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SESQUITERPENOLIDES FROM *MELANOSELINUM DECIPIENS*

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Key Word Index—*Melanoselinum decipiens*; Umbelliferae; sesquiterpene lactones; eudesmanolides.

Abstract—Seventeen new eudesmanolides have been isolated from *Melanoselinum decipiens*, together with the previously known lasolide and the decipienins A, B, D and F. Relative configurations of decipienin B have been assigned by spectroscopic means. © 1997 Elsevier Science Ltd. All rights reserved

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INTRODUCTION

In the course of our research directed toward the isolation and structural elucidation of sesquiterpenolides from the Umbelliferae family [1], we have carried out a reinvestigation of *Melanoselinum decipiens*, a shrub endemic to Madeira Island. The genus *Melanoselinum* is included in the *Laserpitieae* tribe, a group of the Umbelliferae which has been shown to contain sesquiterpene lactones.

This species was first investigated by González *et al.*, who isolated eight sesquiterpene lactones named decipienin A–H [2–4]. In 1986, Holub *et al.* [5], on the basis of spectroscopic studies, corrected their structures.

Recently, we have described the isolation and identification of two eudesmanolides from this species, with a particular stereochemical pattern, not found to date in this Family [1]. In this reinvestigation, 17 new sesquiterpenolides, belonging to the eudesmanolide class, have been isolated together with the previously known lasolide (**16**) [6–8] and the decipienins A (**2**), B (**5**), D (**7**) and F (**8**) [2–4]. We have assigned the relative stereochemistry of decipienin B by means of NOE measurements. NOE experiments led us also to confirm the relative stereochemistry of decipienin A, D and F.

RESULTS AND DISCUSSION

Compounds **1**–**4** exhibited very similar spectra. The IR spectra of **2**–**4** showed absorptions corresponding to a γ-lactone ring (1791–1795 cm^{-1}), an α,β-unsaturated carbonyl group (1594–1663 cm^{-1}) and an α,β-unsaturated ester (1713–1718 cm^{-1}). Compound **1** lacked the latter signal and showed an absorption at 3507 cm^{-1}, characteristic of a hydroxyl group. Mass spectroscopy revealed molecular ions at m/z 262 for **1** and m/z 344 for **2**–**4**. Their ^{1}H NMR spectra were closely related and revealed the presence of two vinylic protons, H-1 and H-2, in addition to a doublet corresponding to the allylic lactone proton.

Taking into account all of these data, we arrived at the basic structure of 11α-hydroxy (or acyloxy)-3-oxo-6αH,7αH,10α,11β-dimethyleudes-1,4-dien-6,12-olide for compounds **1**–**4**. There were only changes in the signals of the ester groups [see Table 1(a) and (b)].

Signals corresponding to H-6 and H-7 are affected by the presence of an ester group at C-11. Such esterification deshielding by 0.7 ppm the signal of H-7 and 0.2 ppm that of H-6. This behaviour confirms the relative stereochemistry assigned to C-6, C-7 and C-11.

Though lactone **5** (decipienin B) was previously described [3], no high resolution ^{1}H NMR data were available and the stereochemistry of the epoxide groups remained unassigned. We, therefore, reanalysed the spectra of this lactone [Table 1(a) and (b)] and assigned the orientation of the oxirane rings by means of NOE measurements (Fig. 1). Irradiation of the H-2 signal showed a positive NOE effect in H-1 and H-3, confirming that these protons are at the same side of the molecule. Irradiation of H-1 also produced an enhancement of the angular methyl signal. NOE interactions between the angular methyl, H-6 and H-7 were also observed.

Compound **6** showed in its ^{1}H NMR spectrum [Table 1(a) and (b)] the signals of a tigloyl group instead of the signals for the angelic ester. The remaining signals were nearly identical to those of **5**.

Compounds **7** and **8** showed IR absorption bands indicating a hydroxyl group, a γ-lactone ring and an α,β-unsaturated ester. The mass spectra showed a

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Table 1(a). ^{1}H NMR spectral data for compounds **1–10**

