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TERPENOIDS FROM *VIGUIERA POTOSINA*

FENG GAO,[1] MAHMUT MISKI, DOUGLAS A. GAGE, JOHN A. NORRIS, and TOM J. MABRY*

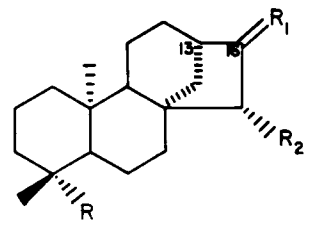
Department of Botany, University of Texas at Austin, Austin, TX 78713-7640

As part of our biochemical systematic investigation of the genus *Viguiera* (Asteraceae, Heliantheae), we report here from *Viguiera potosina* Blake the isolation and structure elucidation of the eudesmanolide sesquiterpene lactone ivalin (1, 2) and several diterpenes: grandifloric acid (**4**) (3), (−)-kaur-16-en-19-oic acid (**3**) (4), 16α-(−)-kauran-17,19-dioic acid (**2**) (5), and 16α-(−)-kauran-19-al-17-oic acid (**1**). This is the first isolation of **1** from a natural source, but it was previously obtained from the oxidation of 16α-(−)-kauran-17,19-diol (5).

The structures of all compounds were determined by spectral analysis, and those of ivalin, grandifloric acid, and (−)-kaur-16-en-19-oic acid were confirmed by direct comparison with authentic samples.

Compound **1** was identified as (−)-kauran-19-al-17-oic acid by analyzing its ir, ms, and ^{1}H-nmr spectra and by a melting point comparison with the previously reported oxidation product (5). In the ^{1}H-nmr spectrum of **1**, the signal at δ 9.74 confirmed the axial substitution of the aldehyde function at C-4 since all equatorial aldehydes reported (6, 7) have the aldehydic proton at higher field (9.23 ppm). The H-16 signal at δ 2.67 ppm (dd, J=6.4, 8.7 Hz) supported a 16α orientation for the carboxyl group.

In order to confirm this assignment, **1** was oxidized to give the dicarboxylic acid **2** (5). For comparison, **6**, the 16β-carboxyl isomer of **2**, was prepared from the readily available **3** via **8** by the procedure of Baker *et al.* (8). Both the dimethyl esters, **5** and **7**, were also compared.



	R	R_1	R_2
1	CHO	α-COOH β-H	H
2	COOH	α-COOH β-H	H
3	COOH	CH_2	H
4	COOH	CH_2	OH
5	COOMe	α-COOMe β-H	H
6	COOH	β-COOH α-H	H
7	COOMe	β-COOMe α-H	H
8	COOH	β-CHO α-H	H

In **6**, the 16α-proton exhibited a signal at δ 3.19 (ddd, J=6.1, 6.1, 12.2 Hz), while the spectrum of **2** displayed a signal at δ 2.94 (dd, J=5.6, 8.6 Hz). Similar results were obtained from **7** and **5**. The ^{13}C-nmr data of **1** as well as the eims and ^{1}H-nmr for **5** also supported the structure assignment of 16α-(−)-kauran-19-al-17-oic acid for **1**.

EXPERIMENTAL

PLANT MATERIAL.—*V. potosina* was collected about 1 km north of Las Tablas, San Luis Potosi, Mexico, in August 1981. A voucher specimen (Norris #78) was deposited in the Herbarium of the University of Texas at Austin.

16α-(−)-KAURAN-19-AL-17-OIC ACID (**1**).—60 mg colorless needles, mp 200-201° (from EtOAc). Ir (in KBr) 3200-2500 (COOH), 2720 (CHO), 1700 (broad, CHO, COOH), 1240, 935 cm^{-1}. Eims *m/z* (%) 318 (M^+, 10.6), 300 (39.3),

[1]Permanent address: South China Institute of Botany, Academia Sinica, Guangzhou, the People's Republic of China.

