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X-RAY STRUCTURAL STUDY OF 3β -ACETOXY-(25R)- 5α -SPIROSTAN-12-ONE

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UDC 548.737:547.918.

An x-ray structural study has been made of a compound with the composition $C_{29}H_{44}O_5$. The bond lengths and valence angles are the usual ones for compounds of this type. All the six-membered rings (A, B, C, and F) have the chair conformation. The five-membered rings D and E have the forms of 14α - and 22α -envelopes, respectively. Rings A, B, C, and D are trans-linked, and D and E cis-linked.

Steroid glycosides are widespread in the vegetable kingdom and possess an extremely interesting spectrum of biological action: they inhibit the growth of malignant neoplasms [1], they exhibit fungicidal action on some pathogenic fungi [2]; they bind cholesterol in the form of insoluble complexes [3]; they possess antimicrobial activity [4]; and they are modifying agents of bilayer lipid membranes [5]. The results of a determination of the dependence of the antitumoral activity of steroid glycosides on their composition and structure have been given previously [1, 6].

In order to establish its molecular structure, an x-ray study has been made of 3β -acetoxy-(25R)- 5α -spirostan-12-one, with the composition $C_{29}H_{44}O_5$. The compound was obtained as the result of the hydrolysis of the steroid glycosides from century-plant agave [7]. After crystallization, the aglycone was acetylated and the product was obtained in the form of single crystals.

Figure 1 gives sketches of the molecule with the bond lengths and the valence and torsional angles. All the six-membered rings have the chair conformation. The greatest deviation from the ideal conformation is observed for ring C. The five-membered ring D forms a 14α -envelope, and E adopts the form of a 22α -envelope. The molecule as a whole is nonplanar. Rings A, B, C, and D are trans-linked, and D and E are cis-linked (Fig. 2). The mean plane of the six-membered ring F is approximately perpendicular to the plane of the neighboring five-membered ring E. This mutual orientation of these rings is determined by the tetrahedral configuration of the C(22) atom common to them. The angle between the planes of the C(20), C(22) and O(2) and the C(23), C(22), and O(3) fragments is 93.3° . The acetate group does not lie in the mean plane of the linked ring A-E. It makes an angle of 73° with the C(2)-C(3)-C(4) plane.

The interatomic distances and valences angles in the structure studied agree with the values observed in other compounds [8-13]. The C-C distances, except for the bonds of C(3) with the neighboring carbon atoms are close to the value for an ordinary $C(sp^3)-C(sp^3)$ bond. The C(12) atom is in a state of sp^2 hybridization, and the distance from it to the C(11) and C(13) atoms correspond to the standard value for bonds of the $C(sp^2)-C(sp^3)$ type. The C(3)-C(2) and C(3)-C(4) distances are shortened in comparison with the length of a corresponding ordinary bond. At the same time, the C(3)-O(1) bond is somewhat lengthened. Close values of the lengths of the bonds of the C(3) atom with the neighboring C and O atoms have been found in methyl 3β -acetoxy- 17α -methyl- 18 -nor- 5α -androstan- 17β -carboxylate [13]. The C(12)-O(4) interatomic distance is close to the value for a double bond. The distances between the intracyclic oxygen atoms O(2) and O(3) and the carbon atoms correspond to ordinary bonds.

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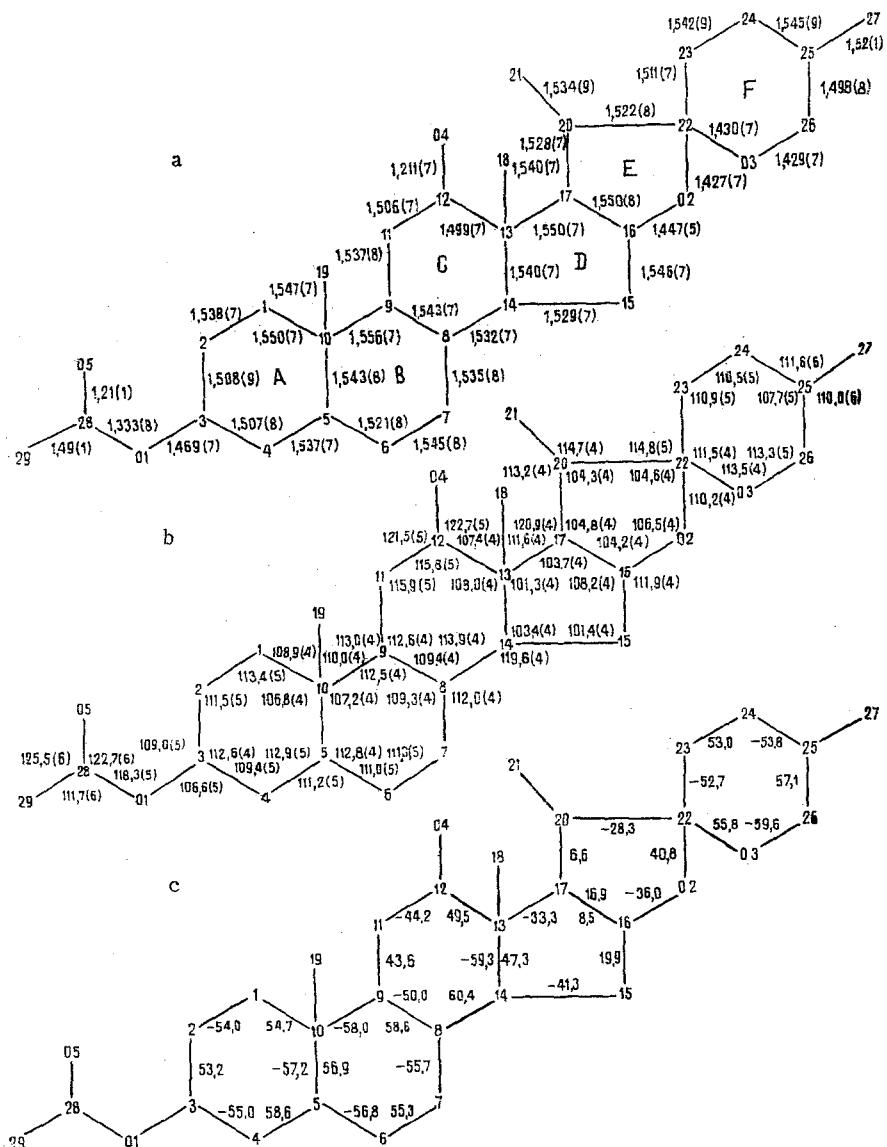


