Table 2 ^{13}C NMR data of compounds **1** and **2** ($CDCl_3$, 100.6 MHz)

C	1	2	C	1	2
1	32.3	31.1	12	25.8	26.5
2	47.2	50.9	13	24.2	24.2
3	25.2	26.3	14	155.4	158.7
4	36.2	36.3	15	14.9	16.1
5	53.1	52.0	1′	97.2	97.2
6	104.1	101.4	2′	73.9	73.8
7	71.1	70.9	3′	72.1	72.0
8	27.5	30.5	4′	71.6	71.6
9	34.4	33.4	5′	70.2	70.1
10	35.1	39.8	6′	16.5	16.6
11	79.2	78.2			

(Table 2) also supported the proposed structure. The glycosides **1** and **2** are most probably formed by an allylic oxidation of hinesol β-fucopyranoside [2]. The isolation of a fucopyranoside of a sesquiterpene alcohol may be of chemotaxonomic relevance as already these compounds have been detected in four different species.

EXPERIMENTAL

^1H NMR, 400 MHz, TMS as internal standard, MS 70 eV. The air-dried aerial parts (950 g), collected near Alexandria, Egypt, were extracted with 95% EtOH at room temp. The resulting extract was separated by CC (silica gel) and further by repeated TLC (silica gel GF 254). Known compounds were identified by comparison of mp, IR, and ^1H NMR spectra with those of authentic materials. Finally, 80 mg taraxasterol, 60 mg stigmasterol, 170 mg β-sitosterol β-D-glycoside, and 100 mg of a mixture of **1** and **2** were obtained. HPLC of 30 mg of the mixture (RP 8, MeOH–H_2O, 7:3) afforded 15 mg **1** (R_t 9.9 min) and 15 mg **2** (R_t 12.3 min). Acetylation of **1** and **2** using Ac_2O and dimethyl aminopyridine at 20° for 1 hr gave the tetraacetates **3** and **4**. Compound **1** and its 7α-epimer **2**, colourless gum, IR ν_{max}^{nujol} cm^{-1} 3400–3600 (OH), MS m/z (rel. int.) 384 $[M]^+$ (0.1) ($C_{21}H_{36}O_6$), 366 $[M-H_2O]^+$ (0.25), 308 $[C_{18}H_{28}O_4]^+$ (1.6), 220 $[C_{15}H_{24}O]^+$ (25), 203 $[C_{15}H_{23}]^+$ (86), 147 (54), 75 (100).

Acknowledgement—We thank Professor Boulos (Department of Botany, University of Cairo) for identification of the plant material.

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Phytochemistry, Vol. 28, No. 4, pp. 1264–1267, 1989
Printed in Great Britain

0031-9422/89 $3.00+0.00
Pergamon Press plc

SESQUITERPENE LACTONES AND AN ELEMANE DERIVATIVE FROM *ONOPORDON CORYMBOSUM*

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(*Received in revised form* 29 *September* 1988)

Key Word Index—*Onopordon corymbosum*, Compositae, sesquiterpene lactones, elemanolides, ^{13}C NMR.

Abstract—The aerial parts of *Onopordon corymbosum* afforded dehydromelitensin, its 8-(4-hydroxymethacryloil)-derivative and a related ester. The ^{13}C NMR of several natural and synthetic elemanolides are discussed.

INTRODUCTION

From the genus *Onopordon* (Compositae, tribe Cynareae) several species have been investigated chemically. Flavonoids [1] and sesquiterpene lactones [2] are the most characteristic isolated constituents. In the present paper we report the isolation and structure elucidation of two elemanolides and an elemane derivative from the hitherto unstudied *Onopordon corymbosum* Willk. The ^{13}C NMR spectral data for several natural and synthetic elemanolides are given also.

