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DIHYDRORIDENTIN FROM *Artemisia pontica* AND ITS STEREOCHEMISTRY

N. A. Talzhanov,[1] R. M. Mukanov,[1] V. A. Raldugin,[2]
M. M. Shakirov,[2] G. A. Atazhanova,[1]
and S. M. Adekenov[1]

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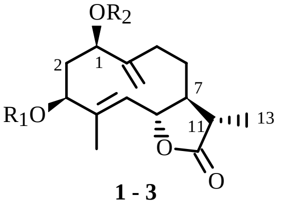
The germacranolide 11,13-dihydroridentin, for which the previously unknown S-configuration of the asymmetric center on C-11 was established, was isolated for the first time from Artemisia pontica *L.*

Key words: *Artemisia pontica*, sesquiterpene lactones, 11,13-dihydroridentin, NMR spectra.

It is well known that the qualitative and quantitative compositions of a natural mixture of sesquiterpene lactones in a plant can vary depending on the vegetation period and habitat. A prime example of this is *Artemisia pontica* L. Thus, one of its Bulgarian populations contains lactones with a new (rotundane) C skeleton [1]; another, only eudesmanolides [2]. Because this *Artemisia* species has a rather wide natural range [3], it seemed interesting to examine its population from a different region.

We found only one lactone in the aerial part of *A. pontica*. It differed from all lactones isolated previously from this species [1, 2]. According to high-resolution mass spectrometry, it had empirical formula $C_{15}H_{22}O_4$. The lactone contained two of the O atoms (IR spectrum: 1775 cm^{-1}); two secondary OH groups, the two others (PMR spectrum of a DMSO-d_6 solution showed two CH–OH systems as doublets at 4.00 and 4.78 ppm with SSCC 5.5 and 4.0 Hz, respectively). Furthermore, the ^{13}C NMR spectrum is consistent with the presence of two C=C double bonds. Thus, the studied lactone, which gives a liquid diacetate, is monocyclic. The three double bonds in it are isolated from each other (UV spectrum lacks maxima at 205-400 nm). The structure **1** was deduced based on PMR and ^{13}C NMR spectra (Table 1), which were interpreted using 2D ^{1}H—^{1}H (COSY) and ^{13}C—^{1}H (COSY and COLOC) spectra. The previously reported 11,13-dihydroridentin [4], the reaction product of the natural lactone ridentin (**2**) with $NaBH_4$ in MeOH, has the same structure but an unknown stereochemistry at C-11. It was proposed in the earlier work [4] that natural 11,13-dihydroridentin was a minor component to ridentin in *A. tridentate* although these same authors did not confirm this later [5].

The configuration at C-7 in ridentin was proposed previously using CD data [5]. The stereochemistry of the asymmetric center at C-11 of its dihydro derivative **1** was established in the present work as *S* based on SSCC $J_{7,11}$ = 12 Hz in the PMR spectrum. This indicates unambiguously the H-7 and H-11 are located *trans* to each other [6].



1 - 3

1: $R_1 = R_2 = H$
2: $R_1 = R_2 = H, \Delta^{11(13)}$
3: $R_1 = Ac, R_2 = H, \Delta^{11(13)}$

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1) Institute of Phytochemistry, Ministry of Education and Science, Republic of Kazakhstan, ul. Gazalieva, 4, 470032, Karaganda, Kazakhstan, fax (3212) 43 37 73, e-mail: arglabin@phyto.kz; 2) N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, 630090, Novosibirsk, ul. Akad. Lavrent′eva, 9, fax (3832) 34 47 52, e-mail: raldugin@nioch.nsc.ru. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 341-342, July-August, 2005. Original article submitted May 31, 2005.

TABLE 1. Chemical Shifts and Multiplicity of Signals for **1** in ^{13}C NMR and PMR Spectra (δ, ppm, 0 = TMS, DMSO-d_6, J/Hz)

C atom	δ (C)	δ (H)
1	73.85 d	3.71 m
2	40.77 t	1.80 m (H-2a); 1.93 m (H-2b)
3	73.52 d	4.02 (ddd, J = 11.0; 4.0; 4.0)
4	146.38 s	-
5	120.80 d	5.19 (br.d, J = 10.0)
6	79.28 d	4.51 (t, J = 10.0)
7	51.58 d	1.80 m
8	26.79 t	1.48 m (H-8a); 1.75 m (H-8b)
9	31.60 t	1.93 m (H-9a); 2.38 m (H-9b)
10	150.45 s	-
11	40.78 d	2.33 (dq, J = 12.0; 7.0)
12	178.16 s	-
13	12.23 q	1.09 (3H, d, J = 7.0)
14	109.41 t	4.76 (1H, br.s, H-14a); 5.02 (1H, br.s, H-14b)
15	11.29 q	1.58 (3H, br.s)
O$\underline{H}$ (1)	-	4.00 (d, J = 5.5)
O$\underline{H}$ (3)	-	4.78 (d, J = 4.0)

The germacranolide subchrysin **3** has a similar structure and was isolated from *A. subchrysolepis* Filat. [7].

EXPERIMENTAL

Melting points were determined on a Boetius instrument. IR spectra were recorded on an Avatar 360 instrument (Thermo Nicolet) in KBr disks. NMR spectra were recorded on a Bruker DRX-500 (working frequency 500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C) in DMSO-d_6 solvent with TMS internal standard on the δ-scale. Column chromatography was performed over SiO_2 (KSK, 1:20). TLC used Silufol plates with development by aqueous $KMnO_4$ solution (1%).

Starting material was the aerial part of *A. pontica* L. collected in mid-July 2003 in the mountains of Kent-Karkaralin region of Karaganda region in the Republic of Kazakhstan. It was dried in air without exposure to direct sunlight and ground to particle size 2-5 mm.

Isolation of 1. Raw material (1.0 kg) was extracted by soaking in $CHCl_3$ (8 L) at 70°C. The extraction was repeated three times (3×8 L). The combined extracts were filtered. Solvent was removed in vacuo. The resulting dry extract (103 g) was treated with EtOH:H_2O (0.9 L, 2:1 by vol), thoroughly mixed, and filtered. The filtrate was extracted with $CHCl_3$ (3×0.2 L). The extracts were combined and evaporated to dryness to afford total compounds (40 g), chromatography of which over SiO_2 (eluent $CHCl_3$ with 0-50% EtOH) isolated **1** (0.4 g, 0.04%), mp 192-194°C (EtOAc), $[\alpha]_D^{18}$ +314° (*c* 0.05, EtOH), lit. [5] mp 193-194°C.

IR spectrum (KBr, ν, cm^{-1}): 3359, 1775, 1732, 1454, 1384, 1209, 1151, 1057, 992, 959, 750, 580, 495.

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