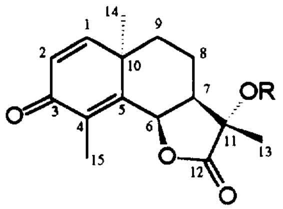
H	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1	6.74 *d* (9.8)	6.72 *d* (9.8)	6.73 *d* (9.7)	6.73 *d* (9.7)	2.78 *d* (3.8)	2.78 *d* (4.0)	3.49 *br d* (5.6)	3.50 *d* (5.5)		
2	6.26 *d* (9.8)	6.24 *d* (9.8)	6.25 *d* (9.7)	6.25 *d* (9.7)	3.41 *dd* (3.8, 2.7)	3.41 *dd* (4.0, 2.9)	6.0 *dd* (9.9, 5.6)	5.94 *dd* (9.8, 5.5)	5.93 *d* (10.2)	5.91 *d* (10.4)
3	—	—	—	—	3.9 *d* (2.7)	3.8 *d* (2.9)	5.60 *d* (9.9)	5.71 *br d* (9.8)	6.63 *d* (10.2)	6.55 *d* (10.4)
5	—	—	—	—	1.77*d* (12.1)	1.78 *d* (11.9)	2.37 *d* (11.5)	2.27 *d* (12.1)	2.31 *d* (11.7)	2.17 *d* (9.1)
6	5.83 *d* (4.3)	5.63 *dq* (8.7, 1.6)	5.62 *dq* (8.5, 1.7)	5.63 *dd* (8.5, 1.7)	4.88 *dd* (12.1, 9.4)	4.86 *dd* (11.9, 9.1)	5.2 *dd* (11.5, 9.4)	5.11 *dd* (12.1, 9.6)	5.23 *t* (11.7, 7.2)	5.44 *dd* (10.4, 9.1)
7	2.32 *m*	3.62 *m*	3.60 *ddd* (8.7, 7.0, 6.4)	3.61 *ddd* (13.6, 7.2, 1.4)	3.34 *ddd* (9.4, 6.8, 3.2)	3.29 *ddd* (9.1, 6.2, 3.5)	3.31 *m*	3.16 *dt* (9.6, 7.0)	3.28 *m*	3.29 *m*
8α	*	*	*	1.55 *m*	*		*	*	*	*
8β	*	*	*	1.89 *m*	*		*	*	*	*
9α	*	*	*	2.0 *ddd* (7.8, 3.5, 2.1)	*		*	*	*	*
9β	*	*	*	1.73 *m*	*		*	*	*	*
13	1.50 *s*	1.40 *s*	1.42 *s*	1.38 *s*	1.45 *s*	1.46 *s*	1.38 *s*	1.45 *s*	1.60 *s*	1.63 *s*
14	1.24 *s*	1.27 *s*	1.27 *s*	1.27 *s*	0.98 *s*	0.97 *s*	0.86 *s*	0.86 is	1.10 *s*	1.21 *s*
15	2.07 *s*	2.11 *d* (1.6)	2.12 *d* (1.7)	2.12 *d* (1.7)	1.58 *s*	1.58 *s*	1.61 *s*	1.62 *s*	1.59 *s*	1.56 *s*
2′	—		—	5.69 *qq* (1.2, 1.2)	—	—	—	—	—	—
3′	—	6.19 *qq* (7.3, 1.4)	6.93 *qq* (6.9, 1.1)	—	6.16 *qq* (7.2, 1.5)	6.92 *qq* (7.0, 1.2)	6.13 *qq* (7.2, 1.4)	6.19 *qq* (7.2, 1.5)	6.21 *qq* (7.2, 1.5)	6.19 *qq* (7.2, 1.5)
4′	—	1.98 *dq* (7.3, 1.4)	1.82 *dq* (6.9, 1.1)	2.17 *d* (1.2)	1.98 *dq* (7.2, 1.4)	1.83 *dq* (7.2, 1.2)	1.98 *dq* (7.2, 1.6)	2.1 *dq* (7.2, 1.2)	2.1 *dq* (7.2, 1.4)	2.0 *dq* (7.2, 1.7)
5′		1.87 *dq* (1.4, 1.4)	1.80 *dq* (1.1, 1.1)	1.92 *d* (1.2)	1.87 *dq* (1.5, 1.4)	1.80 *dq* (1.2, 1.2)	1.87 *dq* (1.6, 1.4)	1.90 *dq* (1.5, 1.2)	1.89 *dq* (1.5, 1.4)	1.89 *dq* (1.7, 1.5)
OH	—	—	—	—					3.10 *br s*	

* Overlapped.

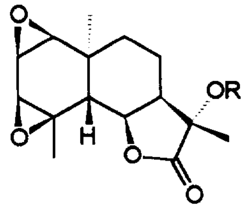
Table 1(b). ^{1}H NMR spectral data for compounds **11**–**17**, **20** and **21**