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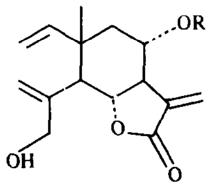
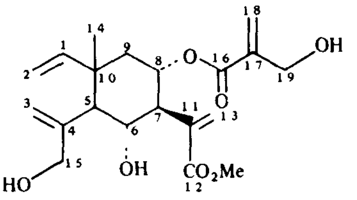


1 R = H
2 R = $COC(=CH_2)CH_2OH$



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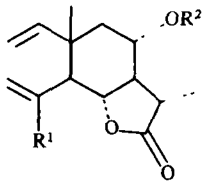
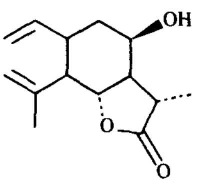


4 R¹ = CH_2OH, R² = H
5 R¹ = CH_2OAc, R² = Ac
6 R¹ = Me, R² = H
7 R¹ = Me, R² = $Si(Me)_2Bu^t$
8 R¹ = CHO, R² = $Si(Me)_2Bu^t$



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RESULTS AND DISCUSSION

The polar fractions of the methanolic extract of the aerial parts of *O. corymbosum* gave a complex mixture of sesquiterpenes which could be separated by repeated column chromatography Dehydromelitensin (**1**), the corresponding 4-hydroxymethacrylate (**2**) and the elemane derivative (**3**) were isolated. The structures of these compounds could be deduced from the ^1H and ^{13}C NMR spectra The ^1H NMR spectral data of compound **1** are included (Table 1) because a high-field spectrum has not been reported previously.

The ^{13}C NMR spectrum of **1** and **2** were very characteristic of elemanolides (Table 2) The C-1, C-2 and C-3 carbons gave signals at *ca* δ146, 113, 115 and 143 respectively. The lactonic carbonyl appeared at *ca* δ170, the exocyclic methylene at 137 (C-11) and at 120 (C-13) The carbon bonded at oxygenated functions appeared between δ65 and 80: C-15 at 67, C-8 at 67–69 depending on the substituents and C-6 at 78 The ester side chain of **2** gave signals at δ126 for the olefinic carbon (C-18) and δ62 for the carbon bonded to hydroxyl group (C-19).

In the ^{13}C NMR spectrum of **3** there is also evidence for the presence of the elemane skeleton (δ146, 112, 115 and 139 for the carbons C-1, C-2, C-3 and C-4 respectively), as well as the two ester carbonyl (at δ167 and 165), the methoxyl (at δ52) and the nature of the ester side chain (δ126 and 62 for C-18 and C-19 respectively) The compound **3** has been isolated previously once only from *Onopordon carmanicum* [3] and it has been named elemacarmanin The two other elemanolides isolated from *O. corymbosum* are characteristic for this genus also Thus, compound **1** has been isolated previously from *O nervosum* [4] as well as from four *Centaurea* species [5–8] (which belong to the same family and tribe as *Onopordon*). The compound **2** has been isolated previously from *O. leptolepis* [9], *O nervosum* [4] and *C. tagananensis* [8]

The ^{13}C NMR spectra of several elemanolides synthesised by us [10] are also included in Table 2. These data could be of great value for identification of natural elemanolides, because several generalizations have been established The chemical shift for C-1, C-2, C-3 and C-4 carbons are very characteristic· δ146–147 and 112–113 for C-1 and C-2 respectively, when the substituent at C-8 is α, while in the epitemisine **9** (OH at C-8 is β) these carbons gave signals at δ148 and 115 The value of C-4 is very characteristic also and depends on the nature of the substituent at this carbon. 139 ppm when this substituent is CH_2OAc, 140 when it is Me, 144 when it is CH_2OH and 145 when it is CHO Likewise C-3 gave a characteristic signal at δ115–116, unless the C-4 substituent is the formyl group, which causes a low-field shift of *ca* 20 ppm. The value of this signal is affected by the stereochemistry of C-8 again (δ121.5 for the epitemisin **9**). The C-6 and C-8 carbons gave characteristic signals also at *ca* δ78 and 68 respectively, a β-substituent at C-8 reduces these values at δ76 and 65, as in compound **9**. The C-9 carbon gave a signal at *ca* 49.5 when at C-8 there is a α-hydroxyl free or as a silyl ether, whilst this signal appeared at *ca* 45 when this hydroxyl is acylated, or at *ca* 46 when it is β-oriented. The quaternary C-10 carbon gave a characteristic signal at *ca* δ42 and the methyl group bonded at C-10 (C-14) gave a signal at *ca* δ19, except when the substituent at C-8 is β, in which case this signal appeared at *ca* δ21. The C-11, C-12 and C-13 carbons gave characteristic signals also. In α,β-unsaturated lactones the C-12 carbon (C=O) gave a signal at *ca* δ170 whilst saturated lactones gave a signal at *ca* δ178. The C-11 and C-13 carbons gave signals at *ca* δ137 and 120 respectively if the lactone is α,β-unsaturated and δ41 and 14 if it is saturated, unless the substituent at C-8 is β again (*ca* δ37 and 12 respectively in compound **9**). Finally the C-15 carbon gave a characteristic signal also A methyl group gave a signal at δ23 5, when it is bonded to a hydroxyl group free or acetylated gave a signal at *ca* δ67 and when it is a formyl group gave a signal at *ca* δ194 The assignment of carbon signals has been made according to the results obtained by distortionless enhancement by polarization transfer (DEPT) experiments Only the signals corresponding to the C-5 and C-7 carbons could not be assigned without ambiguity Nevertheless, it is clear that the generalizations established from ^{13}C NMR spectral data of Table 2 could be of great value for identification of natural elemanolides

