CRYSTAL AND MOLECULAR STRUCTURE OF 20S,24S-DIHYDROXYDAMMAR-25-EN-3-ONE

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UDC 548.737

The complete spatial structure of 20S,24S-dihydroxydammar-25-en-3-one – a triterpenoid isolated from the leaves of a Far-Eastern species of birch, Betula mandschurica – has been established. Intermolecular cooperative hydrogen bonds that are unusual for a triterpenoid system have been detected in crystals of 20S,24S-dihydroxydammar-25-en-3-one, with the participation of both hydroxy groups in one chain of bonds and an orientation of the associated molecules that is characteristic for a bimolecular layer.

In order to establish its spatial structure, a complete x-ray structural investigation has been made of triterpenoid (I) isolated from the Far-Eastern birch species Betula mandschurica [1]. It has been shown that the triterpenoid has the structure of 20S,24S-dihydroxydammar-25-en-3-one. In favor of such a structure are the geometric parameters of the molecule given in Tables 1 and 2 and also the shape of the molecule (Fig. 1) deduced from the coordinates of the atoms determined in the crystal (Table 3).

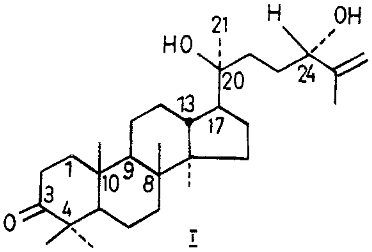
TABLE 1. Bond Lengths d (Å) and Valence Angles ω (degrees)

Bond	d	Angle	ω	Angle	ω
O3—C3	1,19(2)	C2—C1—C10	112,3(9)	C9—C11—C12	113.2(9)
O20—C20	1,43(1)	C1—C2—C3	112,0(9)	C11—C12—C13	109,0(9)
O24—C24	1,43(1)	O3—C3—C2	122(1)	C12—C13—C14	110,7(9)
C1—C2	1,55(2)	O3—C3—C4	123(1)	C12—C13—C17	118,8(9)
C1—C10	1,55(2)	C2—C3—C4	115,5(9)	C14—C13—C17	105,8(8)
C2—C3	1,49(2)	C3—C4—C5	106,7(9)	C8—C14—C13	110.4(8)
C3—C4	1,53(2)	C3—C4—C29	109,2(9)	C8—C14—C15	117,0(8)
C4—C5	1,60(2)	C3—C4—C30	109,4(9)	C8—C14—C28	117,5(8)
C4—C29	1,54(2)	C5—C4—C29	114,1(9)	C13—C14—C15	100,0(8)
C4—C30	1,52(2)	C5—C4—C30	109,3(9)	C13—C14—C28	110,6(8)
C5—C6	1,52(2)	C29—C4—C30	108,1(9)	C15—C14—C28	105,6(8)
C5—C10	1,55(1)	C4—C5—C6	113,8(9)	C14—C15—C16	104,3(8)
C6—C7	1,56(2)	C4—C5—C10	117,7(9)	C15—C16—C17	106,5(8)
C7—C8	1,55(1)	C6—C5—C10	111,3(9)	C13—C17—C16	103,4(8)
C8—C9	1,57(1)	C5—C6—C7	111,3(9)	C13—C17—C20	116,8(9)
C8—C14	1,57(1)	C6—C7—C8	113,1(9)	C16—C17—C20	112,8(8)
C8—C18	1,55(1)	C7—C8—C9	109,2(8)	C17—C20—O20	108.4(8)
C9—C10	1,60(1)	C7—C8—C14	109,9(8)	C17—C20—C21	111.8(9)
C9—C11	1,55(2)	C7—C8—C18	107,2(8)	C17—C20—C22	108,4(9)
C10—C19	1,56(1)	C9—C8—C14	108,0(8)	O20—C20—C21	104.5(8)
C11—C12	1,56(2)	C9—C8—C18	112,3(8)	O20—C20—C22	111,1(8)
C12—C13	1,53(2)	C14—C8—C18	110,1(8)	C21—C20—C22	112,6(9)
C13—C14	1,54(1)	C8—C9—C10	115,3(8)	C20—C22—C23	115,4(9)
C13—C17	1,54(1)	C8—C9—C11	110,6(8)	C22—C23—C24	110.2(9)
C14—C15	1,55(1)	C10—C9—C11	115,4(8)	C23—C24—O24	108.0(8)
C14—C28	1,56(1)	C1—C10—C5	107,6(8)	C23—C24—C25	113,0(9)
C15—C16	1,55(1)	C1—C10—C9	107,4(8)	O24—C24—C25	111,5(9)
C16—C17	1,57(1)	C1—C10—C19	107,2(8)	C24—C25—C26	116(1)
C17—C20	1,56(1)	C5—C10—C9	107,3(8)	C24—C25—C27	122(1)
C20—C21	1,53(1)	C5—C10—C19	114,6(8)	C26—C25—C27	122(1)
C20—C22	1,52(1)	C5—C10—C19	112,4(8)		
C22—C23	1,54(1)				
C23—C24	1,53(1)				
C24—C25	1,51(2)				
C25—C26	1,50(2)				
C25—C27	1,30(2)				