H	11	12	13	14	15	16	17	20	21
1	3.38 *s*	3.39 *d* (1.7)	4.90 *dd* (12.3, 4.6)	3.83 *dd* (12.6, 5.5)	5.6 *dd* (12.6, 5.7)	3.42 *br dd* (11.5, 4.0)	3.64 *br d* (11.5)	4.62 *dd* (11.3, 4.4)	3.35 *dd* (12.0, 3.3)
2α	—	—	*	2.67 *dd* (17.3, 12.6)	2.67 *dd* (17.3, 12.6)	*	*	*	1.62 *m*
2β	—		*	2.77 *dd* (17.3, 5.5)	2.85 *dd* (17.3, 5.7)	*	*	*	1.80 *m*
3	5.91 *m*	5.92 *m*	4.16 *br s*	—	—	2.37 *ddd* (3αH) (13.8, 4.2, 1.9)	2.34 *m* (3αH)	2.37 *ddd* (3βH) (11.5, 4.9, 2.3)	2.12 *ddd* (3αH) (13.7, 13.6, 5.6) 2.35 *ddd* (3βH) (13.7, 4.9, 2.3)
5	2.87 *d* (11.1)	2.89 *d* (11.1)	—	—	—	*	*	2.02 *br s*	1.91 *br s*
6	4.94 *dd* (11.1, 8.3)	4.94 *dd* (11.1, 8.5)	5.42 *d* (4.3)	5.53 *d* (4.7)	5.72 *d* (4.4)	5.03 *dd* (10.8, 9.4)	4.86 *dd* (11.7, 9.6)	5.12 *t* (3.4)	4.87 *t* (3.0)
7	3.27 *ddd* (8.3, 6.6, 6.6)	3.23 *ddd* (8.5, 6.4, 6.4)	2.92 *m*	3.5 *ddd* (11.7, 6.0, 4.7)	2.36 *ddd* (11.5, 6.4, 4.9)	3.32 *m*	3.04 *m*	2.17 *m*	2.99 *ddd* (11.1, 5.9, 3.4)
8α	1.85 *m*	1.87 *m*	*	*	*	*	*	*	1.20 *m*
8β	1.85 *m*	1.87 *m*	*	*	*	*	*	*	1.80 *m*
9α	2.21 *m*	2.23 *m*	*	*	*	*	*	*	2.13 *m*
9β	1.23 *m*	1.25 *m*	*	2.08 *ddd* (13.6, 4.4, 2.5)	1.79 *m*	*	*	*	1.80 *m*
13	1.88 *s*	1.80 *s*	1.68 *s*	1.72 *s*	1.47 *s*	1.60 *s*	1.57 *s*	1.42 *s*	1.67 *s*
14	0.87 *s*	0.88 *s*	1.05 *s*	1.17 *s*	1.22 *s*	0.73 *s*	0.95 *s*	0.90 *s*	0.82 *s*
15	2.19 *s*	2.20 *s*	1.92 *s*	1.90 *s*	1.94 *s*	5.04 *br s* (15aH) 4.93 *br s* (15bH)	4.94 *br d* (15aH) (1.3) 4.78 *br d* (15bH) (1.3)	5.14 *br d* (15aH) (1.4) 4.99 *br d* (15bH) (1.4)	5.09 *d* (15aH) (1.4) 4.96 *d* (15bH) (1.4)
3′	6.18 *qq* (7.2, 1.5)	6.94 *qq* (7.2, 1.1)	6.13 *qq* (7.2, 1.6)	6.17 *qq* (7.2, 1.5)	—	6.15 *qq* (7.4, 1.5)	6.17 *qq* (7.4, 1.5)		6.13 *qq* (7.2, 1.4)
4′	1.99 *dq* (7.2, 1.6)	1.82 *d* (1.0)	1.95 *dq* (7.2, 1.5)	1.97 *dq* (7.5, 1.5)	—	1.98 *dq* (7.4, 1.5)	1.99 *dq* (7.4, 1.5)	—	1.95 *dq* (7.2, 1.4)
5′	1.88 *dq* (1.6, 1.5)	1.80 *m*	1.85 *dq* (1.6, 1.5)	1.87 *dq* (1.5, 1.5)	—	1.87 *dq* (1.5, 1.5)	1.88 *dq* (1.5, 1.5)	—	1.85 *dq* (1.4, 1.4)
OH	2.61 *br s*	—	—	—	—				—
Acetate	—	—	2.04 *s*		2.08 *s*		—	2.04 *s*	—

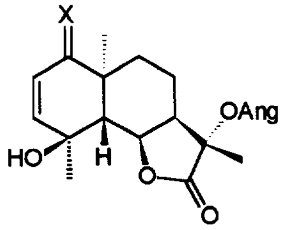
* Overlapped.



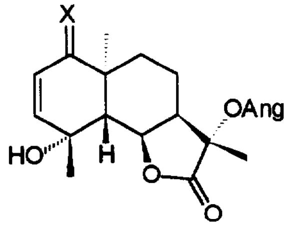
1 R=H
2 R=Ang
3 R=Tig
4 R=Sen



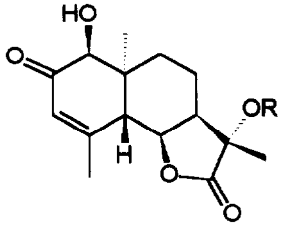
5 R=Ang
6 R=Tig



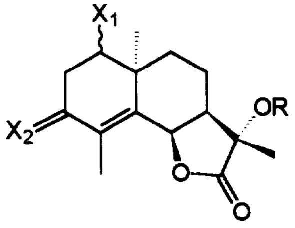
7 X=α-OH, β-H
10 X=O



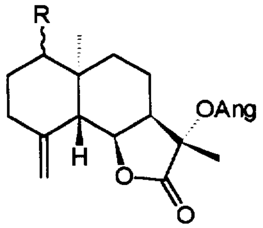
8 X=α-OH, β-H
9 X=O



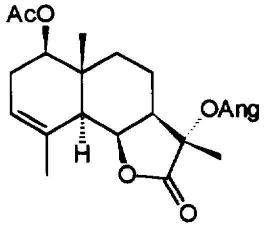
11 R=Ang
12 R=Tig



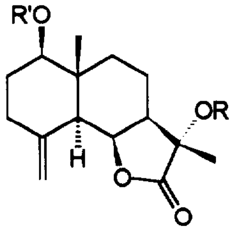
13 X_1=α-OAc; X_2=β-OH, α-H; R=Ang
14 X_1=α-OH; X_2=O; R=Ang
15 X_1=β-OAc; X_2=O; R=H



16 R=α-OH
17 R=β-OH



18



19 R=Ang, R'=Ac
20 R=H, R'=Ac
21 R=Ang, R'=H

molecular ion at m/z 364, in accordance with the molecular formula $C_{20}H_{28}O_6$. In their ^{1}H NMR spectra, signals corresponding to vinylic protons (**7**, 5.60, d, H-3; 6.00, dd, H-2; **8**, 5.71, br d, H-3; 5.94 dd, H-2) were observed and a doublet at δ 3.49 was assigned to H-1 (geminal to a hydroxyl group). The relative configurations were assigned by means of NOE experiments.

