5,7) and a mixture of methyl α- and β-D-glucopyranosides (ratio = 2:3). The cd spectrum of **2**

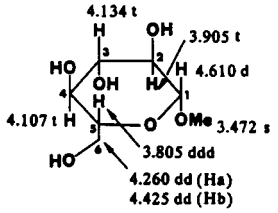




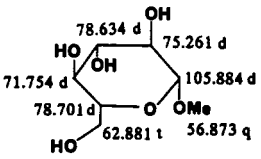
1 $R^1=R^2=H$
3 $R^1=R^2=Glc$

2 R=Glc
5 R=Ac

Glc = β-D-glucopyranosyl



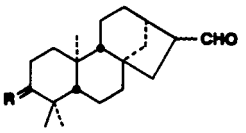
(pyridine-d_5, δ)



4

(pyridine-d_5, δ)

$J_{1,2}=J_{2,3}=J_{3,4}=J_{4,5}=7.0$ Hz
$J_{5,6a}=5.1$ Hz, $J_{5,6b}=2.5$ Hz
$J_{6a,b}=12.0$ Hz



6 R=O
7 R=--OH

showed a negative Cotton effect at 289 nm ($n\rightarrow\pi^*$) in accordance with the 5*S*,10*S* configuration (8,9).

Compound **3**, $C_{32}H_{54}O_{13}$, was obtained as colorless needles, mp>300°, $[\alpha]^{28}D$ −40.74° (pyridine), and showed a positive Molisch color reaction. The structure elucidation was carried out in the same manner as employed for **1** and **2**. Nmr analysis showed that two glucose units are separately present in the molecule and that the aglycone ($3\times C^3$, $9\times C^2$, $4\times C^1$, $4\times C^0$) is a tetracyclic diterpene. Comparisons of the nmr data with those for **1** and **2** suggested **3** to be *ent*-kaurane-3β,16β,17-triol 3β-*O*-β-D-glucopyranosyl-17-*O*-β-D-glucopyranoside. The carbon resonance differences (glycosylation shift) ($\Delta\ \delta_{C\text{-}2}$ **3**–**1** = −4.47 ppm and $\Delta\ \delta_{C\text{-}3}$ **3**–**1** = +6.82 ppm) observed between C-2 and C-3, respectively, in **1** and **3** were in accord with their 3*R* configuration, providing additional evidence to support an *ent*-kaurenoid skeleton (10,11).

Acidic methanolysis of **3** gave *ent*-16ξ-kaurane-3β-ol-17-one [**7**] and a mixture of methyl α- and β-D-glucopyranosides (ratio = 2:1).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points (uncorrected) were determined on a micro hot-stage apparatus. Specific rotations were taken on a JASCO DPI-181 polarimeter. Spectra were recorded on the following spectrometers: uv, Hitachi EPS-2U; cd, JASCO J-20; ir, Hitachi 260-30; ^1H nmr, Varian XL-400 at 400 MHz; ^{13}C nmr, Varian XL-400 at 100.6 MHz; hrms and fabms, JEOL JMS DX-300; elemental analysis, Perkin-Elmer 240B.

All nmr spectra were taken at a probe temperature of 20° in pyridine-d_5 (unless otherwise noted) using a 5-mm tube.

TABLE 1. Nmr Data for Compound **3**.