Pacific Ocean Institute of Bioorganic Chemistry, Far-Eastern Branch, Russian Academy of Sciences, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 667-672, September-October, 1991. Original article submitted December 10, 1990.

TABLE 2. Torsional Angles φ (degrees)

Angle	φ	Angle	φ
C10—C1—C2—C3	—56(1)	C18—C8—C14—C28	173,1 (9)
C2—C1—C10 C5	53(1)	C8—C9—C10—C1	—170,1 (8)
C2—C1—C10—C9	168,1(9)	C8—C9—C10—C5	—55 (1)
C2—C1—C10—C19	—71(1)	C8—C9—C10—C19	72 (1)
C1—C2—C3—O3	—122(1)	C11—C9—C10—C1	59 (1)
C1—C2—C3—C4	56(1)	C11—C9—C10—C5	174,5 (9)
O3—C3—C4—C5	128(1)	C11—C9—C10—C19	—59 (1)
O3—C3—C4—C29	—108(1)	C8—C9 C11—C12	55 (1)
O3—C3—C4—C30	10(1)	C10—C9—C11—C12	—171,5 (9)
C2—C3—C4—C5	—51(1)	C9—C11—C12—C13	—55 (1)
C2—C3—C4—C29	73(1)	C11—C12—C13—C14	58 (1)
C2—C3—C4—C30	—168,9(9)	C11—C12—C13—C17	—179,6 (8)
C3—C4—C5—C6	—176,4(9)	C12—C13—C14—C8	—62 (1)
C3—C4—C5—C10	51(1)	C12—C13—C14—C15	173,9 (8)
C29—C4—C5—C6	63(1)	C12—C13—C14—C28	63 (1)
C29—C4—C5—C10	—70(1)	C17—C13—C14—C8	167,7 (8)
C30—C4—C5—C6	—58(1)	C17—C13—C14—C15	44 (1)
C30—C4—C5—C10	169,0(9)	C17—C13—C14—C28	—67 (1)
C4—C5—C6—C7	163,5(8)	C12—C13—C17—C16	—154,4 (9)
C10—C5—C6—C7	—61(1)	C12—C13—C17—C20	81 (1)
C4—C5—C10—C1	—53(1)	C14—C13—C17—C16	—29 (1)
C4—C5—C10—C9	—168,2(8)	C14—C13—C17—C20	—153,9 (9)
C4—C5—C10—C19	66(1)	C8—C14—C15—C16	—160,0 (8)
C6—C5—C10—C1	173 1(8)	C13—C14—C15—C16	—40,9 (9)
C6 C5—C10—C9	58(1)	C28—C14—C15—C16	74,0 (9)
C6—C5—C10—C19	—68(1)	C14—C15—C16—C17	24 (1)
C5—C6—C7 C8	57(1)	C15—C16—C17—C13	3 (1)
C6—C7—C8 C9	—50(1)	C15—C16—C17—C20	130,2 (9)
C6—C7—C8—C14	—168,7(9)	C13—C17—C20—O20	164,8 (9)
C6—C7—C8—C18	72(1)	C13—C17—C20—C21	50 (1)
C7—C8—C9—C10	51(1)	C13—C17—C20—C22	—74 (1)
C7—C8—C9—C11	—175,7(9)	C16—C17—C20—O20	45 (1)
C14—C8—C9—C10	170,6(8)	C16—C17—C20—C21	—70 (1)
C14—C8—C9—C11	—56(1)	C16—C17—C20—C22	165,9(8)
C18—C8—C9—C10	—68(1)	O20—C20—C22—C23	—54 (1)
C18—C8—C9—C11	66(1)	C17—C20—C22—C23	—172 (8)
C7—C8—C14—C13	179,3(9)	C21—C20—C22—C23	63 (1)
C7—C8—C14—C15	—67(1)	C20—C22—C23—C24	—175,1(8)
C7—C8—C14—C28	55(1)	C22—C23—C24—O24	—63 (1)
C9—C8—C14—C13	60(1)	C22—C23—C24—C25	173,1(9)
C9—C8—C14—C15	173,6(8)	O24—C24—C25—C26	179 (1)
C9—C8—C14—C28	—64(1)	O24—C24—C25—C27	2 (2)
C18—C8—C14—C13	—63(1)	C23—C24—C25—C26	—59 (1)
C18—C8—C14—C15	51(1)	C23—C24 C25—C27	124 (1)