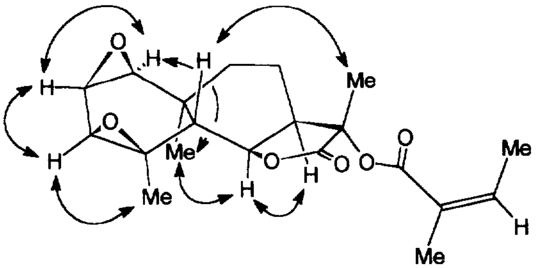


Fig. 1. Observed NOE in decipinin B (**5**).

Compounds **9** and **10** did not give a $[M]^+$ peak. The highest mass spectral fragment appeared at m/z 347, corresponding to $[M - Me]^+$. Their IR and NMR data indicated the presence of an α,β-unsaturated ketone (1714, 1684 cm^{-1}), a tertiary hydroxyl group (3390, 3371 cm^{-1}), a γ-lactone (1790, 1788 cm^{-1}) and an angelate group (1714, 1727 cm^{-1}). They showed in their ^{1}H NMR as more significant signals two doublets corresponding to the olefinic protons H-2 and H-3 (**9**, 5.93, d, H-2; 6.63, d, H-3; **10**, 5.91, d, H-2; 6.55, d, H-3). The stereochemistry at C-4 was confirmed by NOE experiments.

Compounds **11** and **12** showed a $[M]^+$ peak at m/z 362 corresponding to the molecular formula $C_{20}H_{26}O_6$. Their IR spectra contained signals corresponding to a γ-lactone ring, an α,β-unsaturated ketone and a hydroxyl group. The only significant difference in their ^{1}H NMR spectra was the position of the vinylic proton of the ester group, indicating the presence of an angelate group in **11** and a tiglate in **12**. The presence of a narrow multiplet corresponding to the olefinic proton, H-3 (**11**, δ 5.91; **12**, δ 5.92) can be observed in both spectra. The chemical shift of H-1 is almost the same in both compounds, with the only difference being in their multiplicity, a singlet at δ 3.38 in **11** and a doublet at δ 3.39 ($J_{1,3}$ = 1.7 Hz) in **12**. The lactonic proton appears at the same position (δ 4.94, *dd*) in both compounds. A displacement of 0.5 ppm upfield in the signal of H-1 in relation to that in **7** is due to the β-oriented hydroxyl.

Compound **13** was assigned the molecular formula $C_{22}H_{30}O_7$ (MS). It showed in its IR spectrum absorptions at 3411 cm^{-1} (hydroxyl), 1788 cm^{-1} (γ-lactone) and 1722 cm^{-1} (angelate and acetate groups). Its ^{1}H NMR spectrum showed the presence of an allylic hydroxyl group (δ 4.16, *br s*, H-3). ^{1}H–^{1}H COSY established the proton connections of the segment C-1/C-3. The position of the double bond between C-4 and C-5 was deduced from the presence of a methyl at δ 1.92 (*s*, 3H-15) and from the multiplicity of the ring closure (*d*, δ 5.42, $J_{6,7}$ = 4.3 Hz). The relative configuration at C-1 and C-13 was determined by NOE measurements.

Compound **14** showed a $[M]^+$ at *m/z* 362 corresponding to a molecular formula of $C_{20}H_{26}O_6$. It exhibited IR spectral bands corresponding to a hydroxyl group (3454 cm^{-1}), a γ-lactone (1790 cm^{-1}), an α,β-unsaturated ester (1720 cm^{-1}) and an α,β-unsaturated ketone (1678 cm^{-1}). Its ^{1}H NMR spectrum resembled that of **13**. Thus, the signals corresponding to an angelate moiety could be observed and the splitting pattern of H-6 was the same as that of **13** (*d*, δ 5.53, $J_{6,7}$ = 4.7 Hz). There were, however, some differences. The ^{13}C NMR spectrum revealed the presence of a carbonyl group that was assigned to C-3. In its ^{1}H NMR spectrum, there was a double doublet at δ 3.83 assigned to a proton geminal to a hydroxyl group. The splitting pattern of the former signal was only possible of that hydroxyl group was attached to C-1.

The IR spectrum of **15** showed bands corresponding to hydroxyls (3446 cm^{-1}), a γ-lactone (1782 cm^{-1}), an acetate ester (1745 cm^{-1}) and an α,β-unsaturated ketone (1678 cm^{-1}). The downfield part of the ^{1}H NMR spectrum was very simple. Only a narrow doublet at δ 5.72 ($J_{6,7}$ = 4.4 Hz) corresponding to the lactone ring proton and a double doublet of H-1 (δ 5.06, $J_{1,2\alpha}$ = 12.6 Hz, $J_{1,2\beta}$ = 5.7 Hz) could be observed. Other significant signals were those of H-2α (δ 2.67, *dd*, $J_{2\alpha,2\beta}$ = 17.3 Hz, $J_{2\alpha,1}$ = 12.6 Hz) and H-2β (δ 2.85, *dd*, $J_{2\beta,1}$ = 5.5 Hz).

Compound **16**, lasolide, was previously isolated from *Laser trilobum* [6–8]. Together with **16**, we have now isolated its C-1 epimer, 1-*epi*-lasolide (**17**). It showed in its mass spectrum a peak corresponding to $[M+1]^+$ at *m/z* 349 and the fragment $[M+1-H_2O]^+$ at *m/z* 331. It presented an IR spectrum indicating a hydroxyl (3471 cm^{-1}), a γ-lactone (1780 cm^{-1}) and double bonds (1649 cm^{-1}).

