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GERMACRANOLIDES FROM *JURINEA ERIOBASIS*

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Key Word Index—*Jurinea eriobasis*; Compositae; sesquiterpene lactones; pectorolide derivatives.

Abstract—The aerial parts of *Jurinea eriobasis* afforded, in addition to pectorolide, 4′-hydroxypectorolide and alatolide, three further closely related lactones, the structures of which were elucidated by high field ^{1}H NMR spectroscopy.

INTRODUCTION

The large genus *Jurinea* (tribe Cynareae, subtribe Carduinea) with about 250 species is distributed over central and south Europe, and south-west and central Asia. Several species have been studied chemically [1]. Most widespread are germacranolides oxygenated at C-14 and C-15. We now have studied a species from Iran, *J. eriobasis* DC.

RESULTS AND DISCUSSION

The extract of the aerial parts afforded polar fractions which gave by TLC the known germacranolides pectorolide (**1**) [2], 4-hydroxypectorolide (**3**) [3] and alatolide (**6**) [4] as well as three new ones, the acetate **3** and the epoxides **4** and **5**.

The structure of **3** was deduced from its ^{1}H NMR spectrum (Table 1) which differed from that of **2** mainly by the downfiled shift of the H-14 signals and the presence of an acetate methyl singlet (δ 2.08). Spin decoupling allowed the assignment of all signals. The observed couplings further indicated that the stereochemistry was identical with that of **2**.

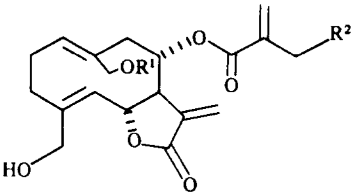
The ^{1}H NMR spectral data of **4** (Table 1) were more pronounced than those of **3** though again a germacranolide with an 8α-hydroxy-methacryloyloxy group had to be present as followed from several characteristic signals. However, one of the olefinic double bonds was replaced by an epoxide group as could be deduced from the double doublet at δ 2.92 and the upfield shift of the H-14 signals. This was supported by the chemical shift of H-5 which could be assigned by spin decoupling. The observed couplings indicated the proposed stereochemistry.

The ^{1}H NMR spectrum of **5** (Table 1) differed from that of **4** by the presence of a lowfield H-1 signal and an upfield shifted H-5 signal. Thus the lactone **5** is probably the isomeric 4,5-epoxide. Again the configurations followed from the observed couplings.

The chemistry of this *Jurinea* species again shows that 14,15-oxygenated germacranolides are characteristic for this genus. These lactones are also present in *Dicoma* species which may indicate the relationship of the tribes *Cynareae* and *Mutisieae*.

EXPERIMENTAL

The plant material was collected in summer 1980, 60 km north of Tehran, Iran, and identified by Dr E. Massumi (Tehran, Iran). The air-dried aerial parts (300 g, voucher, deposited in the Herbarium of the Dept of Botany, Shahid Beheshty University, Tehran, Iran) were cut into small pieces and extracted at room temp. with MeOH–Et_2O–petrol (1:1:1) for 24 hr. After evapn under red. pressure the residue was treated with MeOH to remove long chain saturated hydrocarbons. The extract was separated by CC (silica gel). The polar fractions (1: Et_2O and 2: Et_2O–MeOH, 4:1) were further separated by TLC (silica gel, PF 254). Repeated TLC of fraction 1 (Et_2O) gave 30 mg **1**, 10 mg **6**, 45 mg **3** (R_f 0.64), 5 mg **4** (R_f 0.50) and 5 mg **5** (R_f 0.45). Repeated TLC of fraction 2 (Et_2O–MeOH, 9:1) afforded 50 mg **2**. Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.