Fig. 1. Interatomic distances (\AA) (a), valence angles (b), and torsional angles in the ring (degrees) (c).

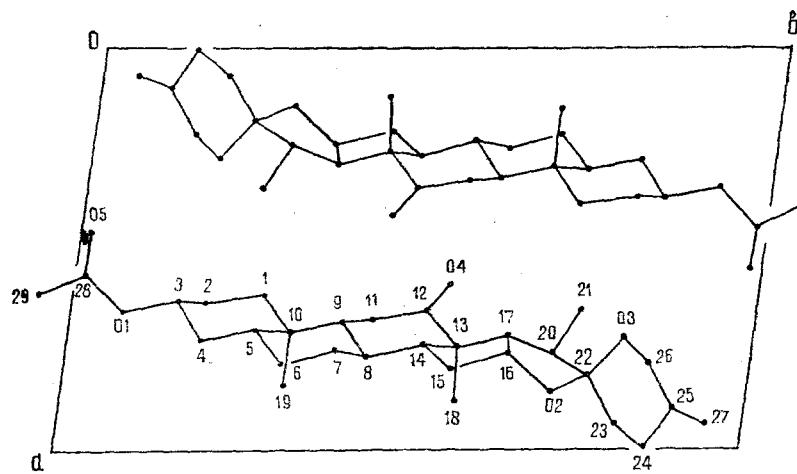


Fig. 2. Projection of the structure on the (001) plane.

TABLE 1. Coordinates of the Basis Atoms ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
O (1)	653 (4)	770 (2)	943	C (13)	7441 (4)	5641 (2)	787 (7)
O (2)	8530 (3)	7051 (2)	-1920 (6)	C (14)	7323 (4)	5172 (2)	-1022 (7)
O (3)	7261 (3)	7973 (2)	-43 (6)	C (15)	8019 (1)	5700 (3)	-2485 (8)
O (4)	5839 (4)	5533 (2)	3168 (7)	C (16)	7548 (5)	6444 (3)	-1968 (8)
O (5)	4469 (5)	0304 (3)	1312 (8)	C (17)	7046 (4)	6384 (3)	77 (7)
C (1)	6091 (5)	2734 (3)	2398 (8)	C (18)	8810 (5)	5756 (3)	1597 (8)
C (2)	6221 (6)	1902 (3)	2587 (9)	C (19)	8445 (5)	3190 (3)	1958 (8)
C (3)	6205 (6)	1526 (3)	698 (9)	C (20)	7591 (5)	7128 (3)	983 (8)
C (4)	7183 (5)	1925 (3)	-634 (9)	C (21)	6578 (7)	7492 (3)	2073 (10)
C (5)	6990 (5)	2747 (3)	-821 (8)	C (22)	8221 (5)	7593 (3)	-633 (8)
C (6)	7861 (5)	3142 (3)	-2326 (9)	C (23)	9402 (5)	8128 (3)	-103 (9)
C (7)	7553 (5)	3948 (3)	-2624 (8)	C (24)	9897 (6)	8623 (3)	-1784 (10)
C (8)	7692 (5)	4339 (2)	-779 (7)	C (25)	8809 (6)	9010 (3)	-2614 (10)
C (9)	6790 (4)	3967 (3)	693 (7)	C (26)	7703 (6)	8417 (3)	-3046 (9)
C (10)	7101 (4)	3165 (3)	1069 (8)	C (27)	9246 (9)	9459 (4)	-4359 (13)
C (11)	6705 (6)	4421 (3)	2498 (8)	C (28)	5580 (8)	212 (3)	1229 (11)
C (12)	6577 (5)	5232 (3)	2232 (8)	C (29)	6065 (8)	-516 (3)	1432 (12)

The packing of the molecule in the elementary cell is shown in Fig. 2. A van der Waals interaction exists between the molecules. There are no anomalously short contacts in the structure.