The presence of the angelate ester was clear, since its ^{1}H NMR spectrum contained a quartet of quartets at δ 6.17 ($J_{3',4'}$ = 7.4 Hz; $J_{3',5'}$ = 1.5 Hz). The signal of the lactone ring closure appeared at δ 4.86 (*dd*, $J_{6,5}$ = 11.7 Hz; $J_{6,7}$ = 9.6 Hz) between the two signals belonging to the exomethylene protons H-15a and H-15b (*br d*, δ 4.90, H-15a; *br d*, δ 4.70, H-15b). H-1 appeared at δ 3.64 as a broad doublet and its relative orientation was determined by NOE measurements. Irradiation of H-1 produced an enhancement of the angular methyl signal.

We described compounds **18** and **19** in a previous paper [1]. Both of them, together with **20** and **21**, present a different stereochemical skeleton since they possess a β-oriented angular methyl.

Compound **20** gave a $[M]^+$ peak at *m/z* 308, corresponding to the molecular formula $C_{17}H_{24}O_5$. This formula is made up of 15 carbons characteristic of the sesquiterpene skeleton plus two more carbons from an acetate group. The presence of this acetate moiety was confirmed by the presence in the mass spectrum of a peak at *m/z* 249 corresponding to the fragment $[M-HOAc]^+$. The presence of this group was also confirmed by a singlet (3H) at δ 2.04 and a double doublet at δ 4.62 that belongs to H-1. The value of the coupling constants $J_{1,2\alpha}$ = 11.3 Hz; $J_{1,2\beta}$ = 4.4 Hz indicated an α-orientation of H-1. The IR spectrum contained the bands of a hydroxyl (3416 cm^{-1}), γ-lactone (1777 cm^{-1}) and an acetate group (1723 cm^{-1}). In the ^{1}H NMR spectrum, two exomethylene protons at δ 5.14 (*br d*, H-15a, $J_{15a,15b}$ = 1.4 Hz) and 4.99 (*br d*, H-15b) were observed. H-6 appeared as a triplet at δ 5.12 ($J_{6,5}$ = $J_{6,7}$ = 3.4 Hz) which partially overlapped with one of the exomethylene signals. The small value of the coupling constant of H-6 indicated a relative equatorial-axial disposition between H-6/H-5 and H-6/H-7, confirming the different stereochemical pattern of this lactone from that of the previously described.

Compound **21**'s spectra resembled those of **20**. The typical signals of the angelate ester (δ 6.13, *qq*, $J_{3',4'}$ = 7.2 Hz; $J_{3',5'}$ = 1.4 Hz) were observed in its ^{1}H NMR spectrum. Signals belonging to the two exomethylenic protons appeared at δ 5.09 (*d*, H-15a, $J_{15a,15b}$ = 1.4 Hz) and 4.96 (*d*, H-15b). The H-6 signal appeared at δ 4.87 (*dd*, $J_{6,5}$ = $J_{6,7}$ = 3.0 Hz), 0.25 ppm upfield compared with the previous compound. The presence of a double doublet at δ 3.35 indicated the presence of an hydroxyl group. Its position at C-1 was determined from the ^{1}H–^{1}H COSY spectrum. The value of its coupling constants indicated that this hydroxyl was β-equatorial. This was confirmed by NOE measurements.

EXPERIMENTAL

General. Mps: uncorr.; HPLC: LiChrosorb Si 60 (Merck) (10 × 250 mm), flow rate 3 ml min^{-1}, differ-

Table 2. ^{13}C NMR spectral data for compounds **2–5**, **9**, **11**, **14**, **16**, **19** and **21**

C	**2**	**3**	**4**	**5**	**9**	**11**	**14**	**16**	**19**	**21**
1	155.5	155.5	155.5	60.8	201.3	78.1	74.9	78.2	80.0	79.1
2	126.0	125.9	126.0	47.7	125.2	196.8	42.6	31.4	32.6	31.3
3	185.8	185.8	185.4	55.0	152.5	125.2	196.7	34.0	33.8	34.2
4	133.6	133.7	133.2	53.0	70.4	162.0	138.4	140.3	142.9	143.6
5	151.5	151.5	151.4	35.2	51.4	48.8	151.0	?	49.0	48.9
6	79.1	79.3	76.4	75.7	76.5	76.6	77.1	75.0	77.3	77.2
7	46.0	52.3	42.1	43.2	43.6	40.3	51.5	49.3	48.9	49.0
8	20.4	19.1	19.2	20.5	20.4	20.5	20.5	20.3	20.5	20.5
9	40.1	40.0	40.0	38.3	30.5	30.0	33.1	37.8	34.1	34.6
10	41.8	41.9	42.0	32.3	48.0	39.7	44.3	40.0	43.5	43.7
11	80.1	?	?	78.1	78.7	79.6	83.5	79.6	80.0	82.7
12	173.9	173.5	173.5	173.9	173.5	174.1	?	?	172.0	173.8
13	19.3	18.4	18.8	19.9	20.2	20.3	?	20.7	20.6	20.4
14	26.4	26.6	26.6	16.7	24.1	18.2	10.8	11.4	11.8	11.7
15	12.0	11.8	12.0	20.5	19.9	23.7	17.5	110.4	111.3	110.9
1′	166.2	166.4	165.0	166.4	166.4	166.5	166.2	166.3	166.3	166.4
2′	126.8	127.8	158.5	126.9	126.6	126.9	126.5	127.2	127.4	127.6
3′	140.8	139.6	115.0	140.5	141.9	140.5	140.4	140.3	140.1	139.7
4′	15.9	12.0	27.6	15.9	15.9	15.9	15.9	15.9	15.3	15.3
5′	18.6	14.5	20.5	18.0	18.2	18.5	17.9	18.2	18.4	18.6
AcO	—	—	—	—	—	—	—	—	170.6 21.1	—

ential refractometer detector; EIMS: direct inlet, 70 eV; ^{1}H NMR: 399.95 MHz, CDCl$_3$, signal of residual CHCl$_3$ centred at δ 7.25 as int. standard; ^{13}C NMR: 100.577 MHz, CDCl$_3$, central signal at CDCl$_3$ at δ 77.0 as int. standard; CC and TLC: silica gel.

