Triterpenoids from *Abies* species.
21.* Crystal and molecular structure of 25,26,27-trinor-7,13-*frido*-9β-lanostane hydroxyketone *p*-bromobenzoate

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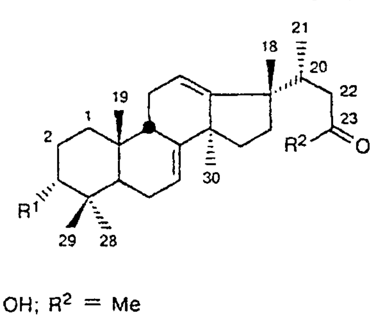
The structure and the absolute configuration of 25,26,27-trinor-17,13-*frido*-9β-lanostane hydroxyketone *p*-bromobenzoate were established by X-ray structural analysis. This compound readily forms a 1 : 1 crystal solvate with *n*-pentane.

Key words: triterpenoids; Siberian fir; X-ray structural analysis.

Hydroxyketone **1** was found among related trinor derivatives that are the products of fragmentation resulting from treatment of a mixture of triterpenic acids from Siberian fir needle (*Abies sibirica Ledb.*) with alkali in an alcohol solution.[1] The structure and the stereochemistry of its precursor, namely, acid **2**, have not been unambiguously established. The probable structure and stereochemistry were suggested by Japanese researchers[2] based on the data of NMR spectra of the corresponding methyl ester **3** and biogenetic considerations. With the aim of establishing the structures of compounds **1—3** and other triterpene derivatives[2] related to **3**, we prepared *p*-bromobenzoate **4**, which is readily crystallized from *n*-pentane (the initial compound **1** and triterpenic ester **3** do not crystallize). It was found that crystals of ester **4** separated from the mother liquor became turbid rather rapidly. These crystals decomposed upon storage at room temperature in several days ("disintegrated"). We suggested that the *p*-bromobenzoate under study forms a crystal solvate with *n*-pentane, which accounts for the effects observed. We succeeded in carrying out X-ray structural analysis only when we used a single crystal sealed in a polyethylene tube. The results of X-ray structural analysis confirmed our suggestions. In the crystal solvate, molecules of compound **4** and *n*-pentane occur in a ratio of 1 : 1.



1: R^1 = OH; R^2 = Me
2: R^1 = OH; R^2 = CH=C(Me)COOH
3: R^1 = OH; R^2 = CH=C(Me)COOMe
4: R^1 = $OCOC_6H_4Br$-*p*; R^2 = Me

The spatial structure of a molecule of compound **4** (and its absolute configuration) is shown in Fig. 1. This structure is consistent with that suggested previously.[1,2] Ring A has a chair conformation, which can be characterized by the following Cremer—Pople parameters:[3] θ = 174°, S = 1.05. Ring B adopts an asymmetrical half-chair conformation (ψ_2 = 6°, θ = 37°, S = 0.77) in which the C(5) and C(10) atoms deviate from the plane of the double bond in opposite directions by 0.46(2) and 0.32(2) Å, respectively. Ring C adopts a conformation intermediate between a sofa and a boat (ψ_2 = 21°, θ = 49°, S = 0.78). The C(8) and C(9) atoms deviate from the plane of the double bond in the same direction by 0.22(2) and 0.90(2) Å, respectively. The five-membered ring D has a twist conformation with the following Cremer—Pople parameters: ψ_2 = 1°, S = 0.55. The results of calculations for the model compound (the *p*-BrC_6H_4 group was replaced by a CH_3 group, and the Ac group at the C(22) atom was replaced by a hydrogen atom) by the molecular mechanics method using the MMX program demonstrated that the conformations of the rings are very close to those determined experimentally, *i.e.*, the deviations from the ideal conformations of the rings observed are determined by intramolecular factors. The orientation of the keto group at the C(23) atom can be characterized by the C(20)—C(22)—C(23)—O(2) torsion angle (11(2)°). The atoms of the ester group C(32)—C(31)(=O(3))—O(1) are in a single plane (the maximum deviation from the plane is 0.01 Å). This group is virtually coplanar with the plane of the phenyl ring (the angle is 4.5(8)°). The bond lengths in compound **4** are close to the normal values.[4]