^{13}C nmr		Correlated proton[a]		^{1}H-^{1}H[c]
Carbon	δ_c	One-bond (δ_H)[b]	Long-range	
C-1	38.650 t	H_a-1 0.597 dt (3.0, 13.5)		H_b-1, H_b-2
		H_b-1 1.573 dt (13.5, 3.0)		H_a-1, H_b-2
C-2	23.898 t	H_a-2 1.648 dm (13.5)		H_b-2, H-3
		H_b-2 1.924 m		$H_{a,b}$-1, H_a-2, H-3
C-3	85.105 d	H-3 3.393 dd (12.0, 4.4)		$H_{a,b}$-2
C-4	38.650 s		H-5, H_3-18, H_3-19	
C-5	55.731 d	H-5 0.513 dm (12.0)		$H_{a,b}$-6, H_3-18
C-6	20.650 t	H_a-6 1.147 tm (13.5)		H-5, H_b-6
		H_b-6 1.283 dm (13.5)		
C-7	42.449 t	H_a-7 1.283 dm (13.5)	H_b-15	H_a-6, H_b-7
		H_b-7 1.488 dm (13.5)		H_a-7, H_b-14, H_b-15
C-8	44.759 s			
C-9	56.814 d	H-9 0.743	H_3-20	H_a-11
C-10	39.198 s			
C-11	18.680 t	H_2-11 1.327 m		H_b-12, H-13
C-12	26.991 t	H_a-12 1.343 m		H-9, H_b-12
		H_b-12 1.731 dm (11.0)		H_a-12
C-13	46.533 d	H-13 2.287 m		H_2-11, $H_{a,b}$-14
C-14	37.580 t	H_a-14 1.731 d (11.0)		$H_{a,b}$-7, H-13, $H_{a,b}$-15
		H_b-14 1.794 dd (11.0, 3.5)		H-13
C-15	53.292 t	H_a-15 1.488 d (13.5)		H_a-7, H_b-14, H_b-15
		H_b-15 1.648 t (13.5)	H_a-14	H_b-7, H_b-14, H_a-15
C-16	80.952 s		H_a-14	
C-17	75.835 t	H_a-17 3.799 d (10.4)		H_b-17
		H_b-17 4.357 d (10.4)		H_a-17
C-18	28.831 q	H_3-18 1.058 s	H-5, H_3-19	H-5, H_3-19
C-19	17.073 q	H_3-19 0.743 s	H-5, H_3-18	H_3-18
C-20	18.014 q	H_3-20 0.760 s	H-5	
C-1′	106.863 d	H-1′ 4.928 d (8.0)		H-2′
C-2′	75.667 d	H-2′ 3.987 t (8.0)		H-1′, H-3′
C-3′	78.759 d	H-3′ 4.145 t (8.0)		H-2′
C-4′	71.755[d] d	H-4′ 4.132 t (8.0)		H-5′
C-5′	78.543[e] d	H-5′ 3.877 dt (2.5, 9.0)		H-4′, $H_{a,b}$-6′
C-6′	62.908[f] t	H_a-6′ 4.293[g] dd (11.0, 5.5)		H-5′, H_b-6′
		H_b-6′ 4.483 dd (11.0, 2.5)		H-5′, H_a-6′
C-1″	102.582 d	H-1″ 4.804 d (8.0)		H-2″
C-2″	75.393 d	H-2″ 3.914 t (8.0)		H-1″, H-3″
C-3″	78.759 d	H-3″ 4.173 t (8.0)		H-2″
C-4″	72.180[d] d	H-4″ 4.132 t (8.0)		H-5″
C-5″	78.896[e] d	H-5″ 3.877 dt (2.5, 9.0)		H-4″, $H_{a,b}$-6″
C-6″	63.350[f] t	H_a-6″ 4.304[g] dd (11.0, 5.5)		H-5″, H_b-6″
		H_b-6″ 4.483 dd (11.0, 2.5)		H-5″, H_a-6″

[a]These data were obtained by the ^{1}H-^{13}C COSY spectrum.
[b]The figures in parentheses are coupling constants (Hz).
[c]These data were obtained by ^{1}H-^{1}H COSY spectrum.
[d–g]Values with the same superscript are exchangeable.

The values in parentheses are referred to compounds **2** and **3** for DEPT and one-bond (^{1}H-^{1}H and ^{1}H-^{13}C) correlation and to compound **3** for long-range (^{1}H-^{13}C) correlation.

The DEPT spectra were recorded using the $\theta = 90°$ and 142° pulses to separate the CH/CH$_3$ and CH$_2$ lines phased up and down, respectively. Aquisition data were number of scans 1024–32K (256–32K, 1024–32K); relaxation delay for protons 2 sec and 90° pulse widths 30.0 (31.0, 30.0) μsec and 9.6 (9.7, 9.1) μsec for ^{13}C and ^{1}H, respectively. The delay between pulses (3.57 msec) was set to $\frac{1}{2}J$(CH), where J(CH) was taken to be 140 Hz.

