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TWO NEW GERMACRANOLIDES FROM *ONOPORDON LEPTOLEPIS*[*]

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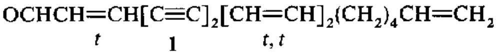
Key Word Index—*Onopordon leptolepis*; Compositae; new germacranolides.

Abstract—The investigation of the aerial parts of *O. leptolepis* afforded, in addition to a known polyynaldehyde and onopordopicrin, two further germacranolides. The structures are elucidated by spectroscopic methods and by conversion to the corresponding acetates.

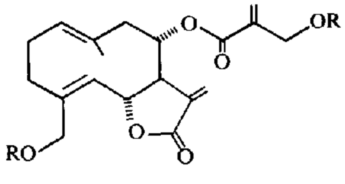
INTRODUCTION

From the genus *Onopordon*, tribe Cynareae, already several species have been investigated. The roots of seven species afforded mainly C_{17}-acetylenes [1], while the aerial parts also from seven species yielded onopordopicrin [2–4]. Furthermore several flavones have been isolated. *Onopordon leptolepis* DC. growing in Iran, has not been investigated before. The aerial parts also contain onopordopicrin (**2**), the aldehyde **1** and two new germacranolides (**4** and **6**), closely related to **2**.

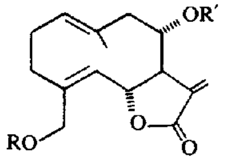


$$\underset{t}{OCHCH{=}CH}[C{\equiv}C]_2\underset{t,t}{[CH{=}CH]_2}(CH_2)_4CH{=}CH_2$$

1



2 R = H
3 R = Ac



4 R = H, R' = COC(Me) = CH_2
5 R = Ac, R' = COC(Me) = CH_2
6 R = H, R' = COCHMe$_2$
7 R = Ac, R' = COCHMe$_2$

RESULTS AND DISCUSSION

The extract of the aerial parts of *Onopordon leptolepis* DC. afforded the known aldehyde **1** and as the main component, onopordopicrin (**2**) [2–4]. While the ^{1}H-NMR of the diol could not be interpreted even at 270 MHz, in the spectrum of the corresponding diacetate in $CDCl_3/C_6D_6$ at 50° all signals could be assigned. The observed coupling constants establish the given stereochemistry [2–4].

The less polar fraction afforded in mixture two further lactones, which, however, could not be separated, even after acetylation. High resolution mass spectroscopy of the acetates gave the elemental formulae $C_{21}H_{26}O_6$ and $C_{21}H_{28}O_6$ showing that the two lactones only differ by two hydrogens. The ^{1}H NMR spectrum of the mixture clearly indicates the presence of a methacrylic and an isobutyric acid ester. All the other signals in the spectrum of the acetates at 50° are very similar to those of the diacetate **3** (see Table 1). The identical stereochemistry at C-8 clearly follows from the observed coupling constants ($J_{7\alpha,8\beta} = 8$; $J_{8\beta,9\alpha} = 10.5$ and $J_{8\beta,9\beta} = 2.5$). Some of the signals are always overlapping; however, by using solvent shift and double resonance experiments all signals could be assigned.

Investigation of further *Onopordon* species are desirable to see whether these lactones are characteristic of this genus.

EXPERIMENTAL

IR: Beckman IR 9, $CHCl_3$; ^{1}H NMR: Bruker WH 270; MS: Varian MAT 711. The fresh plant material was extracted with $CHCl_3$ and the extract separated first by column chromatography (Si gel, act. grade II) and further by repeated TLC (Si gel, GF 254) using Et_2O–petrol-mixtures as solvents. 1 kg of aerial parts afforded 50 mg **1**, 1.5 g **2** and 36 mg **4** and **6** (*ca* 4:1) (Et_2O–petrol 4:1).