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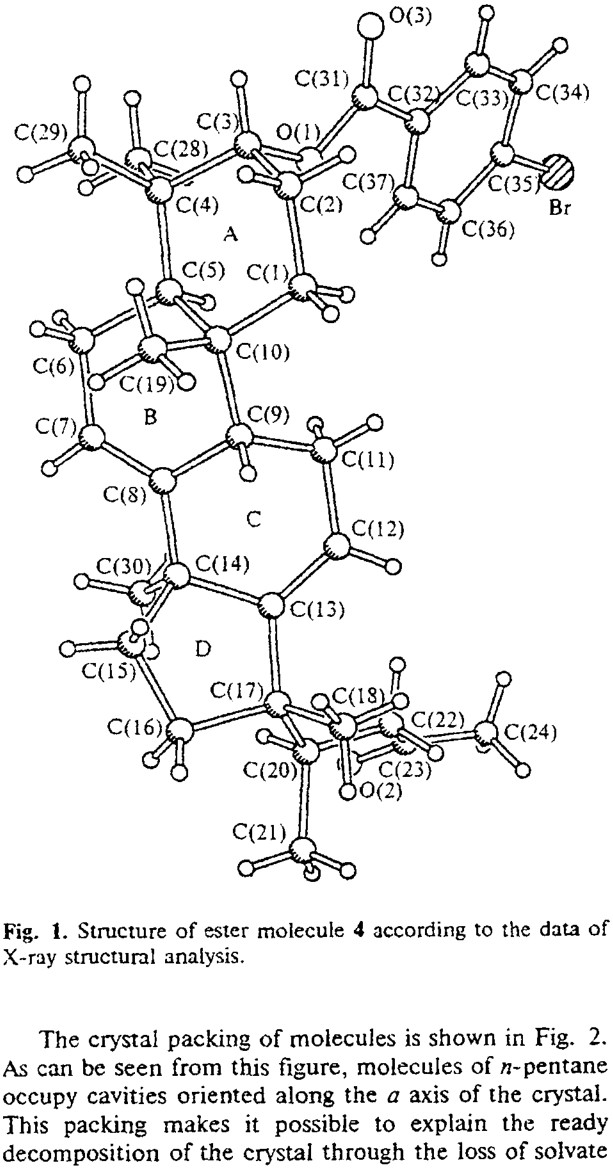

Fig. 1. Structure of ester molecule **4** according to the data of X-ray structural analysis.

The crystal packing of molecules is shown in Fig. 2. As can be seen from this figure, molecules of *n*-pentane occupy cavities oriented along the *a* axis of the crystal. This packing makes it possible to explain the ready decomposition of the crystal through the loss of solvate molecules. The intermolecular distances in the crystal solvate correspond to the sum of the van der Waals radii of the atoms. According to the Cambridge Structural Database,[5] the cases of involvement of a solvent such as *n*-pentane in the crystals of organic compounds are scarce. It is interesting to note that we failed to obtain crystals of ester **4** from *n*-hexane.

Experimental

The melting point was determined on a Kofler stage. Chromatography was carried out on KCK silica gel; the ratio of the compound and the sorbent was 1 : 20. A 98 : 2 hexane—ether mixture was used as the eluent.

Synthesis of (3*R*,17*S*,20*R*)-3-*p*-bromobenzoyloxy-25,26,27-*frido*-9β-lanosta-7,12-dien-23-one (4). *p*-Bromobenzoyl chloride (0.3 g) was added to a solution of hydroxyketone **1**[1] (0.10 g) in Py (4 mL). The reaction mixture was stirred at 60° C for 48 h. The usual workup of the reaction mixture and chromatography gave compound **4** in a yield of 0.11 g. Crystallization from *n*-pentane gave crystals of *n*-pentane solvate **4** in a yield of 0.05 g, m.p. 96—104° C (with decomposition; darkening of the crystals was observed even at 54—62° C).

