

DITERPENOID ACIDS FROM *ELAEOSELINUM FOETIDUM*

MARIANO PINAR\* and MARIANO P. GALAN

*Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

In previous communications (1-3), we reported several diterpene acids from the roots of *Elaeoselinum foetidum* (L) Boiss. (Umbelliferae), and from the aerial parts of this plant, we also reported a new seco-norkaurane, foetidin (4). A study of a new extract of the aerial parts has now allowed the isolation of three diterpene acids, one of which is a new compound, 5, whose structure was elucidated by <sup>1</sup>H-nmr and <sup>13</sup>C-nmr spectroscopic studies of its methyl ester derivative (6). The other two materials, 1 and 2, were previously identified in the roots but in mixtures (2); they have now been isolated for the first time, also as methyl derivatives, in their pure state.

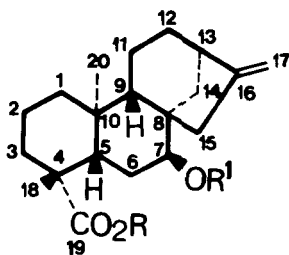
The methyl ester 6 had a molecular formula C<sub>21</sub>H<sub>32</sub>O<sub>3</sub>. Its ir spectrum was consistent with the presence of an hydroxyl (3620 cm<sup>-1</sup>), an ester (1732 cm<sup>-1</sup>), and an exocyclic methylene (3070, 1650, 903 cm<sup>-1</sup>) group. The <sup>1</sup>H-nmr spectrum of 6 showed signals at δ 5.04 and 4.96 assigned to an exocyclic methylene group. A signal at δ 3.56 was assigned to the geminal proton of the hy-

droxyl group, shifting to δ 4.90 on acetylation to yield 7. Double resonance experiments at δ 3.56 affected the signals of δ 5.04 and 4.96 and vice versa. There were also signals characteristic of a methyl ester group at δ 3.64 and of two tertiary methyl groups at δ 1.16 and 0.79.

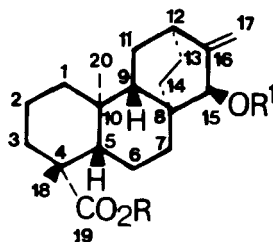
In the ms, the peak at *m/z* 314 [M-H<sub>2</sub>O]<sup>+</sup> also indicates the presence of the hydroxyl group in 6. The <sup>13</sup>C-nmr spectrum of 6 (see Experimental) corresponded almost exactly with that reported for the methyl *ent*-15 $\alpha$ -senecioyatis-16-en-19-oate (1), taking into account the substitution of the ester function by the hydroxyl group on the 15 $\beta$ -position (*ent*-15 $\alpha$ ) (5). In agreement with these data, the new compound can be identified as the *ent*-15 $\alpha$ -hydroxyatis-16-en-19-oic acid (5).

The *enantio* absolute configuration of this new natural compound is based on the co-occurrence of gummiferolic and *ent*-kaur-16-en-19-oic acids (2,6).

It is necessary to note that compound 5 has a free hydroxyl group, and the ex-



|   | R  | R'  |
|---|----|-----|
| 1 | H  | Ang |
| 2 | H  | Sen |
| 3 | Me | Ang |
| 4 | Me | Sen |



|   | R  | R' |
|---|----|----|
| 5 | H  | H  |
| 6 | Me | H  |
| 7 | Me | Ac |

Ang = CO.C(Me)=CH(Me)  
Sen = CO.CH=C(Me)<sub>2</sub>

traction and isolation procedures exclude completely the possibility of this arising as an artifact.

### EXPERIMENTAL

**PLANT MATERIAL.**—Aerial parts of *E. foetidum* were collected between Arcos de la Frontera and Tabernas de Ribera, Cádiz, Spain, in June 1980. Voucher specimens (No. 177215) are deposited at the Herbarium of the Royal Botanic Garden of Madrid.

**EXTRACTION AND SEPARATION.**—Air-dried and finely powdered aerial parts (400 g) were extracted overnight with Et<sub>2</sub>O in a Soxhlet apparatus. The extract was worked up and chromatographed in the usual way (4). Elution with *n*-hexane-EtOAc (20:1) yielded *ent*-kaur-16-en-19-oic acid (40 mg) and foetidid (15 mg). Elution with CHCl<sub>3</sub> afforded an acid fraction which was treated with CH<sub>2</sub>N<sub>2</sub> in the usual procedure. The methylation fraction on preparative tlc developed with *n*-hexane-EtOAc (5:1) yielded the compounds **3** (10 mg), **4** (8 mg), and **6** (5 mg).

