

SHIRAZOLIDE AND 14 α -O DIHYDROSHIRAZOLIDE TWO NEW ELEMANOLIDES FROM JURINEA LEPTOLOBA

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Abstract

The less polar fractions of the extract of the aerial parts of *Jurinea leptoloba* afforded two new elemanolides. The structures were elucidated by high field NMR techniques.

Introduction

From the large Eurasian genus *Jurinea* (Compositae, tribe *Cynareae*, subtribe *Carduinae*) with about 250 species so far only 14 have been studied chemically.

Most widespread are *sesquiterpene* lactones similar to those from the genus *centaurea*.

However, derivatives of the germacranolides albicolide are not common in the latter genus but are widespread in *Jurinea* [1-7]. We have now studied a further species from Iran, *J. leptoloba* DC.

Results and Discussion

The less polar fractions of the extract of the aerial parts gave by column chromatography and HPLC the elemanolides **3** and **4**. The ^1H NMR spectrum of **3** (Table 1) indicated the presence of an elemanolide by the characteristic signals of protons of two vinylic groups. Spin decouplings led to the proposed substitution pattern. The stereochemistry followed in part from the observed couplings. NOED gave effects between H-5 H-7 (6%) and H-1 (3%), between OH, H-14 (10%), H-6 (22%) H-15 (2%) and H-8 (3%), between H-15 and H-6 (4%), between H-6 and H-8 (6%), between H-1, H-5 (2%) and H-14 (2%) as well as between H-14, H-1 (5%), OH (5%) and H-9 (5%).

Obviously, lactone **2** was formed by cope reaction of germacranolide **1** affording the elemanolide **3** which

Keywords: - *Jurinea leptoloba*, *Sesquiterpene* lactones, Elemanolides

when further oxidized leads to the dilactone **4**, also present in the plant. Its structure followed from the ^1H -NMR data (Table 1) which in part was similar to that of **3**.

However, due to the presence of a carbonyl group at C-14 several signals were shifted. The shift of H-6 is especially, remarkable. Obviously due to the shielding effect of the C-14 carbonyl the shifts of H-6 by 1.14 ppm in the compounds **3** and **4**.

A deshielding effect is responsible for the down field shift of H-9 β .

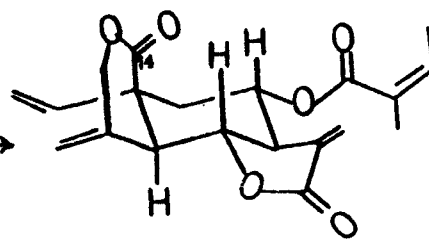
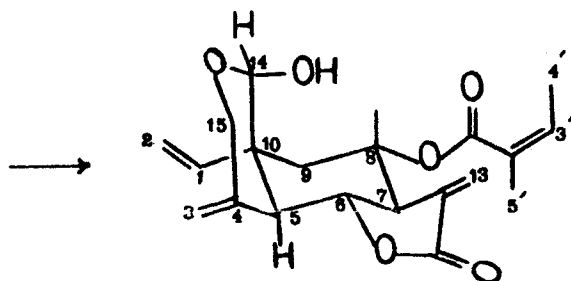
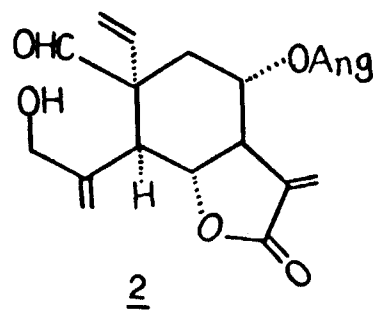
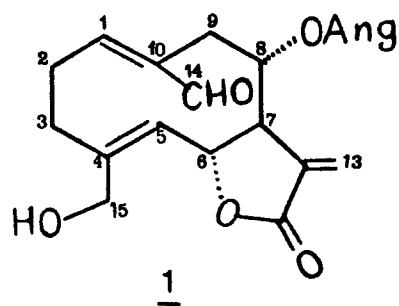
The observed NOE'S further supported the proposed stereochemistry with a *cis* oxadecaline system.

We have named the dilactone **4** shirazolide.

Experimental Section

The air-dried aerial parts (500g, collected in Aug. 1989, in Iran, voucher number 324 R, deposited in the Herbarium of the Department of Botany, Shahid Beheshti University, Tehran, I. R. Iran) were extracted with Et₂O-MeOH-Petrol (1:1:1) The extract obtained was defatted with MeOH and first separated by column chromatography (silica gel).

The fractions obtained with Et₂O-Petrol (1:3) were separated by prep. TLC (silica gel, HF 254) affording a mixture which was further separated by HPLC (RP 8, MeOH-H₂O) 7.5 : 2.5, Ca 100 bar, flow rate,



14- α -O-Dihydroshirazolide

Shirazolide

Table 1. ^1H NMR spectral data of compounds 3 and 4
(400 MHz, CDCl_3 , δ - values)

H	3		4	
1	5.97	dd	5.81	dd
2	5.16	d	5.34	d
2'	5.14	d	5.31	d
3	5.17	brs	5.36	brs
3'	5.07	brs	5.28	brs
5	2.61	brs	3.02	dd
6	4.85	dd	3.71	dd
7	2.80	dddd	2.91	dddd
8	5.64	ddd	5.27	ddd
9	2.40	dd	3.03	dd
9'	1.50	dd	2.46	dd
13	6.15	d	6.18	d
13'	5.59	d	5.61	d
14	4.95	d	---	-
15	4.63	brd	4.98	dt
15'	3.94	d	4.87	dt
-O Ang				
3'	6.19	qq	6.17	qq
4'	2.04	dq	2.03	dq
5'	1.91	dq	1.90	dq
OH	3.02	d		

$J[\text{Hz}]$: 1,2=10; 1,2'=17; 3,15=2; 5,6=6,7=7, 8=11;
8,9- 4.5; 8,9'=10; 9,9'=13; 3',4'=7; 3',5'=4',5'=1.5
compound 3:14,OH = 3.5

3ml/min to give 8 mg 4 (R_t 7.5 min) and 12 mg (3) (R_t 8.5 min).

14 α -O-Dihydroshirazolide (3). IR CHCl_3 , Cm^{-1} :
max
3580 (OH), 1770 (γ -lactone), 1720 (ester); MS m/z
(rel. int.): 360[M]⁺ (o.1) ($\text{C}_{20}\text{H}_{24}\text{O}_6$), 260.105

[M- CO_2H]⁺ (4) (calc for $\text{C}_{15}\text{H}_{16}\text{O}_4$: 260.105),
214 [260-HCOOH]⁺ (50), 83 [C₄H₇CO]⁺ (100);
[α]_D^{24°} + 48 (CHCl_3 ; C o.3).

Shirazolide (4). IR CHCl_3 , Cm^{-1} : 1770 (γ -
max
lactone) 1725 (ester), 1710 (C=O); Ms m/z (rel. int.):
358. 141 [M]⁺ (6) (calc. for $\text{C}_{20}\text{H}_{22}\text{O}_6$: 358.141), 258
[M- CO_2H]⁺ (5), 214 [258-CO₂]⁺ (6), 83
[C₄H₇CO]⁺ (100); [α]_D^{24°} + 80 (CHCl_3 ; C o.1)

Acknowledgements

A. Rustaiyan thanks: Professor F. Bohlmann, from the Technical University of Berlin for ^1H NMR and mass spectra, and Eng. A. Mozaffarian, from the Research Institute of Forests and Rangelands, Tehran, for the collection and identification of plant material.

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