Table 1 ^{1}H NMR spectral data of compound **1**

H	δ
1	5 76 *dd*
2	5 02 *d*
2′	4 96 *d*
3	5 38 *s*
3′	4 92 *s*
5	2 49 *d*
6	4 12 *t*
7	2 62 *tt*
8	4 09 *dt*
9β	1 85 *dd*
13	6 15 *d*
13′	5 96 *d*
14	1 08 *s*
15	4 06 *d*
15′	3 96 *d*

Coupling constants (Hz) $J_{1,2} = 10\ 7$, $J_{1,2'} = 17\ 3$, $J_{5,6} = J_{6,7} = 11\ 5$, $J_{7,13} = J_{7,13'} = 3$, $J_{7,8} = J_{8,9\beta} = 4\ 1$, $J_{9\alpha,9\beta} = 13\ 0$, $J_{15,15'} = 14\ 0$

EXPERIMENTAL

^{1}H and ^{13}C NMR were run at 200 13 and 50 32 MHz respectively in Cl$_3$CD, using the solvent signals at δ7 24 (^{1}H) and δ77 0 (^{13}C) as ref The DEPT experiments were performed using polarization transfer pulses of 25° and 17 , obtaining in the first case positive signals for CH and CH$_3$ and negative signals for CH$_2$, in the second case only signals for the CH groups

Plant material Aerial parts of *O corymbosum* were collected at the Valencia-Teruel road (Barracas, Castellón, Spain) and authenticated by Prof J Alcover (Botany Department of the Faculty of Biological Sciences, University of Valencia) A voucher specimen is deposited in the herbarium of the above mentioned department

Extraction and chromatography The plant material (12 kg) was extracted exhaustively firstly with hexane and afterwards with MeOH This extract was reduced *in vacuo* to *ca* 1 5 l, diluted with H$_2$O (3 l) and re-extracted with Et$_2$O Evaporation of

Table 2 ^{13}C NMR spectral data of compounds **1**–**9**

C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1	146 11	145 59	146 31	146 36	145 70	146 94	147 17	146 00	148 14
2	112 69	113 15	112 03	112 56	113 09	111 86	111 59	112 31	115 60
3	114 90	115 20	114 95	114 59	116 67	115 75	115 44	137 72	121 52
4	143 92	143 65	139 33	144 42	138 87	140 26	140 36	145 33	140 70
5	50 61^a	50 58^a	55 37^a	50 49^a	51 33^a	58 26^a	58 29^a	46 59^a	59 75^a
6	78 82	78 64	70 92*	78 70	77 99	78 56	78 56	77 37	75 88
7	55 04^a	52 34^a	54 66^a	58 43^a	55 98^a	55 19^a	55 21^a	58 56^a	56 64^a
8	67 47	69 67	70 92*	68 93	69.91	69 13	69 54	69 51	65 47
9	49 77	45 04	43 53	49 55	44 99	49 56	49 72	49 39	46 12
10	41 92	41 92	40 24	41 71	41 63	42 03	41 80	41 71	42 69
11	137 44	136 63	137 97	41 57	41 02	41 46	41 23	41 36	36 94
12	169 68	?	167 13^b	178 44	177 69	178 72	178 85	178 56	178 92
13	120 49	120 22	128 35	14 36	13 90	14 41	14 40	14 45	12 32
14	18 88	18 68	18 36	18 99	18 88	19 71	19 53	18 32	21 19
15	67 31	67 36	67 84	67 35	67 25	23 79	23 65	193 73	23 52
16	—	?	165 42^b	—	—			—	
17	—	?	?	—	—			—	
18	—	126 74	126.01	—	—	—	—	—	
19	—	62 32	62 47	—	—	—	—		—
OMe	—	—	52 03	—	—	—		—	—