**Compound 3.**—Syrup; [ $\alpha$ ]<sub>D</sub> -45° (CHCl<sub>3</sub>, c=0.21); uv (EtOH)  $\lambda$  max 215 (log  $\epsilon$  4.01); ir (CHCl<sub>3</sub>) 3080, 2950, 2880, 1720, 1665, 1605, 1445, 1380, 1158, 992, 960, 880 cm<sup>-1</sup>; 360 MHz <sup>1</sup>H nmr (CDCl<sub>3</sub>) and 90.5 MHz <sup>13</sup>C nmr (CDCl<sub>3</sub>). The chemical shifts of both spectra coincide exactly with those reported in (2); ms *m/z* (% rel. int.) 414 (M<sup>+</sup> 0.5), 374 (1), 359 (4), 355 (4), 314 (98), 255 (80), 254 (79), 121 (74), 83 (97), 55 (100); C<sub>26</sub>H<sub>38</sub>O<sub>4</sub>; mw 414.

**Compound 4.**—Syrup; [ $\alpha$ ]<sub>D</sub> -38° (CHCl<sub>3</sub>, c=0.25); uv (EtOH)  $\lambda$  max 216 (log  $\epsilon$  4.15); ir (CHCl<sub>3</sub>) 3070, 2940, 2880, 1720, 1655, 1605, 1440, 1380, 1152, 992, 962, 880 cm<sup>-1</sup>; 360 MHz <sup>1</sup>H nmr (CDCl<sub>3</sub>) and 90.5 MHz <sup>13</sup>C nmr (CDCl<sub>3</sub>). The chemical shifts of both spectra coincide exactly with those reported in (2); ms *m/z* (% rel. int.) 414 (M<sup>+</sup> 0.1), 354 (1), 314 (70), 255 (30), 254 (25), 239 (18), 211 (10), 185 (15), 150 (20), 121 (14), 105, (30), 83 (100), 55 (93); C<sub>26</sub>H<sub>38</sub>O<sub>4</sub>; mw 414.

**Compound 6.**—Mp 194-196° (MeOH); ir (CCl<sub>4</sub>) 3620, 3070, 1728, 1650, 1260, 1192, 1140, 900 cm<sup>-1</sup>; 90 MHz <sup>1</sup>H nmr (CDCl<sub>3</sub>)  $\delta$  5.04 (t, *J*=1.5 Hz, H-17), 4.96 (m, H-17'),

3.64 (s, COOMe), 3.56 (m, H-15), 1.16 (s, 3H-18), 0.78 (s, 3H-20); 22.5 MHz <sup>13</sup>C nmr  $\delta$  (ppm) C-1, 39.8 t, C-2 18.8 t, C-3 38.1 t, C-4 43.8 s, C-5 56.4 d, C-6 19.7 t, C-7 33.0 t, C-8 37.8\* s, C-9 42.3 d, C-10 37.7\* s, C-11 26.2 t, C-12 36.3 d, C-13 27.0 t, C-14 28.6 t, C-15 76.6 d, C-16 157.2 s, C-17 109.3 t, C-18 28.7 q, C-19 178.2 s, C-20 12.2 q, C-21 51.3 q; C<sub>21</sub>H<sub>32</sub>O<sub>3</sub>; mw 332.

$$[\alpha]^{20} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365 \text{ nm}}{-30^\circ \quad -32^\circ \quad -36^\circ \quad -58^\circ \quad -87^\circ} \quad (\text{CHCl}_3, c 0.21)$$

**Compound 7.**—Treatment of **6** with Ac<sub>2</sub>O-pyridine, 24 h room temperature, usual work up gave **7**. Mp 134-136° (MeOH); [ $\alpha$ ]<sub>D</sub> -74° (CHCl<sub>3</sub>, c=0.15); ir (CCl<sub>4</sub>) 3075, 2935, 2864, 1738, 1728, 1634, 1468, 1445, 1370, 1140, 1018, 985, 850 cm<sup>-1</sup>; 90 MHz <sup>1</sup>H nmr (CDCl<sub>3</sub>)  $\delta$  5.10 (t, *J*=1.8 Hz, H-17), 5.00 (m, H-17'), 4.90 (m, H-15), 3.67 (s, COOMe), 2.15 (s, MeCO), 1.20 (s, 3H-18), 0.83 (s, 3H-20); ms *m/z* 374 (M<sup>+</sup>); C<sub>23</sub>H<sub>34</sub>O<sub>4</sub>; mw 374.

$$[\alpha]^{20} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365}{-74^\circ \quad -78^\circ \quad -89^\circ \quad -154^\circ \quad 16^\circ} \quad (\text{CHCl}_3, c 0.12)$$

Full details of the isolation and identification of the compounds are available on request to the senior author.

### ACKNOWLEDGMENTS

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