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ISOLATION AND CRYSTAL STRUCTURE OF TARAXASTERYL ACETATE FROM *Onopordum acanthium*

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Taraxasteryl acetate was isolated for the first time from Scotch thistle Onopordum acanthium. *Its crystal and molecular structure was found using x-ray structure analysis.*

Key words: *Onopordum acanthium,* taraxasteryl acetate, x-ray structure analysis.

Scotch thistle (*Onopordum acanthium* L.) is a biennial herbaceous plant of the Asteraceae family that is used in medical practice as a bactericide, cardiotonic, hemostatic, and antihypotensive agent [1-3].

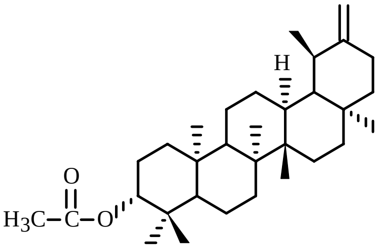
The lactones arctiopicrin and onopordopicrin were isolated from its leaves [1]; alcohols lupeol and amyrin as type of their acetates, from the seeds [4].

Our goal was to isolate and establish the structure of new biologically active terpenoid compounds from *O. acanthium* L.

The aerial part of the plant was investigated for the presence of biologically active compounds. Extraction by $CHCl_3$ and column chromatography over silica gel using ethylacetate:hexane (1:15) afforded a crystalline compound. IR and ^{13}C NMR spectra were consistent with functional groups and spectral properties of taraxasteryl acetate **1** [5, 6]. The index of refraction (+102.5°, $CHCl_3$) was close to the reported value (+100.5°, $CHCl_3$) [7]. However, the melting point of **1** (232-234°C) was substantially different from that reported in the literature (256-257°C).

In order to refine the physicochemical properties and determine unambiguously the structure of the compound isolated by us, we performed a single-crystal x-ray structure analysis. Table 1 lists the principal geometric parameters of **1**.

It was found that the molecule of **1** has the structure taraxasteryl acetate, the geometry of the triterpene fragment of which is practically the same as that of taraxasterol [8].



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Four of the six-membered rings have the chair conformation and are *trans*-fused to each other (Fig. 1). The acetate on C3 is equatorial. The six-membered ring with sp^2-hybridized C20 has a slightly asymmetrical (twisted) boat conformation. The fragment C18C19C21C22 is planar within 0.092(5) Å. The deviations of C17 and C20 from this plane are 0.652(4) and 0.526(5) Å. The C20 methylene is pseudoaxial and is situated in the plane of C20 bonds.

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TABLE 1. Atomic Coordinates of **1** and Equivalent Isotropic Temperature Factors of Nonhydrogen Atoms $B = 4/3\ \Sigma\Sigma(a_ia_j)B(i,j)(\text{Å}^2)$, i = 1, 2, 3, j = 1, 2, 3