^{1}H-^{1}H COSY was done with a ^{1}H single probe; relaxation time 1 sec; 90° (^{1}H) = 14.3 (15.0, 14.3) μsec; 90° mixing pulse; $F_1 = F_2 = 2327$ (3300, 1904) Hz; data matrix 1024 × 128; 16 scans during 128 time increments (zero filling in F_1); 2 dummy scans; spectra were symmetrized about diagonal axis using FOLDT command after 20 transformations.

^{1}H-^{13}C COSY was done under the following conditions: ^{13}C, 30~105 MHz probe; relaxation time 1 sec; 1 dummy scan; 90° ^{1}H and ^{13}C pulse were calibrated at 30.0 (31.0, 30.0) and 9.6 (9.7, 9.1) μsec, respectively. One-bond correlation: $F_1 = 2342$ (3312, 1925) Hz, $F_2 = 14245$ (13850, 14347) Hz; data matrix 2048 × 48; 640 (64, 256) scans during 48 time increments; acquisition time 0.072 (0.074, 0.071) sec; $^1J_{CH}$ (average) 140 Hz; size of final data points 2K. Long-range correlation: $F_1 = 1813$ (1925) Hz, $F_2 = 21097$ (14347) Hz; data matrix 2048 × 64; 640 (2816) scans during 64 time increments (zero filling in F_1); 1 dummy scan; acquisition time 0.049 (0.071) sec; $^{LR}J_{CH}$ (average) 7.0 Hz; size of final data points 2K.

EXTRACTION AND ISOLATION.—The aerial parts of *A. sacrorum* were collected in the Northeast District of China in 1988. Plant material was identified in the Department of Medical Plants, Shenyang College of Pharmacy, and a herbarium specimen is deposited there. The air-dried, powdered plant material (6 kg) was extracted four times with boiling H_2O (8 liters) for 1 h. The H_2O layer was concentrated in vacuo to ca. 3 liters, and EtOH (9 liters) was added. The precipitate produced was filtered off. The filtrate was concentrated in vacuo to ca. 3 liters and successively extracted with petroleum ether, $CHCl_3$, EtOAc, and *n*-BuOH. The $CHCl_3$ extract (91 g) was chromatographed over Si gel (3.5 kg) eluting with petroleum ether/EtOAc. The petroleum ether-EtOAc (5:1) eluates gave compound **1** (12.0 mg). The EtOAc extract (126 g) was chromatographed over Si gel (5 kg), eluting with $CHCl_3$/Me_2CO. Compound **2** (250 mg) was obtained from the $CHCl_3$-Me_2CO (5:1) eluates. Compound **3** (300 mg) was obtained by chromatography of the *n*-BuOH extract (300 mg) over polyamide (4.2 kg), eluting with 30% EtOH.

