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A DITERPENOID FROM *ELAEOSELINUM FOETIDUM*

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Key Word Index—*Elaeoselinum foetidum*; Umbelliferae; diterpenoid; *ent*-7α-senecioxy-15α-hydroxy-atis-16-en-19-oic acid.

Abstract—A new diterpene acid has been isolated from the roots of *Elaeoselinum foetidum*. Its structure was established as *ent*-7α-senecioxy-15α-hydroxy-atis-16-en-19-oic acid by ^{1}H NMR and ^{13}C NMR spectroscopic studies of its methyl ester derivative and confirmed by correlation with a margotianin derivative.

INTRODUCTION

In previous communications, we reported four new diterpene acids [1, 2] and the new seco-nor-kaurane, foetidin [3], from *Elaeoselinum foetidum*, an umbelliferous plant endemic at the Iberian Peninsula. A study of a more polar fraction of an extract of the root of this plant, has now allowed the isolation of three minor diterpenoid constituents. These are the already known grandiflorolic acid [4] and 17-hydroxy-(−)-kaur-15-en-19-oic acid [5], and a new diterpenoid which possesses the *ent*-atis-16-ene skeleton.

RESULTS AND DISCUSSION

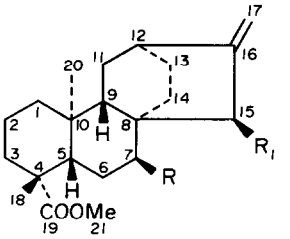
The compound **1** had a molecular formula $C_{26}H_{38}O_5$. Its IR spectrum (see Experimental) was consistent with the presence of an ester, exocyclic methylene and hydroxyl groups. The ^{1}H NMR spectrum (see Experimental) showed characteristic signals for a senecioate group and the signal of its geminal equatorial proton appeared as a triplet at δ4.82 (J = 2, 9 Hz). A broad one proton singlet at δ3.90, shifting to δ5.38 on acetylation to yield **2**, is assigned to the geminal proton of the hydroxyl group. The signals attributed to the exocyclic methylene group appeared as a broadened singlet at δ4.95. Double resonance experiments showed on irradiation at the frequency corresponding to δ4.95 affected the signal at 3.90 and *vice versa*. There also appear signals in the spectrum of a methyl ester group and two tertiary methyl groups. The UV absorption of **1** (see Experimental) was also indicative of the presence of the senecioate group. In the mass spectrum (see Experimental) the peak at m/z 412 [M $-H_2O]^+$ also reveals the presence of the hydroxyl group.

The ^{13}C NMR spectrum of **1** (Table 1) provided decisive proof for the *ent*-atis-16-ene hydrocarbon skeleton and for the presence of a C-19 carbomethoxyl group, an *ent*-7α-senecic ester group and an *ent*-15α-hydroxyl group [1, 2].

Finally, alkaline hydrolysis of **1** yielded the hydroxy-ester, which was acetylated to give **3**. This compound was identified by comparison with an authentic sample of methyl-*ent*-7α,15α-diacetoxy-atis-16-en-19-oate **3** [6]. From a consideration of all above data, the new compound can be identified as *ent*-7α-senecioxy-15α-hydroxy-atis-16-en-19-oic acid.

EXPERIMENTAL

The extract of the root of this plant was chromatographed on a silica gel column to obtain the terpene acids reported in refs [1, 2]. The more polar acid fraction was treated with ethereal CH_2N_2



	R	R_1
1	O−CO−CH=C(Me)$_2$ (1′ 2′ 3′ 4′ 5′)	OH
2	O−CO−CH=C(Me)$_2$	O−CO−Me
3	O−CO−Me	O−CO−Me

Table 1 ^{13}C NMR chemical shifts of compound **1**

C-1	39.8 *t**	C-11	26.5 *t*†
C-2	18.8 *t*	C-12	35.6 *d*
C-3	38.2 *t*	C-13	26.7 *t*†
C-4	43.3 *s*	C-14	25.9 *t*†
C-5	49.1 *d*	C-15	76.7 *d*‡
C-6	26.7 *t*†	C-16	153.2 *s*
C-7	77.9 *d*‡	C-17	110.3 *t*
C-8	37.6 *s*	C-18	28.4 *q*
C-9	39.1 *d*	C-19	177.7 *s*
C-10	39.7 *s*	C-20	12.3 *q*
C-1′	165.0 *s*	C-21	51.2 *q*
C-2′	115.7 *d*		
C-3′	158.4 *s*		
C-4′	27.5 *q*		
C-5′	20.4 *q*		