Plant material. Melanoselinum decipiens was collected near Funchal (Madeira) in the summer of 1993 and was identified by Dr Susana Sá Fontinha. A voucher specimen (MADJ no. 02676) is deposited in the Botanical Garden of Madeira.

Extraction and isolation. The dried aerial parts of *M. decipiens* (1.2 kg) were extracted with EtOH in a Soxhlet apparatus for 12 hr, affording 25 g of syrup. This crude material was chromatographed on a silica gel column and eluted with mixts of petrol and EtOAc of increasing polarity. Frs of 100 ml were collected and combined on the basis of TLC monitoring. These frs were further rechromatographed on silica gel columns and the products were purified by HPLC using the same eluants.

11α-*Hydroxy*-3-*oxo*-6α*H*,7α*H*,10α*Me*-*eudesm*-1,4-*dien*-6,12-*olide* (**1**). $C_{15}H_{18}O_4$. $[\alpha]_D^{25}$ −20.0° (CHCl$_3$; *c* 0.10). IR ν_{max}^{film} cm^{-1}: 3507 (hydroxyl), 2937, 1795 (γ-lactone), 1659 (ketone); MS *m/z* (rel. int.): 262 $[M]^+$ (0.2), 218 $[M-CO_2]^+$ (0.6), 191 (3.4), 165 (4.8), 149 (8.6), 123 (11.0), 69 (71.5), 55 (100).

11α-*Tigloyloxy*-3-*oxo*-6α*H*,7α*H*,10α*Me*-*eudesm*-1,4-*dien*-6,12-*olide* (**3**). $C_{20}H_{24}O_5$. $[\alpha]_D^{25}$ +7.9° (CHCl$_3$; *c* 0.29). IR ν_{max}^{film} cm^{-1}: 2938, 1793 (γ-lactone), 1713 (tigloyl ester), 1660 (α,β-unsaturated ketone); MS *m/z* (rel. int.): 345 $[M+1]^+$ (2.1), 327 $[M+1-H_2O]^+$ (1.0), 245 $[M+1-HOTig]^+$ (13.3), 201 $[M+1-HOTig-CO_2]^+$ (20.0), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (35.8).

11α-*Senecioyloxy*-3-*oxo*-6α*H*,7α*H*,10α*Me*-*eudesm*-1,4-*dien*-6,12-*olide* (**4**). $C_{20}H_{24}O_5$. $[\alpha]_D^{25}$ +28.3° (CHCl$_3$; *c* 0.10). IR ν_{max}^{film} cm^{-1}: 2944, 1793 (γ-lactone), 1714 (senecioyl ester), 1657 (α,β-unsaturated ketone); MS *m/z* (rel. int.): 344 $[M]^+$ (1.6), 244 $[M-HOSen]^+$ (24.0), 207 (100), 83 $[C_4H_7CO]^+$ (53.7), 55 $[C_4H_7]^+$ (11.1).

11α-*Angeloyloxy*-1α,2α-3α,4α-*diepoxy*-5β*H*,6α*H*,7α*H*,10α*Me*-*eudesman*-6,12-*olide* (**5**). $C_{20}H_{26}O_6$. $[\alpha]_D^{25}$ −31.6° (CHCl$_3$; *c* 0.62). IR ν_{max}^{film} cm^{-1}: 2936, 1784 (γ-lactone), 1717 (angeloyl ester); MS *m/z* (rel. int.): 363 $[M+1]^+$ (0.2), 263 $[M+1-HOAng]^+$ (1.71), 249 $[M+1-HOAng-Me]^+$ (2.57), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (70.2).

11α-*Tigloyloxy*-1β,2β-3β,4β-*diepoxy*-5β*H*,6α*H*,7α*H*,10α*Me*-*eudesman*-6,12-*olide* (**6**). $C_{20}H_{26}O_6$. $[\alpha]_D^{25}$ −22.0° (CHCl$_3$; *c* 0.20). IR ν_{max}^{film} cm^{-1}: 2936, 1784 (γ-lactone), 1717 (angeloyl ester); MS *m/z* (rel. int.): 263 $(M-OTig]^+$ (0.6), 262 $[M-HOTig]^+$ (0.2), 248 $[M-HOTig-Me]^+$ (0.35), 83 $[C_4H_7CO]^+$ (85.9), 55 $[C_4H_7]^+$ (75.4).

11α-*Angeloyloxy*-1α,4β-*dihydroxy*-5β*H*,6α*H*,7α*H*,10α*Me*-*eudesm*-2,3-*en*-6,12-*olide* (**7**). $C_{20}H_{28}O_6$. $[\alpha]_D^{25}$ −15.3° (CHCl$_3$; *c* 0.17). IR ν_{max}^{film} cm^{-1}: 3413 (hydroxyl), 2929, 1779 (γ-lactone), 1721 (angeloyl ester), 1657 (double bonds); MS *m/z* (rel. int.): 364 $[M]^+$ (0.1), 349 $[M-CH_3]^+$ (0.2), 346 $[M-H_2O]^+$ (0.3), 265 $[M-OAng]^+$ (0.8), 264 $[M-HOAng]^+$ (1.0), 83 $[C_4H_7CO]^+$ (66.3), 55 $[C_4H_7]^+$ (40.1).