EXPERIMENTAL

Crystals acicular, colorless, well-faceted. Parameters of the monoclinic cell: $a = 10.537(5)$, $b = 18.109(9)$, $c = 7.132(4)$ Å, $\gamma = 98.28(4)^\circ$, $V = 1347(1)$ Å³, $\mu(\text{CuK}\alpha) = 5.43$ cm⁻¹, $d_{\text{calc}} = 1.16$ g/cm³, sp. gr. p2₁, Z = 2. The experimental results were obtained with a specimen having dimensions of $0.3 \times 0.25 \times 1.0$ mm on a DAR-UMB diffractometer with a graphite monochromator in CuK α radiation. The calculations were performed with 2023 independent reflections having intensities greater than 2σ .

The search for a model of the structure was carried out by the direct method using the programs of the "Rentgen-75" group and was begun in the automatic regime: from 346 $|E_{\text{hkl}}| \geq 1.28$, 1750 ternary derivatives were formed, and with $P_{\text{min}} = 0.95$ and $\sigma = 0.75$ a calculation was made of 512 phase variants for 8 ($3K + 5a_1$) reference reflections. In the six best variants with R estimates of 0.904-0.900 and R-Φ (E) of 0.45-0.48 that were analyzed it was impossible to isolate even a fragment of the molecule.

After this, the search for the structure was carried out in the "manual regime." The selection was made of 8 ($3K + 5a_1$) reference reflections and, using the previous set of ternary derivatives with $P_{\text{min}} = 0.96$ and $\sigma = 0.75$, 512 phase variants were calculated. The ten best variants were analyzed. However, none of them led to an interpretation of the structure.

It was decided to repeat the direct method with different indices. From 349 $|E_{\text{hkl}}| \geq 1.28$, 2000 ternary derivatives were formed. It was observed that in the first 50 variants of the preceding group the 020 reflection had the phase $\varphi_{\text{hkl}} = 180^\circ$ and it was therefore included in the new starting set of reflections as known. From eleven reference magnitudes with $P_{\text{min}} = 0.98$ and $\sigma = 0.75$ we calculated 1024 phase variants. In this way, two variants E₁ and E₂ with the same R estimate of 0.942 and R(E) factors of 0.448 and 0.358, respectively, were isolated. From the E₂ synthesis analyzed in detail, 24 of the nonhydrogen atoms were located. In the following electron density synthesis constructed from the whole group of reflections we found the missing atoms. The initial coordinates for refinement by the method of least squares were those of the basis atoms with R = 0.198.

The structure was refined by the method of least squares, taking the anisotropy of the thermal vibrations of the nonhydrogen atoms into account, to a factor R = 0.061. In the least-squares procedure, an experimental weighting scheme was used.

The CH, CH₂, and CH₃ groups were refined as rigid fragments with fixed C-H distances (1.08 Å) and H-C-H angles (109.5°). At the same time, the general isotropic temperature parameters for the hydrogen atoms in the CH₃ groups and for the other H atoms were refined separately. The coordinates of the atoms are given in Table 1.

R. P. Shibaeva participated in the performance of the investigation and in a discussion of the results.

SUMMARY

An x-ray structural study has been made of 3β -acetoxy- $25R$ - 5α -spirostan-1-one. The bond lengths and valence angles are the usual ones for compounds of this type. All the six-membered rings have the chair conformation and the five-membered rings the envelope form. Rings A, B, C, and D are trans-linked and D and E are cis-linked.

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ISOLATION OF FRUTITSIN FROM THE SEEDS OF *Amorpha fruticosa*

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UDC 547.918

The conditions for the isolation and purification of frutitsin by various solvents and mixture of solvents have been studied. The proposed method for the isolation of frutitsin permits the yield of the substance to be increased.

In the Institute of the Chemistry of Plant Substances of the Academy of Sciences of the Uzbek SSR, an original drug, frutitsin, isolated from the seeds of the plant *Amorpha fruticosa* L. [1, 2] has been created, and it is recommended as a sedative in vegetative neuroses, neuroses of the cardiovascular system, and paroxysmal tachycardia [3]. A method for its production has been developed [4] in which ethanol-dichloroethane (1:1, by volume) is used as the extractant for the plant raw material. Dichloroethane has a fairly high toxicity (the MAC for dichloroethane in a working area is 10 mg/m^3), and therefore in large-tonnage manufacturers it is desirable not to use this solvent in the industrial process.

We have developed a new method of obtained frutitsin using less toxic solvents. We used the seeds of *Amorpha fruticosa* of the 1977 and 1978 harvests grown in the *Gazety "Pravda" sovkhoz*, Tashkent province.

In order to select the solvents for the extraction and subsequent purification of frutitsin, in model experiments we selected an extractant and studied the process of extracting fru-

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from *Khimiya Prirodykh Soedinenii*, No. 5, pp. 619-621, September-October, 1982. Original article submitted November 18, 1981.