Chemistry of Natural Compounds, Vol. 35, No. 2, 1999

LESTERONE, A NEW PHYTOECDYSTEROID FROM THE SEEDS OF *Leuzea carthamoides*

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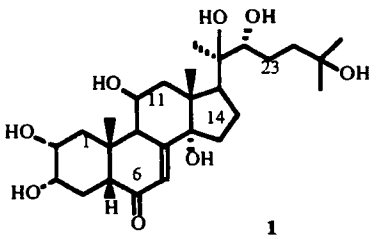
UDK 547.926

A new phytoecdysteroid, lesterone has been isolated from the seeds of Leuzea *(Rhaponticum)* carthamoides. *It has been unambiguously identified as 5b-cholest-7-en-2a,3a,11b,14a,20R,22R,25-heptahyrdoxy-6-one with the aid of NMR and mass spectroscopies.*

A systematic study of *Leuzea carthamoides* D.C. [syn. Rhaponticum carthamoides (Willd) Iljin] [1-4] has led to the isolation of a new phytoecdysteroid, which we named lesterone (1).

In the high mass region of the EI-mass spectrum of ecdysteroid 1 peaks of the dehydrated ions with *m/z* 460 $[M-2H_2O]^+$, 442 $[M-3H_2O]^+$, 424 $[M-4H_2O]^+$, 409 $[M-4H_2O-Me]^+$, 406 $[M-5H_2O-Me]^+$, 388 $[M-6H_2O]^+$, and 373 $[M-6H_2O]^+$, are observed. On cleavage of the C-20-C-22 bond, ions with *m/z* 379 $[M-117]^+$, 361 $[M-117-H_2O]^+$, 343 $[M-117-2H_2O]^+$, and 325 $[M-117-3H_2O]^+$, are formed. The ions with *m/z* 316 and 301 correspond to break of the C-17-C-20 bond. The mass spectral fragmentation of the side chain is shown by ions with m/z 99 $[C_6H_{11}O]^+$ and 81 $[C_8H_9O]^+$. These data are analogous to the mass spectral fragmentation of turkesterone [5] and rapisterone D [3]. Data of the mass-spectrum of ecdysteroid **1** indicate the presence of four hydroxyl groups in the steroid part of the molecule and three hydroxyl groups in the side chain.

In the ^1H NMR spectrum of lesterone at 4.25 ppm as the doublet of triplets with constants J=12 and 4 Hz is a signal of an axial proton, geminal to a secondary hydroxyl group. A signal of an equatorial proton, geminal to a secondary hydroxyl group, is observed at 4.14 ppm as a quartet with constant J=3.5 Hz. These fact are analogous to the data of rapisterone D; therefore the two hydroxyl groups are located at C-3 and C-2 and possess the α-orientation in ecdysteroid **1**. A signal of unknown proton, geminal to a secondary hydroxyl group is observed in contrast to rapisterone D in the NMR spectrum of lesterone at 4.04 ppm as the doublet of quartets. The signal of C-18 and C-19 the methyl groups are screened and occur at 1.01 ppm and 1.05 ppm, respectively. The data are evidence of an unknown hydroxyl group, probably present in the molecule steroid part in C-ring.



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Its position in the C-ring was considered to be C-12 and C-11 carbon atoms. In comparison with rapisterone D, the signal of the proton at C-17 was observed to change and therefore the unknown proton and hydroxyl group are assumed to be preferably located at C-11. A comparison of signals of the angular methyl groups at C-18 and C-19 and of the proton at C-9 in the 1H NMR spectra (Table 1) of turkesterone and ecdysteroid 1 has shown the β- orientation of hydroxyl group at C-11.

Institute of Petrochemistry and Catalysis, Academy of Sciences of the Bashkortostan Republic, prospekt Oktyabrya 141, Ufa 450075, Russia. Published in Khimiya Prirodnykh Soedinenii, No. 2 pp. 205-206, March-April, 1999. Original article submitted December 21, 1998.

 0009-3130/99/3502-0182$22.00

TABLE 1. Chemical Shifts of ^{1}H NMR Spectra of Turkesterone and Lesterone (δ, ppm)

Protons	Turkesterone	Lesterone
2-H	4.45	4.14
3-H	4.06	4.25
7-H	6.12	6.11
9-H	3.75	3.53
11-H	4.45	4.04
17-H	-	2.81
18-Me	1.12	1.01
19-Me	1.18	1.05
21-Me	1.45	1.44
26-Me	1.24	1.24
27-Me	1.24	1.24

The chemical shifts values of C-21, C-26 and C-27 methyl groups of turkesterone and ecdysteroid 1 combined with the data described for the side-chain mass spectral decay have revealed the identity of the side-chains of there substances.

Thus, the new ecdysteroid lesterone is 5β-cholest-7-en-2α,3α,11β,14α,20R,22R,25-heptahydroxy-6-one.

EXPERIMENTAL

The mass spectrum was recorded on an MKh-1310 instrument supplied with a system of direct introduction of substances into the ion source at an ionizing current of 60 eV, collector current of 50 μA, and temperature of the evaporating ampule and ionization chamber 100-160°C.

Extraction. The air dried seeds of *Leuzea carthamoides* (1.2 kg) were milled and then extracted with MeOH. The combined extracts were evaporated under vacuum at 40-45°C to a volume of 250 ml and this was then diluted with 375 ml H_2O. After extraction of the hydrophobic compounds by partitioning against hexane, the phytoecdysteroids were extracted with n-BuOH. The solvent was removed under vacuum to give 30.4 g of crude material. After isolation of the known ecdysteroids, the fractions (125 mg) containing lesterone were chromatographed on a column with SiO_2, eluted with $CHCl_3$-MeOH (15:1). The yield of lesterone was 8 mg (0.00066 %).

Lesterone 1. $C_{27}H_{44}O_8$, amorphous. IR(ν_{max}^{KBr}, cm^{-1}): 3360-3470 (OH), 1650 (Δ^7 -6-keto group).^{1}H NMR spectrum (C_5D_5N, 400 MHz, δ ppm): 1.01 (CH_3-18, s); 1.05 (CH_3-19, s); 1.24 (2 CH_3-26/27); 1.44 (CH_3-21, s); 3.72 (H-22, dd); 4.14 (H-2, q, J=3.5 Hz); 4.25 (H- 3, dt, J=12 and 4 Hz); 3.53 (H-9, m); 4.04 (H-11, dq); 2.81 (H-17, t); 6.11 (H-7, broad singlet).

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