15-Hydroxy-8α-[α-methylacryloyl]-respectively isobutyryloxy-costunolide(**4** *and* **6**). Colourless gum, which could not be separated, IR cm^{-1}: OH 3400; γ-lactone 1760, $C{=}CCO_2R$ 1715, 1640; CO_2R 1740. The mixture was heated for 30 min at 70° in 1 ml Ac_2O. After evapn the residue was purified by TLC (Et_2O–petrol 3:2). The resulting acetates **5** and **7** again could not be separated, colourless gum; MS: M^+ *m/e* 376 and 374 ($C_{21}H_{28}O_6$ and $C_{21}H_{26}O_6$); $-$HOAc 316 and 314; 316 and 314 $-$ RCO_2H 228; $C_3H_7CO^+$ 71; $C_3H_5CO^+$ 69; $MeCO^+$ 43.

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[*] Part 190 in the series "Naturally Occurring Terpene Derivatives". For Part 189 see Bohlmann, F. and Suwita, A. (1979) *Phytochemistry* **18**, 677.

Table 1. ^{1}H NMR data of **2–5** and **7** (270 MHz, TMS as internal standard)

	2 ($CDCl_3$)	**3** ($CDCl_3/C_6D_6$, 50°)	**4**	**5/7** (C_6D_6, 50°)	**5/7** ($CDCl_3$)
1-H	*dd*(*br*) 5.02	*dd*(*br*) 4.80		*ddq* 4.58	*m* 5.14
2-H	*m* 2.24	*m* 2.11		*m* 1.92	*m* 2.07
3α-H	*m* 2.24	*m* 1.9		*ddd* 1.71	*m* 2.07
3β-H	*m* 2.6	*ddd* 2.39		*ddd* 2.26	*m* 2.5
5-H	*d* 4.83	*m* 4.77		*d* 4.47*	*m* 4.94
6β-H	*dd* 5.13	*m* 4.77		*dd* 4.43*	*m* 4.97
7α-H	*m* 3.09	*dddd* 2.85		*dddd* 2.61	*m* 3.11
8β-H	*dd*(*br*) 5.20	*ddd* 5.05		*ddd* 5.04	*m* 4.97
9α-H	*m* 2.6	*d*(*br*) 2.51		*d*(*br*) 2.48	*m* 2.5
9β-H	*m* 2.01	*dd* 2.32		*dd* 2.13	*m* 2.07
13-H	*d* 6.30	*d*(*br*) 6.27	*dd* 6.38	*dd* 6.42	*d*(*br*) 6.31
13′-H	*d* 5.78	*d*(*br*) 5.65	*dd* 5.65	*dd* 5.67	*d*(*br*) 5.79
14-H	*s*(*br*) 1.52	*s*(*br*) 1.42	*s*(*br*) 1.27	*s*(*br*) 1.29	*s*(*br*) 1.53
15-H	*d* 4.32	*s*(*br*) 4.53		*d* 4.42*	*s*(*br*) 4.62
15′-H	*d* 4.11			*d* 4.48*	
OCOR	*s*(*br*) 6.29	*dt* 6.25	*dq* 5.29	*qq* 2.34	*s*(*br*) 6.15
	s(*br*) 5.97	*dt* 5.77	*dq* 6.04	*d* 1.07	*d* 1.22
	s(*br*) 4.36	*m* 4.73	*dd* 1.85	*d* 1.08	*s*(*br*) 1.97
OAc	—	*s* 1.96		*s* 1.78	*s* 2.11
		s 1.94			

* Overlapping signals.

J(Hz): 1,2β = 10; 1,2α = 6.5; 1,14 = 1; 2α,3α = 6.5; 2α,3β = 3; 2β,3α = 12; 2β,3β = 4; 3α,3β = 12.5; 5,6 = 10; 6,7 = 9; 7,8 = 9; 7,13 = 3.5; 7,13 = 3; 8,9β = 10.5; 9α,9β = 12.5; 13,13 = 1†; COC(Me) = CH_2 3′,4′ = 1 bzw. 1.5; 3′,3′ = 1.5; COCH Me_2 = 7.

† Proved by double resonance experiments.

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