δ-values (ppm) from TMS, at 20.5 MHz in $CDCl_3$ solution.
*SFORD multiplicity.
†,‡Values may be interchanged.

and the mixture of the methyl esters was carefully and repeatedly chromatographed over silica gel (Merck, N° 5554). Elution with $CHCl_3$–MeOH (99:1) yielded in order of elution: 60 mg of **1**, 56 mg of methyl-17-hydroxy-(−)-kaur-15-en-19-oate and 42 mg of methyl-15α-hydroxy-(−)-kaur-16-en-19-oate. The previously known compounds were identified by their mp, IR, ^{1}H NMR and [α] data.

Compound **1**. Syrup; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3613 (free OH), 3575 (intramolecular associated), 3080, 1657, 905 (exocyclic methylene) and 1732 (ester); UV λ_{max}^{EtOH} nm (log ε): 220 (4, 27); ^{1}H NMR (90 MHz, $CDCl_3$): δ4.95 (*br s*, $W_{1/2}$ = 3 Hz, 2H-17), 4.82 (*t*, *J* = 2, 9, H-7), 3.90 (*br s*, $W_{1/2}$ = 3 Hz, H-15), 3.65 (*s*, COOMe), 1.08 (*s*, 3H-18) and 0.85 (*s*, 3H-20); sen. ester 5.69 (*qq*, $J_{2'Me\,(cis)} = J_{2'Me\,(trans)}$ = 1, 2 Hz, H-2'), 2.16 (*d*, $J_{2'Me\,(trans)}$ = 1, 2 Hz, 3H-4') and 1.92 (*d*, $J_{2'Me\,(cis)}$ = 1, 2 Hz, 3H-5'); ^{13}C NMR (20.5 MHz, $CDCl_3$): see Table 1; EIMS (direct inlet, 75 eV) *m/z* (rel. int.): 430 $[M]^+$ (0, 3), 412 (5), 347 (8), 330 (100), 312 (75), 302 (24), 270 (71), 255 (49), 253 (39), 237 (18), 212 (21), 173 (20), 162 (30), 121 (19), 109 (15), 83 (74), 55 (26), 43 (25). $C_{26}H_{38}O_5$ MW 430.

nm	589	578	546	436	365	
$[\alpha]^{20}$	+31°	+33°	+38°	+67°	−2°	($CHCl_3$, *c* 1.59).

Compound **2**. Treatment of **1** with Ac_2O–pyridine in the usual manner gave compound **2**. Syrup; IR $\nu_{max}^{CCl_4}$: 3080, 1658, 910; 1746, 1732 and 1725 (sh) (acetate, senecioate and methyl ester); UV λ_{max}^{EtOH} nm (log ε): 218 (4.04); ^{1}H NMR (90 MHz, $CDCl_3$): δ5.38 (*br s*, H-15), 4.98 (*br s*, H-17), 4.92 (*br s*, H-17'), 4.79 (*t*, *J* = 3 Hz, H-7), 3.65 (*s*, COOMe), 1.90 (*s*, OAc), 1.08 (*s*, 3H-18), 0.84 (*s*, 3H-20), 5.76 (*qq*, H-2'), 2.21 (*d*, 3H-4'), 1.93 (*d*, 3H-5'). EIMS *m/z* (rel. int.): 472 $[M]^+$ (1), 412 (80), 397 (5), 372 (3), 330 (90), 312 (40), 269 (30), 253 (32), 83 (100). $C_{28}H_{40}O_6$ MW 472.

nm	589	578	546	436	365	
$[\alpha]^{20}$	−2°	−2°	−3°	−5°	−8°	($CHCl_3$; *c* 1.03).

Compound **3**. A soln of **1** (30 mg) in 2.5 N ethanolic KOH was refluxed under the same conditions described in ref. [6]. The residue (22 mg) was treated with Ac_2O–pyridine in the usual manner and purified by prep. TLC on silica gel (Merck, N° 5554) developed with $CHCl_3$, to yield **3**, which was identical by mmp and comparison of IR, ^{1}H NMR, MS and optical rotation with an authentic sample of methyl-*ent*-7α,15α-diacetoxy-atis-16-en-19-oate [6].

nm	589	578	546	436	365	
$[\alpha]^{20}$	−15°	−16°	−18°	−33°	−38°	($CHCl_3$; *c* 1.05).

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