I

Each of the six-membered rings of the molecule has the chair conformation. The smallest values of the asymmetry parameters [2] of the six-membered rings are the following: $\Delta C_s(2)$ = 1.6°, $\Delta C_s(5)$ = 2.2°, $\Delta C_s(11)$ = 1.6°. The distorted conformations of rings A and B are caused mainly by stresses arising through the presence of three β-methyl groups, in positions 4, 8, and 10. The distances between the carbon atoms of these methyl groups, C19—C29 and C18—C19 are, respectively, 3.24 and 3.15 Å. Ring D has the conformation of a 14α-envelope distorted in the direction of a 13β, 14α-half-chair. The minimum value of the asymmetry parameter of ring D is $\Delta C_s(14)$ = 4.1°.

The side chain of compound (I) has a (+)-antiperiplanar conformation, judging from the value of the torsional angle C13—C17—C20—O20. The form of the major part of the side chain in this compound is that of an anti-zigzag. A chain of atoms in a complete transoid conformation begins at C16 and ends at C25. The double bond in the side chain is present in an eclipsed conformation with the C24—O24 bond.

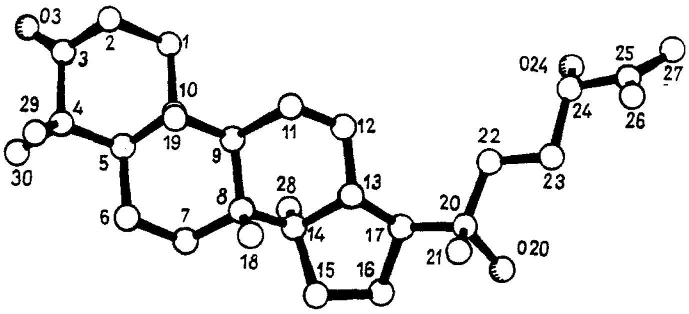


Fig. 1. Spatial structure of the (I) molecule and the numbering of the atoms.