ent-KAURANE-3β,16β,17-TRIOL [**1**].—Colorless needles, mp 220–222° (EtOH) [lit. (4) mp 218–220°, lit. (5) mp 218°, lit. (6) mp 217° (MeOH)]; $[\alpha]^{28}D$ −38.89° (*c* = 0.36, pyridine) [lit. (4) $[\alpha]D$ −39° (*c* = 0.59, MeOH)]; ir ν max (KBr) cm^{-1} 3400, 2925, 2850, 1460, 1450, 1440, 1040, 1035; ^{1}H nmr δ 6.030 (17-OH, t, *J* = 4.5 Hz), 5.667 (3-OH, d, *J* = 5.5 Hz), 5.095 (16-OH, s), 4.228 (Hb-17, dd, *J* = 10.5, 4.5 Hz), 3.949 (Ha-17, dd, *J* = 10.5, 4.5 Hz), 3.318 (H-3, dt, *J* = 11.0, 5.5 Hz), 2.359 (H-13, m), 1.929 (Hb-14, dd, *J* = 12.0, 4.0 Hz), 1.867 (Ha-14, d, *J* = 12.0 Hz), 1.767 (Hb-2, Hb-12, Hb-15, m), 1.648 (Hb-1, dt, *J* = 13.0, 5.0 Hz), 1.605 (Ha-2, Hb-7, m), 1.588 (Ha-15, m), 1.487 (Ha-12, m), 1.468 (H_2-11, m), 1.424 (Hb-6, Ha-7, m), 1.260 (Ha-6, m), 1.087 (H_3-18, s), 0.917 (H_3-20, s), 0.913 (H_3-19, s), 0.864 (H-9, d, *J* = 8.2 Hz), 0.772 (Ha-1, dt, *J* = 5.0, 13.0 Hz), 0.660 (H-5, dd, *J* = 12.0, 2.0 Hz); ^{13}C nmr δ 81.703 (s, C-16), 78.282 (d, C-3), 66.612 (t, C-17), 57.167 (d, C-9), 55.532 (d, C-5), 54.026 (t, C-15), 46.188 (d, C-13), 44.837 (s, C-8), 42.775 (t, C-7), 39.562 (s, C-4, C-10), 39.193 (t, C-1), 37.867 (t, C-14), 29.017 (q, C-18), 28.367 (t, C-2), 26.969 (t, C-12), 20.798 (t, C-6), 18.925 (t, C-11), 18.243 (q, C-19), 16.497 (q, C-20); hrms *m/z* $[M]^+$ 322.2530 (322.2508 for $C_{20}H_{34}O_3$).

ent-KAURANE-16β,17-DIOL-3-ONE 17-*O*-β-D-GLUCOPYRANOSIDE (ABBEOKUTONE 17-*O*-β-D-GLUCOPYRANOSIDE, SUGEROSIDE) [**2**].—Colorless needles, mp 216–218° (EtOH) [lit. (7) mp 208°]; $[\alpha]^{28}D$ −61.64° (*c* = 1.1, pyridine) [lit. (7) $[\alpha]D$ −58.1° (*c* = 1.0, pyridine)]; uv λ max (EtOH) (log ε) 283 (2.14); cd (*c* = 1 × 10^{-3}, EtOH) $[\theta]^{28.5}$ (nm) −3181 (289) (negative maximum); ir ν max (KBr) cm^{-1} 3400, 2900, 2850, 1700, 1100–1000; ^{1}H nmr δ 4.922 (H-1′, d, *J* = 8.1 Hz), 4.480 (Hb-6′, dd, *J* = 11.5, 1.5 Hz), 4.362 (Hb-17, d, *J* = 10.7 Hz), 4.300 (Ha-6′, dd, *J* = 11.5, 5.2 Hz), 4.134 (H-3′, m), 4.127 (H-4′, m), 3.980 (H-2′, t, *J* = 8.1 Hz), 3.885 (H-5′, m), 3.815 (Ha-17, d, *J* = 10.7 Hz), 2.377 (H_2-2, dd, *J* = 8.0, 6.5 Hz), 2.310 (H-13, m), 1.823 (Hb-14, dd, *J* = 10.5, 3.5 Hz), 1.725 (Hb-12, m), 1.662 (Hb-1, Hb-15, m), 1.648 (Ha-14, m), 1.493 (Hb-7, m), 1.462 (Ha-15, m), 1.265 (Ha-12, m), 1.223 (Ha-7, m), 1.220 (H_2-6, m), 1.200 (H-5, H_2-11, m), 1.110 (Ha-1, m), 0.963 (H_3-19, s), 0.890 (H_3-18, s), 0.830 (H-9, d, *J* = 8.2 Hz), 0.799 (H_3-20, s); ^{13}C nmr δ 216.871 (s, C-3), 106.779 (d, C-1′), 80.924 (s, C-16), 78.893 (d, C-5′), 78.753 (d, C-3′), 75.731 (t, C-17), 75.664 (d, C-2′), 71.805 (d, C-4′), 62.947 (t, C-6′), 55.606 (d, C-9), 54.325 (d, C-5), 52.953 (t, C-15), 47.255 (s, C-4), 46.370 (d, C-13), 44.615 (s, C-8), 41.373 (t, C-7), 38.705 (s, C-10), 37.373 (t, C-1), 37.243 (t, C-14), 34.368 (t, C-2), 27.402 (q, C-18), 26.735 (t, C-12), 21.995 (t, C-6), 21.230 (q, C-19), 19.069 (t, C-11), 17.885 (q, C-20); hrms *m/z* $[M]^+$ 482.2865 (482.2879 for $C_{26}H_{42}O_8$). *Anal.* calcd for $C_{26}H_{42}O_8$, C 64.73, H 8.74; found C 64.52, H 8.93.