Atom	X	Y	Z	B
O1	0.1575 (3)	1.13352 (8)	0.3218 (3)	4.13 (6)
O2	-0.0591 (4)	1.1201 (1)	0.4448 (3)	6.09 (8)
C1	0.1830 (5)	1.0177 (1)	0.2495 (4)	3.49 (9)
C2	0.1245 (5)	1.0634 (1)	0.2428 (4)	4.2 (1)
C3	0.2166 (5)	1.0900 (1)	0.3362 (3)	3.15 (8)
C4	0.4101 (4)	1.0900 (1)	0.3212 (4)	3.19 (8)
C5	0.4658 (4)	1.0424 (1)	0.3205 (3)	2.92 (8)
C6	0.6582 (5)	1.0366 (1)	0.3138 (4)	4.3 (1)
C7	0.7031 (5)	0.9918 (1)	0.3522 (4)	4.0 (1)
C8	0.6172 (4)	0.9569 (1)	0.2772 (3)	2.76 (8)
C9	0.4255 (4)	0.9674 (1)	0.2699 (3)	2.70 (8)
C10	0.3726 (4)	1.0124 (1)	0.2312 (3)	3.17 (9)
C11	0.3343 (5)	0.9323 (1)	0.1991 (4)	4.0 (1)
C12	0.3579 (5)	0.8890 (1)	0.2539 (4)	4.1 (1)
C13	0.5476 (5)	0.8780 (1)	0.2670 (4)	3.21 (9)
C14	0.6430 (4)	0.9121 (1)	0.3395 (3)	3.20 (8)
C15	0.8337 (5)	0.9004 (1)	0.3475 (4)	3.9 (1)
C16	0.8592 (5)	0.8560 (1)	0.3924 (4)	4.6 (1)
C17	0.7740 (5)	0.8229 (1)	0.3150 (4)	4.4 (1)
C18	0.5842 (5)	0.8329 (1)	0.3130 (4)	3.9 (1)
C19	0.4751 (6)	0.7991 (1)	0.2416 (5)	5.6 (1)
C20	0.5719 (5)	0.7580 (1)	0.2292 (5)	5.7 (1)
C21	0.6753 (6)	0.7455 (1)	0.3352 (5)	6.7 (1)
C22	0.7982 (6)	0.7792 (1)	0.3753 (5)	5.8 (1)
C23	0.4841 (5)	1.1111 (1)	0.4316 (4)	4.2 (1)
C24	0.4708 (6)	1.1152 (1)	0.2087 (4)	4.8 (1)
C25	0.4116 (6)	1.0221 (1)	0.0979 (4)	4.2 (1)
C26	0.7072 (5)	0.9571 (1)	0.1548 (3)	3.70 (9)
C27	0.5746 (6)	0.9136 (1)	0.4680 (4)	4.7 (1)
C28	0.8544 (5)	0.8222 (1)	0.1899 (4)	5.2 (1)
C29	0.3099 (7)	0.7889 (2)	0.3081 (7)	9.5 (2)
C30	0.5558 (8)	0.7346 (2)	0.1334 (7)	9.3 (2)
C31	0.0139 (6)	1.1429 (1)	0.3799 (4)	5.1 (1)
C32	-0.0457 (7)	1.1861 (2)	0.3461 (7)	8.8 (2)

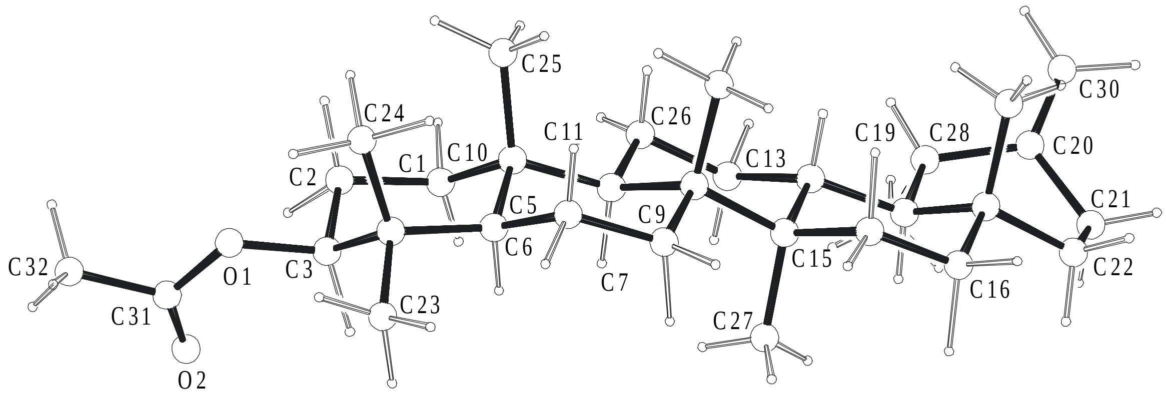

Fig. 1. Geometry of **1** in the crystal.

Thus, the C20=C30 double bond experiences no steric hindrance and is not twisted. As a result, the C=C bond length of 1.316(9) Å is normal for double bonds. Since **1** has no free hydroxyls, the molecular packing in the crystal is determined by ordinary van-der-Waals interactions.

EXPERIMENTAL

We collected *O. acanthium* L. in Bashkortostan Republic 100 km to the west of Ufa. It was identified taxonomically based on the herbarium collection of the Institute of Biology of Ufa Scientific Center, RAS.