TABLE 3. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) of the (I) Molecule

Atom	x	y	z
O3	4641(13)	6723(8)	3873(3)
O20	8426(10)	8379(6)	191(2)
O24	2053(9)	8750(6)	33(2)
C1	4340(15)	8284(10)	2879(3)
C2	4039(15)	8323(11)	3358(4)
C3	5247(17)	7468(11)	3583(3)
C4	7308(15)	7608(10)	3503(3)
C5	7572(14)	7643(9)	3009(3)
C6	9569(16)	7702(9)	2821(3)
C7	9781(16)	7368(9)	2400(4)
C8	8607(14)	8147(9)	2107(3)
C9	6586(14)	8181(9)	2273(3)
C10	6366 (15)	8514(9)	2757(3)
C11	5342 (15)	8876(11)	1969(4)
C12	5399 (16)	8392(11)	1514(3)
C13	7396 (15)	8366(9)	1364(3)
C14	8581 (15)	7605(9)	1657(3)
C15	10412(15)	7611(9)	1413(3)
C16	9831 (15)	7469(9)	950(3)
C17	7810 (15)	7925(9)	919(3)
C18	9502 (15)	9390(9)	2099(3)
C19	6766 (16)	9843(9)	2843(3)
C20	7528 (14)	8827(9)	556(3)
C21	8490 (16)	10000(9)	645(3)
C22	5478(15)	8973(9)	483(3)
C23	4951(15)	9716(9)	99(3)
C24	2878(14)	9885(9)	82(3)
C25	2281(16)	10725(10)	−256(4)
C26	3040(20)	11949(11)	−228(5)
C27	1108(21)	10423(10)	−542(4)
C28	7917(16)	6301(9)	1653(3)
C29	8005(16)	8722(10)	3730(3)
C30	8322(18)	6518(11)	3680(3)

The bond lengths in compound (I) have the usual values for triterpenoids of the dammarane series [3-7]. The maximum value for bonds of the Csp^3–Csp^3 type is 1.60 Å, and the minimum value 1.52 Å. The length of the C4–C5 and C9–C10 bonds, 1.60 Å, differs from the corresponding bond lengths in other triterpenoids of this series studied previously by not more than 3σ (where σ is the standard deviation).

The steric hindrance connected with the presence in the triterpenoid of three axial methyl groups in the β-positions at C4, C8, and C10 leads to an increase in the endocyclic valence angles C4–C5–C10, and C8–C9–C10 to 117.7° and 115.3°. The difference in the positions of the methyl groups in steroids (13β) and in triterpenoids of the dammarane series (14α) correlate well with the change in the valence angles at the linkage of rings C and D. Thus, while in steroids with the trans-linkage of rings C and D the valence angle C8–C14–C15 has the maximum value and the angle C14–C13–C17 the minimum value [2], in compound (I) the largest deviation from tetrahedral values is observed for the angles C12–C13–C17 (118.8°) and C13–C14–C15 (100.0°). Values of the valence angles close to these in the linkage of rings C and D are observed in other triterpenoids of the dammarane series [3-7].

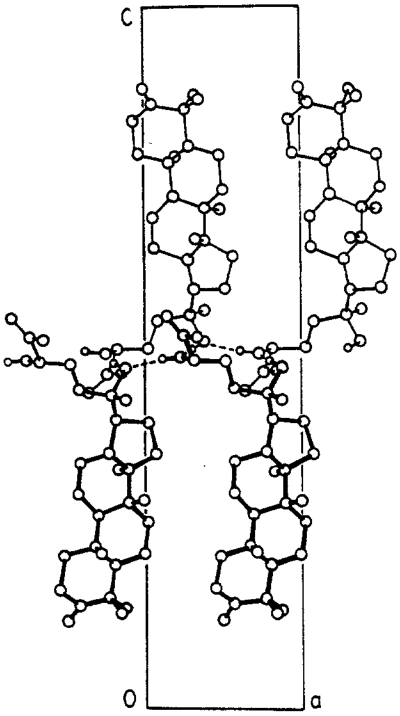


Fig. 2. Fragment of the packing of (I) molecules in the crystal. Hydrogen bonds are shown by broken lines.

A fragment of the packing of the (I) molecules in the crystal is shown in Fig. 2. The molecules, linked "tail to tail" by hydrogen bonds, form chains parallel to the crystallographic axis *a*. All the hydroxy groups of the molecules of such a chain participate in a linear system of intermolecular cooperative O—H...O bonds. The distances in the chains of atoms O24—H...O20'—H'...O24" are, respectively, 0.96, 1.78, 0.97, and 1.82 Å, while the O...O distances are 2.73(1) and 2.710(9) Å.