Acidic Methanolysis of **2**.—A mixture of **2** (5.0 mg), 2 N HCl (0.5 ml), and MeOH (1 ml) was refluxed for 6 h. MeOH was removed in vacuo to leave an aqueous residue, which was extracted with $CHCl_3$. Workup of the organic layer, followed by preparative tlc (Si gel, $CHCl_3$), gave **6** (2.2 mg) as a colorless oil: R_f 0.40; ir ν max ($CHCl_3$) cm^{-1} 2721, 1717 (CHO), 1701 (C=O); nmr ($CDCl_3$) δ 9.680 (1H, d, *J* = 1.7

Hz, CHO), 1.029, 1.053, 1.082 (each 3H, s, 3 × Me); hrms *m/z* $[M]^+$ 302.2247 (302.2246 for $C_{20}H_{30}O_2$).

The aqueous layer was neutralized with Ag_2CO_3, filtered, and concentrated in vacuo to dryness, giving a mixture of methyl α- and β-D-glucopyranosides (1.5 mg); tlc (Si gel) R_f 0.60 [$CHCl_3$-MeOH-H_2O (6:4:0.5)], 0.70 [*n*-BuOH–pyridine–H_2O (6:4:3)]; nmr for α compound δ 5.043 (1H, d, J = 3.7 Hz, H-1), 4.012 (1H, dd, J = 9.8, 3.7 Hz, H-2), 4.438 (1H, dd, J = 9.8, 8.3 Hz, H-3), 4.076 (1H, dd, J = 9.7, 8.3 Hz, H-4), 4.142 (1H, ddd, J = 9.7, 5.0, 2.3 Hz, H-5), 4.242 (1H, dd, J = 11.5, 5.0 Hz, Ha-6), 4.381 (1H, dd, J = 11.5, 2.3 Hz, Hb-6), 3.318 (3H, s, OMe); nmr for β compound see structure **1**; each signal intensity of H-1 and OMe in α and β compounds, 2:3.

ent-KAURANE-3β,16β,17-TRIOL 3β-*O*-β-D-GLUCOPYRANOSYL-17-*O*-β-D-GLUCOPYRANOSIDE [**3**].—Colorless needles, mp > 300° (EtOH); $[\alpha]^{28}D$ −40.74° (*c* = 0.54, pyridine); ir ν max (KBr) cm^{-1} 3400, 2950, 1070, 1020; fabms (glycerol matrix) *m/z* $[M + Na]^+$ 669 (646 for $C_{32}H_{54}O_{13}$). *Anal.* calcd for $C_{32}H_{54}O_{13}\cdot 2\frac{1}{2}H_2O$, C 55.55, H 8.59; found C 55.64, H 8.11. Nmr see Table 1.

Acidic Methanolysis of **3**.—A mixture of **3** (2.0 mg), 2 N HCl (0.5 ml), and MeOH (1 ml) was treated in the same manner as above.

The aglycone **7** (1.0 mg) was obtained as a colorless oil: ir ν max ($CHCl_3$) cm^{-1} 3600 (OH), 2740, 1719 (CHO); nmr ($CDCl_3$) δ 9.655 (1H, d, J = 1.7 Hz, CHO). Sugar (0.9 mg) was obtained as a mixture of methyl α- and β-D-glucopyranosides (ratio = 2:1) and identified by tlc and nmr analyses.

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