11α-*Angeloyloxy*-1α,4α-*dihydroxy*-5β*H*,6α*H*,7α*H*,10α*Me*-*eudesm*-2-*en*-6,12-*olide* (**8**). $C_{20}H_{28}O_6$. $[\alpha]_D^{25}$ −56.0° (CHCl$_3$; *c* 0.10). IR ν_{max}^{film} cm^{-1}: 3371 (hydroxyl), 2929, 1782 (γ-lactone), 1717 (angeloyl ester), 1658 (double bonds); MS *m/z* (rel. int.): 264

$[M-HOAng]^+$ (0.1), 249 $[M-HOAng-Me]^+$ (0.3), 231 $[M-HOAng-Me-H_2O]^+$ (0.3), 213 $[M-Me-2H_2O]^+$ (0.2), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (96.3).

11α-*Angeloyloxy*-4α-*hydroxy*-1-*oxo*-5β*H*,6α*H*,7α*H*,10α*Me-eudesm*-2-*en*-6,12-*olide* (**9**). $C_{20}H_{26}O_6$. $[\alpha]_D^{25}$ −25.3° ($CHCl_3$; *c* 0.47). IR ν_{max}^{film} cm^{-1}: 3390 (hydroxyl), 2931, 1790 (γ-lactone), 1714 (angeloyl ester), 1714 (α,β-unsaturated ketone), 1682 (double bonds); MS *m/z* (rel. int.): 347 $[M-Me]^+$ (0.2), 263 $[M-OAng]^+$ (1.7), 245 $[M-OAng-H_2O]^+$ (3.3), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (91.7).

11α-*Angeloyloxy*-4β-*hydroxy*-1-*oxo*-5β*H*,6α*H*,7α*H*,10α*Me-eudesm*-2-*en*-6,12-*olide* (**10**). $C_{20}H_{26}O_6$. $[\alpha]_D^{25}$ −4.0° ($CHCl_3$; *c* 0.10). IR $[\nu]_{max}^{film}$ cm^{-1}: 3371 (hydroxyl), 2922, 1788 (γ-lactone), 1727 (angeloyl ester), 1684 (α,β-unsaturated ketone), 1639 (double bonds); MS *m/z* (rel. int.): 347 $[M-Me]^+$ (0.8), 263 $[M-OAng]^+$ (2.7), 245 $[M-OAng-H_2O]^+$ (6.1), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (59.7).

11α-*Angeloyloxy*-1β-*hydroxy*-2-*oxo*-5β*H*,6α*H*,7α*H*,10α*Me-eudesm*-3-*en*-6,12-*olide* (**11**). $C_{20}H_{26}O_6$. $[\alpha]_D^{25}$ −90.0° ($CHCl_3$; *c* 0.35). IR ν_{max}^{film} cm^{-1}: 3391 (hydroxyl), 2933, 1786 (γ-lactone), 1717 (angeloyl ester), 1683 (ketone); MS *m/z* (rel. int.): 362 $[M]^+$ (0.3), 264 $[M-C_6H_{10}O]^+$ (0.3), 262 $[M-HOAng]^+$ (1.1), 244 $[M-HOAng-H_2O]^+$ (1.9), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (39.3).

11α-*Tigloyloxy*-1β-*hydroxy*-2-*oxo*-5β*H*,6α*H*,7α*H*,10α*Me-eudesm*-3-*en*-6,12-*olide* (**12**). $C_{20}H_{26}O_6$. $[\alpha]_D^{25}$ −40.0° ($CHCl_3$; *c* 0.10). IR ν_{max}^{film} cm^{-1}: 3391 (hydroxyl), 2933, 1788 (γ-lactone), 1715 (tigloyl ester), 1685 (α,β-unsaturated ketone); MS *m/z* (rel. int.): 362 $[M]^+$ (0.4), 347 $[M-Me]^+$ (0.1), 264 $[M-C_6H_{10}O]^+$ (0.5), 262 $[M-HOTig]^+$ (1.8), 244 $[M-HOTig-H_2O]^+$ (1.8), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (86.9).

1α-*Acetoxy*-11α-*angeloyloxy*-3β-*hydroxy*-6α*H*,7α*H*,10α*Me-eudesm*-4-*en*-6,12-*olide* (**13**). $C_{22}H_{30}O_7$. $[\alpha]_D^{25}$ −10.7° ($CHCl_3$; *c* 0.45). IR ν_{max}^{film} cm^{-1}: 3411 (hydroxyl), 2946, 1788 (γ-lactone), 1722 (angelate and acetate groups); MS *m/z* (rel. int.): 347 $[M-OAc]^+$ (0.2), 346 $[M-HOAc]^+$ (1.0), 306 $[M-HOAng]^+$ (0.1), 247 $[M-HOAc-HOAng]^+$ (5.4), 246 $[M-HOAc-HOAng]^+$ (19.0), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (25.6).