The very fact of the detection of cooperative H-bonds in the crystals of compound (I) is of interest. Connected with them are, on the one hand, a number of specific properties (or a specific anisotropy of the properties) of the crystals [8], and, on the other hand, an arrangement of the molecules linked by the cooperative H-bonds in the crystals of compound (I) that is similar to the orientation of the molecules in the bimolecular layers of membranes. The formation of such systems in biological membranes may substantially affect their physical properties.

EXPERIMENTAL

The crystals of compound (I) ($C_{30}H_{50}O_3$) belong to the rhombic system, space group $P2_12_12_1$, Z = 4. The parameters of the unit cell were measured on a Syntex $P2_1$ four-circle diffractometer and are given below, together with other crystallographic information: a = 7.294(1), b = 11,336(2), c = 32.056(4) Å, V = 2650.4 Å³, M = 458, d_{calc} = 1.15 g/cm³.

The integral intensities of the 1606 independent reflections observed were measured on the same diffractometer (Mo Kα radiation, graphite monochromator, 2θ/ω scanning) in the interval of 2θ from 2 to 46°. The structure was determined by the direct method and was refined by the method of least squares in the anisotropic full-matrix approximation to R = 0.067 (for all the reflections observed). In the calculation of the divergence factors the positions of the hydrogen atoms in the crystal (determined from difference syntheses in the hydroxy and methyl groups and given geometrically for the CH_2 and CH_3 groups) were taken into account. The coordinates of the atoms are given in Table 3. All the calculations were made on an Eclipse S-200 computer by the INEXTL programs [9].

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STEROIDS OF THE SPIROSTAN AND FUROSTAN SERIES FROM Nolina microcarpa

1. STRUCTURES OF NOLINOSPIROSIDE C AND NOLINOFUROSIDES A AND C

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UDC 547.918:547.926

In addition to the known steroid sapogenin (25S)-ruscogenin (I), three new glycosides have been isolated from the leaves of *Nolina microcarpa* S. Wats. (family Dracaenacea), and the following structures are suggested for them: (25S)-spirost-5-ene-1β,3β-diol 1-O-β-D-fucopyranoside (nolinospiroside C, II), (25S)-furost-5-ene-1β,3β,22α,26-tetraol 1-O-β-D-fucopyranoside (nolinofuroside A, III), and (25S)-furost-5-ene-1β,3β,22α,26-tetraol 1-O-β-D-fucopyranoside 26-O-β-D-glucopyranoside (nolinofuroside C, V).

Among plants of the Dracaenaceae family there are a few saponin-bearing ones [1, 2]. However, not one of the species of the genus *Nolina* belonging to this family has been studied as a producer of steroids of the spirostan and furostan series. In a methanolic extract of the leaves of *Nolina microcarpa* S. Wats. growing on the southern coast of the Crimea as a decorative plant we have established the presence of at least ten substances, most of which were assigned to derivatives of the spirostan and furostan series.

The present paper is devoted to proofs of the structures of three previously undescribed steroid glycosides. They have been called nolinospiroside C (II) and nolinofurosides A (III) and C(V).

On TLC, compounds (I) and (II) were revealed with vanillin/phosphoric acid in the form of yellow spots [2, 3] and were not stained by Ehrlich's reagent [4]. Their IR spectra contained in the 800-1000 cm^{-1} region a series of bands corresponding to the absorption of a (25S)-spiroketal grouping [5, 6].

Substances (III) and (V) were isolated in the form of mixtures – (III and IV) and (V and VI), respectively. The products of the color reactions of compounds (III)-(VI) with vanillin/phosphoric acid had a green coloration, and those with Ehrlich's reagent a red coloration. Heating aqueous solutions of the mixtures (II, IV) and (V, VI) led to the chromatographically homogeneous glycosides (III) and (V). Their IR spectra each contained a weak broadened band at 915 cm^{-1}. When solutions of the mixtures (III, IV) and (V, VI) in absolute methanol were heated they were transformed into the less polar components (IV) and

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