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TWO NEW ELEMANOLIDES FROM *ONOPORDON LEPTOLEPIS**

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Key Word Index—*Onopordon leptolepis*; Compositae; new elemanolides; Cope rearrangement; sesquiterpene lactones.

Abstract—The investigation of the polar fractions of the aerial parts of *O. leptolepis* afforded two new elemanolides, their structures being elucidated by spectroscopic methods and by partial synthesis starting with onopordopicrin.

INTRODUCTION

From the aerial parts of *Onopordon leptolepis* DC. three sesquiterpene lactones have already been isolated: onopordopicrin, which seems to be present in all species; and two closely related esters, where the hydroxy methacrylate is replaced by methacrylate and isobutyrate*. The investigation of the polar fractions has now afforded two further lactones, which turn out to be elemanolides.

RESULTS AND DISCUSSION

Careful separation of the polar fractions of the extract of *O. leptolepis* DC. afforded two new sesquiterpene lactones, the elemanolides **1** and **3**. The structures clearly follow from the ^{1}H NMR data and those of the acetates. Furthermore, the aldehyde **3** and the diacetate of **2** have been synthesized from onopordopicrin (**4**). Cope rearrangement of the diacetate **5** at 150° affords high yield of the diacetate **2**, identical with the diacetate of the natural lactone, while partial oxidation of onopordopicrin yields the monoaldehyde **6**, which also could be transformed by Cope rearrangement to an elemanolide (**3**), which was completely identical with the natural compound. As the rearrangement only proceeds at temperatures above 100° and no trace of the corresponding ten-membered ring compound could be detected in the extract, the two elemanolides must be real natural products. The stereochemistry of the two lactones clearly follows from the ^{1}H NMR data and furthermore from the known stereochemistry of onopordopicrin as the Cope rearrangements proceeds stereospecifically.

1 and **3** are derivatives of dehydro-melitensin [1], which has the same stereochemistry at all asymmetric centres and has been isolated from *Centaurea pullata*, belonging to the same tribe as *Onopordon*, but to a different subtribe [2].

EXPERIMENTAL

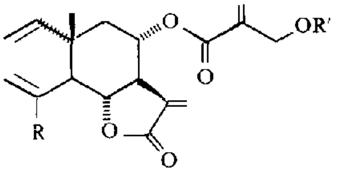
IR: Beckman IR 9, $CHCl_3$; ^{1}H NMR: Bruker WH 270; MS: Varian MAT 711 and 311A; optical rotation: Perkin-Elmer polarimeter, $CHCl_3$. The polar fractions of the $CHCl_3$ extract of 1 kg of aerial parts was separated first by column chromatography (Si gel, act. grade II) and further by repeated TLC (Si gel, GF 254) using $Et_2O–C_6H_6$ mixtures as solvents. 500 mg **1** ($Et_2O–C_6H_6$ 4:6) and 80 mg **3** ($Et_2O–C_6H_6$ 1:2) were obtained.

Dehydromelitensin-8-(O)-4[4′-*hydroxymethacrylate*] (**1**). Colourless gum, IR: OH 3460; γ-Lactone 1770; $C{=}CCO_2R$ 1730 cm^{-1}.

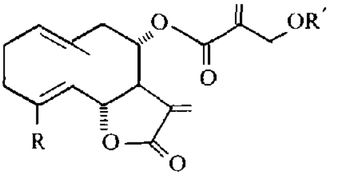
$$[\alpha]^{\lambda}_{24^\circ} = \frac{589}{+74}\ \frac{578}{+76}\ \frac{546}{+88}\ \frac{436\ \text{nm}}{+152}\ (c = 0.68).$$

Acetylation (Ac_2O, 30 min 70°) afforded **2**, colourless gum. IR: γ-lactone 1760; OAc 1745; $C{=}CCO_2R$ 1715 cm^{-1}; MS (CI, isobutene): M^+ +H 433 ($C_{23}H_{28}O_8$ +H); −ketene 391 (EI-MS does not show a molecular ion).