11α-*Angeloyloxy*-1α-*hydroxy*-3-*oxo*-6α*H*,7α*H*,10α*Me-eudesm*-4-*en*-6,12-*olide* (**14**). $C_{20}H_{26}O_6$. $[\alpha]_D^{25}$ −18.0° ($CHCl_3$; *c* 0.20). IR ν_{max}^{film} cm^{-1}: 3454 (hydroxyl), 2942, 1790 (γ-lactone), 1720 (angeloyl ester), 1678 (α,β-unsaturated ketone); MS *m/z* (rel. int.): 362 $[M]^+$ (0.2), 344 $[M-H_2O]^+$ (0.5), 263 $[M-OAng]^+$ (10.4), 262 $[M-HOAng]^+$ (36.2), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (4.2).

1β-*Acetoxy*-11α-*hydroxy*-3-*oxo*-6α*H*,7α*H*,10α*Me-eudesm*-4-*en*-6,12-*olide* (**15**). $C_{17}H_{22}O_6$. $[\alpha]_D^{25}$ +3.3° ($CHCl_3$; *c* 0.10). IR ν_{max}^{film} cm^{-1}: 3446 (hydroxyl), 2934, 1782 (γ-lactone), 1745 (acetate), 1678 (α,β-unsaturated ketone); MS *m/z* (rel. int.): 263 $[M-OAc]^+$ (0.5), 248 $[M-OAc-Me]^+$ (0.4), 230 $[M-OAc-Me-H_2O]^+$ (0.4), 83 $[C_4H_7CO]^+$ (14.5), 55 $[C_4H_7]^+$ (10.7), 43 (100).

11α-*Angeloyloxy*-1α-*hydroxy*-5β*H*,6α*H*,7α*H*,10α*Me-eudesm*-4,15-*en*-6,12-*olide* (**16**). $C_{20}H_{28}O_5$. $[\alpha]_D^{25}$ −16.7° ($CHCl_3$; *c* 0.18). IR ν_{max}^{film} cm^{-1}: 3476 (hydroxyl), 2937, 1786 (γ-lactone), 1720 (angelate), 1655 (double bond); MS *m/z* (rel. int.): 349 $[M+1]^+$ (0.1), 331 $[M+1-H_2O]^+$ (0.1), 249 $[M-OAng]^+$ (3.0), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (63.9).

11α-*Angeloyloxy*-1β-*hydroxy*-5β*H*,6α*H*,7α*H*,10α*Me-eudesm*-4,15-*en*-6,12-*olide* (**17**). $C_{20}H_{28}O_5$. $[\alpha]_D^{25}$ −1.4° ($CHCl_3$; *c* 0.22). IR ν_{max}^{film} cm^{-1}: 3471 (hydroxyl), 2939, 1780 (γ-lactone), 1714 (angelate), 1649 (double bond); MS *m/z* (rel. int.): 349 $[M+1]^+$ (2.25), 331 $[M+1-H_2O]^+$ (0.2), 249 $[M+1-HOAng]^+$ (7.0), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (52.4).

1β-*Acetoxy*-11α-*hydroxy*-5α*H*,6α*H*,7α*H*,10β*Me-eudesm*-4,15-*en*-6,12-*olide* (**20**). $C_{17}H_{24}O_5$. $[\alpha]_D^{25}$ −97.5° ($CHCl_3$; *c* 0.10). ν_{max}^{film} cm^{-1}: 3416 (hydroxyl), 2938, 1777 (γ-lactone), 1723 (acetate), 1657 (double bond); MS *m/z* (rel. int.): 308 $[M]^+$ (0.2), 264 $[M-CO_2]^+$ (0.7), 249 $[M-OAc]^+$ (0.4), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (57.9).

11α-*Angeloyloxy*-1β-*hydroxy*-5α*H*,6α*H*,7α*H*,10β*Me-eudesm*-4,15-*en*-6,12-*olide* (**21**). $C_{20}H_{28}O_5$. $[\alpha]_D^{25}$ −11.9° ($CHCl_3$; *c* 0.16). IR ν_{max}^{film} cm^{-1}: 3364 (hydroxyl), 2934, 1787 (γ-lactone), 1720 (angelate), 1657 (double bond); MS *m/z* (rel. int.): 248 $[M-HOAng]^+$ (6.9), 83 $[C_4H_7CO]^+$ (100.0), 55 $[C_4H_7]^+$ (95.2).

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REFERENCES

1. Massanet, G. M., Guerra, F. M., Dorado, J. M., Jorge, Z. D. and Valerga, P., *Phytochemistry*, 1995, **39**, 1123.
2. González, A. G., Bretón-Funes, J. L., Galindo, A. and Rodríguez-Luis, F., *Anales Quimica*, 1973, **69**, 1339.
3. González, A. G., Bretón-Funes, J. L., Galindo, A. and Rodríguez-Luis, F., *Anales Quimica*, 1974, **70**, 1028.
4. González, A. G., Bretón-Funes, J. L., Galindo, A. and Cabrera, I. *Revista Latinoamericana Quimica*, 1976, **7**, 37.
5. Holub, M. and Budesinsky, M., *Phytochemistry*, 1986, **25**, 2015.
6. Holub, M., De Groote, R., Herout, V. and Sorm, F., *Collection Czechoslovak Chemical Communications*, 1968, **33**, 2911.
7. Holub, M., Budesinsky, M., Smitalova, Z., Saman, D. and Rychlewska, U., *Tetrahedron Letters*, 1984, 3755.
8. Holub, M., Budesinsky, M., Smitalova, Z., Saman, D. and Rychlewska, U., *Collection Czechoslovak Chemical Communications*, 1985, **51**, 903.