Ground air-dried raw material (flower torus) collected during the second-half of flowering was exhaustively extracted with $CHCl_3$. The total products were chromatographed over a column of KSK silica gel at a 1:50 product:silica-gel ratio.

The process was monitored by TLC using SiO_2 plates (Silufol) and crystalline I_2 developer.

IR spectra were recorded on a Specord 75-IR spectrometer using mineral oil suspensions; PMR and ^{13}C NMR, on a Bruker AMX-300 (working frequency 75 MHz for ^{13}C, $CDCl_3$ solvent). The ^{13}C spectra were edited using the standard JMOD regime.

The rotation angle was measured on a Perkin—Elmer 141 polarimeter. The melting point was determined on a miniature Boetius heating stage.

The x-ray structure analysis of single crystals of **1** was performed at the Division of X-ray Structure Research of the RFBR User Center (UC SAC, RFBR grant No. 00-03-40133) in the laboratory of diffraction method research at Arbuzov IOPC, KSC RAS. The experiment was carried out on a CAD-4 (Nonius B.V.) automated x-ray diffractometer.

Crystals of **1**, $C_{32}H_{52}O_2$, are orthorhombic, at 20°C $a = 7.901(6)$, $b = 31.83(2)$, $c = 11.242(6)$ Å, $V = 2827(3)$ Å^3, $d_{calc} = 1.10$ g/cm^3, $Z = 4$, space group $P2_12_12_1$. Cell constants and intensities of 5731 reflections, 3139 of which had $I \geq 3\sigma$, were measured at 20°C (diffractometer, graphite monochromator, λ Cu Kα, $\omega/2\theta$ scanning, $\theta \leq 72°$). Intensities of three standard reflections did not decrease during the experiment. Absorption corrections were not applied ($\mu = 4.7$ cm^{-1}).

The structure was solved by direct methods using the SIR program [9] and refined initially by isotropic and then anisotropic approximations. H atoms were found in difference electron-density syntheses. Their contributions to the structure factors were calculated using fixed positional and isotropic temperature parameters. The absolute configuration of the molecule was set based on the known configuration of taraxasterol. The final agreement factors were $R = 0.057$ and $R_w = 0.061$ for 2487 independent reflections with $F^2 \geq 3\sigma$. Calculations were performed using the MOLEN program set [10]. Intermolecular contacts were analyzed and drawings were made using the PLATON program [11].

Table 1 gives coordinates of nonhydrogen atoms. The cell constants, atomic coordinates, and bond lengths and angles were deposited in the Cambridge Crystallographic Database (reference No. CCDC238753. The data can be obtained for free upon request to www.ccdc.cam.ac.uk/data_request/cif; by e-mail to data_request@ccdc.cam.ac.uk; or to the address: The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or from the authors).

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REFERENCES

1. *Plant Resources of the USSR. Flowering Plants, Their Chemical Composition and Use. Asteraceae Family* [in Russian], Nauka, St. Petersburg (1993).
2. *Atlas of Medicinal Plants of the USSR* [in Russian], Moscow (1962).
3. V. N. Kortikov and A. V. Kortikov, *Secrets of Healing Herbs*, in two volumes [in Russian], Minsk (1995), Vol. 1.

4. N. T. Ulʹchenko, E. I. Gigienova, and U. A. Abdullaev, *Khim. Prir. Soedin.*, 612 (1979).
5. A. Patra, A. K. Mukhopadhyay, and A. K. Mitra, *Org. Magn. Reson.*, **17**, 166 (1981).
6. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, 2nd Ed., Methuen & Co., London (1958).
7. *Dictionary of Organic Compounds*, 5th Ed., New York, London, and Toronto (1982).
8. W. F. Reynolds, J. F. Sawyer, R. G. Enriquez, L. I. Escobar, M. A. Chaves, and J. N. Shoolery, *Can. J. Chem.*, **63**, 1048 (1985).
9. A. Altomare, G. Cascarano, C. Giacovazzo, and D. Viterbo, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, **47**, No. 4, 744 (1991).
10. L. H. Straver and A. J. Schierbeek, *MOLEN. Structure Determination System*, **1**, Program Description, B. V. Nonius, (1994).
11. A. L. Spek, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, **46**, No. 1, 34 (1990).