289 (M-CHO, 100). ^{1}H nmr (200 MHz in $CDCl_3$, TMS) δ 0.86 (3H, s, H-20), 1.00 (3H, s, H-18), 2.54 (1H, m, H-13), 2.67 (1H, dd, J=6.4, 8.7 Hz, H-16β), 9.74 (1H, d, J=1.3 Hz, H-19). ^{13}C nmr (22.6 MHz $CDCl_3$, TMS) δ 41.0 (t) C_1, 18.5 (t) C_2, 38.3 (t) C_3, 48.5 (d) C_4, 56.7 (d) C_5, 20.5 (t) C_6, 44.5 (t) C_7, 45.1 (s) C_8, 54.6 (d) C_9, 39.4 (s) C_{10}, 18.5 (t) C_{11}, 31.0 (t) C_{12}, 45.4 (d) C_{13}, 39.9 (t) C_{14}, 34.3 (t) C_{15}, 41.3 (d) C_{16}, 183.5 (s) C_{17}, 24.3 (q) C_{18}, 206.0 (d) C_{19}, 16.3 (q) C_{20}.

16α-(−)KAURAN-17,19-DIOIC ACID (**2**).—34 mg white powder. Ir (in KBr) 3200-2500, 1690, 1240, 1020, 950, 930 cm^{-1}. Eims *m/z* (%) 334 (4.1), 316 (12.4), 288 (100). ^{1}H nmr (90 MHz, in pyridine-*d*5, TMS) δ 1.15 (3H, s, H-20); 1.35 (3H, s, H-18); 2.92 (1H, dd, J=6, 9 Hz, H-16).

(−)-KAURENIC ACID (**3**).—475 mg colorless prism. The identity was confirmed by direct comparison of the ^{1}H nmr, ms, mp, and mmp with an authentic sample.

GRANDIFLORIC ACID (**4**).—22 mg white crystals. Its ^{1}H-nmr and ms data were the same as those of an authentic sample.

IVALIN.—3.419 g. It was identified by direct comparison of its mp, mmp, ^{1}H nmr and eims with an authentic sample.

OXIDATION OF **1**.—30 mg of **1** was dissolved in 3 ml of distilled Me_2CO. Four drops of Jones Reagent were added under stirring at a temperature of 15-20°. One h later, iPrOH was added to decompose excess reagent. Workup in the usual way yielded **2** (31 mg). The ir, ^{1}H nmr, and eims of this product were the same as those of natural product **2**.

METHYLATION OF THE OXIDATION PRODUCT **2**.—28 mg of **2** was methylated with CH_2N_2 in the usual manner. After purifying over a Sephadex LH-20 column (cyclohexane-CH_2Cl_2-MeOH, 7:4:1), 20 mg of **5** was obtained. Eims *m/z* (%) 362 (11.3), 347 (1.9), 330 (24.5), 303 (100). ^{1}H nmr (90 MH, $CDCl_3$, TMS) δ 0.83 (3H, s, H-20), 1.18 (3H, s, H-18), 2.44 (1H, m, H-13), 2.62 (1H, dd, J=6, 8.7 Hz, H-16), 3.65 (6H, s, 2×OCH_3). The same compound was obtained by methylating the natural compound **2**.

COMPOUND **6**.—Prepared by the published method (8), compound **6** had the following properties: ^{1}H nmr (2.00 MHz pyridine-*d*5, TMS) δ1.16 (3H, s, H-20), 1.36 (3H, s, H-18), 2.73 (1H, m, H-13), 3.19 (1H, ddd, J=6.1, 6.1, 12.2 Hz, H-16α). The dimethyl ester of **6**, i.e. **7**, was obtained with CH_2N_2. ^{1}H nmr (90 MHz, $CDCl_3$, TMS) δ 0.81 (3H, s, H-20), 1.16 (3H, s, H-18), 2.50 (1H, m, H-13), 2.82 (1H, ddd, J=6, 6, 12 Hz, H-16α), 3.64 (3H, s, OCH_3), 3.68 (3H, s, OCH_3). Eims *m/z* (%) 362 (12.4), 347 (2.4), 330 (22.9), 303 (100).

Full details of the extraction and isolation of the compounds are available from the senior author on request.

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