	1	**2**	**3**	**4**	**5**
R^1	H	H	Ac	Ac	Ac
R^2	H	OH	OH	OH	OH
				1β,10α epoxide	4α,5β epoxide

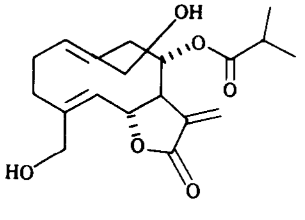


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Table 1. ^{1}H NMR spectral data of compounds **3**–**5** (400 MHz, $CDCl_3$)

H	3	4	5
1	5.28 *br dd*	2.92 *dd*	5.62 *dd*
2	2.39 *dddd*	2α 1.52 *dddd*	2.38 *m*
2°	2.35 *dddd*	2β 2.24 *dddd*	
3α	2.63 *ddd*	2.55 *ddd*	1.38 *m*
3β	2.15 *ddd*	2.41 *ddd*	2.11 *m*
5	4.93 *br d*	5.39 *br d*	2.86 *d*
6	5.18 *ddd*	5.20 *dd*	4.75 *dd*
7	3.11 *dddd*	3.08 *dddd*	3.28 *dddd*
8	5.19 *ddd*	5.21 *ddd*	4.90 *ddd*
9α	2.51 *dd*	1.56 *dd*	2.41 *dd*
9β	2.78 *br d*	2.76 *br d*	2.61 *br d*
13	6.29 *d*	6.29 *d*	6.38 *d*
13′	5.73 *d*	5.74 *d*	5.75 *d*
14	4.60 *br d*	4.49 *d*	4.77 *br d*
14′	4.47 *br d*	3.78 *d*	4.65 *br d*
15	4.24 *br d*	4.44 *d*	4.37 *br d*
15′	4.16 *br d*	4.33 *d*	3.82 *br d*
OCOR			
	6.26 *br* s	6.26 *br s*	6.26 *br s*
	5.92 *br s*	OR 5.97 *br s*	OR 5.94 *br s*
	4.33 *br s*	4.35 *br s*	4.30 *br s*
OAc	2.08 *s*	2.15 *s*	2.09 *s*

J[Hz]: Compound **3**: 1,2α = 6.5; 1,2β = 11; 2α,3α = 6.5; 2α,3β = 3; 2β,3α = 12; 3α,2β = 12; 5,6 = 10; 6,7 = 8; 7,8 = 9; 7,13 = 7,13′ = 3; 8,9α = 10.5; 8,9β = 12; 9α,9β = 13; compound **4**: 1,2α = 2.5; 1,2β = 12; compound **5**: 5,6 = 9.

4′-Hydroxypectorolide-14-O-*acetate* (**3**). Colourless oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3590 (OH), 1760 (γ-lactone), 1720 (ester); MS *m/z* (rel. int.): 406 $[M]^+$ (0.2) ($C_{21}H_{26}O_8$), 346.141 $[M - HOAc]^+$ (4) (calcd for $C_{19}H_{22}O_6$: 346.141), 244 $[346 - R - COOH]^+$ (22), 226 $[244 - H_2O]^+$ (24), 85 (100); $[\alpha]_D^{24}$ × 110 ($CHCl_3$; *c* 0.8).

1β,10α-*Epoxy-4′-hydroxypectorolide*-14-O-*acetate* (**4**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590 (OH), 1760 (γ-lactone), 1725 (ester); MS *m/z* (rel. int.): 422 $[M]^+$ (0.1) ($C_{21}H_{26}O_9$), 349 $[M - AcOCH_2]^+$ (0.5), 247 $[349 - RCOOH]^+$ (8), 69 (100); $[\alpha]_D^{24°}$ +34 ($CHCl_3$; *c* 0.25).

4α,5β-*Epoxy-4′-hydroxypectorolide*-14-O-*acetate* (**5**). Colourless oil; IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3590 (OH), 1760 (γ-lactone), 1720 (ester); MS *m/z* (rel. int.): 422 $[M]^+$ (3) ($C_{21}H_{26}O_9$), 391 $[M - CH_2OH]^+$ (25), 279 $[391 - RCOOH - ketene]^+$ (65), 197 (100); $[\alpha]_D^{24°}$ +28 ($CHCl_3$; *c* 0.1).

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