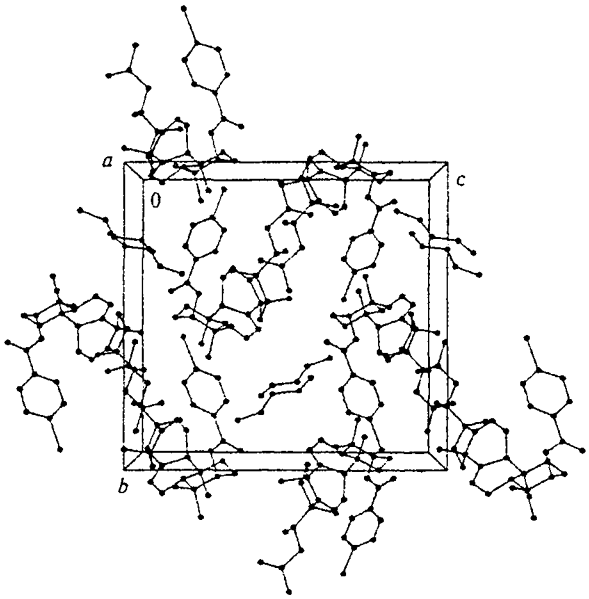

Fig 2. Crystal packing of molecules in the pentane solvate of ester **4** (projection along the *a* axis). The conformer **B** of *n*-pentane molecules is shown (see the Experimental section and Table 1).

X-ray structural analysis of a single crystal of the solvate of compound 4 was carried out on a Syntex P2$_1$ diffractometer (Cu-Kα radiation, graphite monochromator). A crystal of dimensions 3.5 mm×0.2 mm×0.1 mm was placed in a polyethylene tube, which was then sealed. The solvate crystals are orthorhombic; at 25° C a = 11.878(6), b = 17.225(7), c = 18.048(7) Å, V = 3693(3) Å^3, space group $P2_12_12_1$, Z = 4, $C_{34}H_{45}O_3Br + C_5H_{12}$, μ = 1.761 mm^{-1}, d_{calc} = 1.176 g cm^{-3}. The intensities of 2630 independent reflections with θ/2 < 110° were measured using the θ/2θ scanning technique. Absorption correction was applied taking into account the crystal faceting (the transmission factor was 0.67—0.84) and then using the DIFABS program (the correction was 0.72—1.29). The structure was solved by the direct method using the SHELX-86 program.[6] Refinement of the structure by the full-matrix least-squares method with anisotropic thermal parameters (H atoms were placed in geometrically calculated positions) using the SHELXL-93 program[7] (wR_2 = 0.1842 based on all F^2, R = 0.0614 using 1532 reflections with $F_0 > 4\sigma$) gave severely distorted geometry and very high thermal parameters for the pentane molecule, which was indicative of disorder. These data in combination with the peaks of the difference synthesis made it possible to interpret the disorder as a superposition of a number of conformers of *n*-pentane. Therefore, *n*-pentane was further refined isotropically (without H atoms) as four conformers (two *trans-trans* forms and two *gauche-trans* forms) with fixed geometry calculated by the molecular mechanics method. The ratios of the conformers were refined, and the final portions were 21(2), 31(3), 27(3),

Table 1. Atomic coordinates (×10^4) and equivalent thermal parameters (×10^3) for nonhydrogen atoms of compound **4** (solvate with *n*-pentane)*