Transformation of onopordopicrin to **2**. 20 mg of **4** was heated in 1 ml Ac_2O for 30 min at 70°. The purified diacetate **5*** (TLC) was heated for 10 min under N_2 at 150°. TLC ($Et_2O–C_6H_6$ 1:2) afforded 15 mg **2**, identical with the diacetate of the natural product.



	1	2	3
R	CH_2OH	CH_2OAc	CHO
R′	H	Ac	H



	4	5	6
R	CH_2OH	CH_2OAc	CHO
R′	H	Ac	H

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* Part 191 in the series "Naturally Occurring Terpene Derivatives". For part 190 see Rustaiyan, A., Nazarians, L. and Bohlmann, F. (1979) *Phytochemistry* **18**, 883 (and refs. cited therein).

Table 1. ^{1}H NMR data of **1**–**3** and **6** (270 MHz, TMS as internal standard)

	1 ($CDCl_3/CD_3OD$) 1:1	**2** ($CDCl_3$)	**3** ($CDCl_3$)	**6** ($CDCl_3$)
1-H	*dd* 5.82	*dd* 5.78	*dd* 5.68	*dd* 5.13
2*t*-H	*d* 5.03	*d* 5.03	*d* 4.87	*m* 2.25
2*c*-H	*d* 5.07	*d* 5.08	*d* 4.97	
3-H	*s*(*br*) 5.45	*s*(*br*) 5.44	*s*(*br*) 6.32	*d*(*br*) 3.08
3′-H	*s*(*br*) 4.99	*s*(*br*) 5.05	*s*(*br*) 6.29	*m* 2.25
5α-H	*d* 2.54	*d* 2.49	*d* 3.20	*dd* 5.88
6β-H	*dd* 4.37	*dd* 4.22	*dd* 4.44	*dd* 5.36
7α-H	*dddd* 3.03	*dddd* 2.95	*dddd* 3.01	*dddd* 3.16
8β-H	*ddd* 5.32	*ddd* 5.31	*ddd* 5.33	*ddd* 5.21
9α-H	*dd* 1.74	*dd* 1.69	*dd* 1.74	*d*(*br*) 2.65
9β-H	*dd* 2.05	*dd* 2.07	*dd* 2.12	*dd* 2.48
13-H	*d* 6.13	*d* 6.16	*d* 6.18	*d* 6.38
13′-H	*d* 5.54	*d* 5.57	*d* 5.61	*d* 5.86
14-H	*s* 1.21	*s* 1.17	*s* 1.11	*s* 1.31
15-H	*d* 3.97	*d* 4.55	*s* 9.48	*s* 10.01
15′-H	*d* 4.08	*d* 4.49		
OCOR	*s*(*br*) 6.33	*s*(*br*) 6.42	*s*(*br*) 6.32	*s*(*br*) 6.30
	s(*br*) 5.99	*s*(*br*) 5.95	*s*(*br*) 5.96	*s*(*br*) 5.99
	d 4.30	*d* 4.85	*d* 4.36	*s*(*br*) 4.37
	d 4.35	*d* 4.79	*d* 4.42	—
OAc	—	*s* 2.10	—	—
	—	*s* 2.09	—	—

J(Hz) 1, 2*c* = 10.5; 1, 2*t* = 17; 5, 6 = 11; 6, 7 = 11; 7, 8 = 10.5; 7, 13 = 3; 8, 9α = 11; 8, 9β = 4.5; 9α, 9β = 13; 15, 15′ = 13; 4′, 4′ = 14.

Synthesis of **3**. 20 mg **4** in 3 ml $CHCl_3$ was stirred with 200 mg MnO_2 for 30 min. TLC (Et_2O–C_6H_6 1:1) afforded 15 mg **6** (^{1}H NMR see Table 1), which was heated in DMSO for 15 min at 125°. After evapn of the solvent *in vacuo* 5 mg **3** were obtained by TLC, identical with the natural product.

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