Other signals: compound **5** 170 55, 170 24 for $-\mathrm{O\underline{C}O\underline{Me}}$ and 21 01 for $-\mathrm{OCO\underline{Me}}$ Compound **7**, 25 69 for $(\underline{\mathrm{Me}})_3$ C-Si 17 84 for (Me)$_3$ $\underline{\mathrm{C}}$-Si and −4 42 and −4 71 for $\underline{\mathrm{Me}}$ −Si Compound **8**, 25 72 for $(\underline{\mathrm{Me}})_3$ C-Si, 17 90 for (Me)$_3$ $\underline{\mathrm{C}}$-Si and −4 36 and −4 66 for $\underline{\mathrm{Me}}$ -Si

* Overlapped signals

$^{a\ b}$Chemical shifts denoted by the same letter in each column may be interchanged solvent yielded 70 g of crude syrup which was chromatographed on silica gel Elution of the column with mixtures of increasing polarity (hexane–CH_2Cl_2–EtOAc) and repeated CC of the fractions eluted from CH_2Cl_2–EtOAc (3 17) to EtOAc afforded **1** (7 mg), **2** (3 mg) and **3** (25 mg)

Dehydromelitensin (**1**). Colourless oil; IR ν_{max} cm^{-1}: 3600–3100, 1760, 1640 MS m/z (rel. int.) 249 $[M-15]^+$ (0.42), 246 $[M-18]^+$ (0.94), 231 (1 65).

8-(4-hydroxymethacryloil)-Dehydromelitensin (**2**) Colourless oil IR ν_{max} cm^{-1} 3600–3150, 1770, 1730 MS m/z (rel int.) 246 $[M-RCO_2H]^+$ (6.1), 85 $(RCO)^+$ (60).

Elemacarmanin (**3**) Colourless oil, IR ν_{max} cm^{-1} 3550–3150, 1715, 1630 MS m/z (rel int) 278 $[M-RCO_2H]^+$ (49), 85 $[RCO]^+$ (57)

Acknowledgements—Financial support by the Comisión Asesora de Investigación Cintífica y Técnica (CAICYT, Grant No 559/84) is gratefully acknowledged We thank Prof Dr J Alcover (Department of Botany, Faculty of Biological Sciences, University of Valencia, Spain) for identification of plant material.

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Phytochemistry, Vol 28, No 4, pp 1267–1268, 1989
Printed in Great Britain

0031–9422/89 $3.00+0.00

A DERIVATIVE OF *ENT*-13-*EPI*-MANOYL OXIDE ISOLATED FROM *SIDERITIS JAVALAMBRENSIS*

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(*Received* 5 *July* 1988)

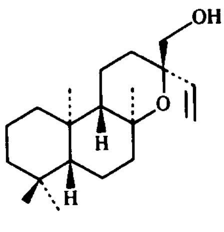
Key Word Index—*Sideritis javalambrensis*; Labiatae, diterpenoid; *ent*-13-*epi*-manoyl oxide derivative; *ent*-16-hydroxy-13-*epi*-manoyl oxide.

Abstract—*ent*-16-Hydroxy-13-*epi*-manoyl oxide, a new derivative of *ent*-13-*epi*-manoyl oxide, has been isolated from the hexanic extract of *Sideritis javalambrensis* aerial parts.

INTRODUCTION

Sideritis javalambrensis Pau is a plant endemic to Sierra Javalambre (Teruel, Spain) whose chemical content has not been previously studied. The hexanic extract obtained from the aerial parts of this species exerts anti-inflammatory effects in animals [1] In the present work, it has been studied to establish the principle responsible for the pharmacological activity thus leading to the isolation of a new diterpenoid

The diterpenoid was found to have the molecular formula $C_{20}H_{34}O_2$. The ^1H NMR spectrum showed an AB quartet centred at δ3.05 ($J = 10.8$ Hz) assigned to two protons geminal to a primary hydroxyl group, as well as a vinylic ABX system and four methyl singlet signals at 0.79 (6H), 0.71 (3H) and 0 66 (3H) The ^{13}C NMR data of C-1 to C-11 and C-17 to C-20 were identical to those of *ent*-13-epi-manoyl oxide [2] whereas the carbon resonances of C-12 to C-16 led us to place the hydroxyl function at C-16.



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