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Br	711(1)	4367(1)	7006(1)	94(1)
O(1)	2617(6)	744(4)	7769(4)	77(2)
O(2)	8510(8)	3142(5)	4261(5)	109(3)
O(3)	1413(9)	844(5)	8705(5)	118(3)
C(1)	4901(9)	318(6)	8064(6)	78(3)
C(2)	3915(10)	−32(7)	8468(6)	88(4)
C(3)	2882(10)	−42(6)	7969(8)	77(3)
C(4)	3069(9)	−487(5)	7243(6)	65(3)
C(5)	4168(9)	−217(5)	6872(6)	64(3)
C(6)	4492(10)	−700(6)	6191(6)	84(3)
C(7)	5533(10)	−411(6)	5800(7)	75(3)
C(8)	6246(8)	70(6)	6114(6)	60(3)
C(9)	6126(8)	351(5)	6917(6)	63(3)
C(10)	5220(9)	−99(6)	7360(6)	63(3)
C(11)	6039(8)	1245(5)	6888(6)	61(3)
C(12)	7101(10)	1533(6)	6554(6)	65(3)
C(13)	7693(9)	1147(6)	6042(6)	60(3)
C(14)	7230(9)	414(6)	5705(6)	64(3)
C(15)	8294(9)	−88(6)	5709(7)	75(3)
C(16)	9249(10)	461(6)	5497(7)	84(4)
C(17)	8906(8)	1273(6)	5826(6)	60(3)
C(18)	9608(9)	1410(7)	6538(7)	88(4)
C(19)	5772(10)	−888(6)	7581(7)	99(4)
C(20)	9115(9)	1933(6)	5256(6)	73(3)
C(21)	10346(10)	1978(7)	5001(8)	109(5)
C(22)	8735(10)	2723(6)	5512(6)	72(3)
C(23)	8533(10)	3325(7)	4915(8)	80(4)
C(24)	8375(12)	4137(6)	5131(6)	97(4)
C(28)	2088(10)	−326(6)	6715(7)	90(4)
C(29)	2997(11)	−1358(5)	7443(7)	96(4)
C(30)	6903(10)	575(7)	4884(5)	79(3)
C(31)	1866(12)	1121(7)	8164(8)	86(4)
C(32)	1665(9)	1918(6)	7896(6)	65(3)
C(33)	922(11)	2385(7)	8277(7)	91(4)
C(34)	650(11)	3123(7)	8029(7)	91(4)
C(35)	1125(9)	3364(5)	7370(6)	64(3)
C(36)	1893(8)	2926(5)	6987(6)	63(3)
C(37)	2161(9)	2204(6)	7258(5)	67(3)
C(1A)	5253(72)	1861(52)	−539(49)	200
C(2A)	4041(74)	2186(65)	−555(35)	200
C(3A)	3610(61)	2355(37)	239(34)	200
C(4A)	2530(59)	2859(56)	216(44)	200
C(5A)	2272(72)	3204(59)	992(51)	200
C(1B)	4269(55)	2106(45)	−826(34)	200
C(2B)	3288(44)	2519(35)	−434(31)	200
C(3B)	3528(43)	2634(29)	402(29)	200
C(4B)	2702(45)	3224(42)	742(38)	200
C(5B)	3111(67)	3509(48)	1504(37)	200
C(1C)	4490(64)	1688(38)	−60(41)	200
C(2C)	3343(61)	2089(38)	−222(34)	200
C(3C)	2820(50)	2422(35)	500(41)	200
C(4C)	3506(56)	3154(32)	759(41)	200
C(5C)	2877(79)	3590(47)	1380(51)	200
C(1D)	4314(80)	2224(60)	−302(60)	200
C(2D)	3215(77)	1906(41)	35(53)	200
C(3D)	2465(57)	2559(47)	347(51)	200
C(4D)	2968(72)	2909(44)	1064(42)	200
C(5D)	2371(90)	3668(49)	1282(58)	200

* The atoms from C(1A) to C(5D) correspond to conformers **A**, **B**, **C**, and **D** of the solvate *n*-pentane molecule.

and 21(2)% (in Table 1, they are denoted as conformers **A**, **B**, **C**, and **D**, respectively). The final values of the factors were as follows: R_1 = 0.0582 using 1529 reflections with $F_0 > 4\sigma$, wR_2 = 0.1626 based on all F^2, S = 1.003, 372 parameters.

The absolute configuration of ester **4** was unambiguously established. Flack's parameter was −0.10(6).[8] The atomic coordinates and equivalent thermal parameters for nonhydrogen atoms are given in Table 1.

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