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CRYSTAL AND MOLECULAR STRUCTURE OF METHYL β-L-ARABINOPYRANOSIDE

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UDC 548.737

The crystal and molecular structure of methyl β-L-arabinopyranoside has been determined. The geometric parameters of the glycosidic bond have been found and the presence of an O(2)—H...O(1) intramolecular hydrogen bond in the molecule has been established.

The crystal and molecular structure of β-D-arabinose was determined in 1957 [1] and was later refined by Hordvik [2] with respect to two projections. More accurate results on the structure of the molecule were obtained in 1967 by Kim and Jeffrey in an investigation of

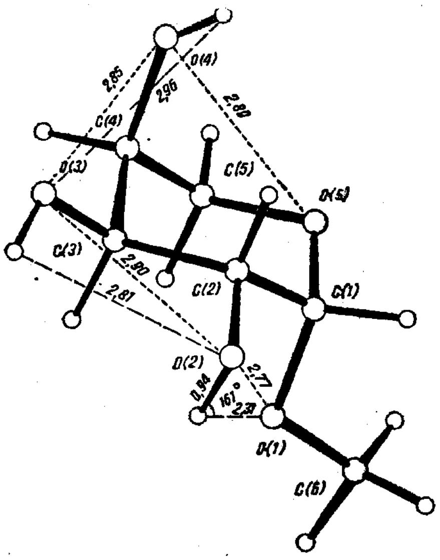

Fig. 1. Form of the molecule of methyl β-L-arabinopyranoside. The dashed lines show the O(H)...O distances that are less than 3 Å.

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TABLE 1. Bond Lengths (Å) in Methyl β-L-Arabinopyranoside, β-DL-Arabinose, and β-D-Arabinose

Bond	Length		
	Me β-L-arabinopyranoside	β-DL-arabinose [3]	β-D-arabinose [2]
C(1)—C(2)	1,54(1)	1,532(4)	1,524(9)
C(2)—C(3)	1,53(1)	1,528(4)	1,523(9)
C(3)—C(4)	1,54(1)	1,543(4)	1,554(9)
C(4)—C(5)	1,50(1)	1,515(4)	1,537(10)
C(5)—O(5)	1,41(1)	1,447(4)	1,440(8)
C(1)—O(5)	1,42(1)	1,434(4)	1,421(8)
C(1)—O(1)	1,40(1)	1,392(4)	1,382(12)
C(2)—O(2)	1,41(1)	1,417(4)	1,454(8)
C(3)—O(3)	1,43(1)	1,432(4)	1,426(9)
C(4)—O(4)	1,43(1)	1,425(4)	1,431(12)
C(6)—O(1)	1,45(1)		

TABLE 2. Valence Angles (degrees) in Methyl β-L-Arabinopyranoside, β-DL-arabinose, and β-D-Arabinose

Bond	Angle		
	Me β-L-arabinopyranoside	β-DL-arabinose [3]	β-D-arabinose [2]
C(2)—C(1)—O(5)	110,7(6)	109,5(3)	109.4(6)
O(1)—C(1)—O(5)	112,5(7)	112,9(3)	113,1(7)
C(2)—C(1)—O(1)	107,9(7)	108,3(2)	108,9(7)
C(1)—C(2)—C(3)	110,0(6)	109,3(2)	109,2(6)
C(1)—C(2)—O(2)	111,6(7)	111,5(2)	107,3(6)
C(3)—C(2)—O(2)	111,7(6)	112,2(2)	110.8(6)
C(2)—C(3)—C(4)	108,7(7)	109,9(2)	109,7(6)
C(2)—C(3)—O(3)	111,7(7)	111,7(2)	109,2(6)
C(4)—C(3)—O(3)	109,5(7)	109,4(2)	110,1(6)
C(3)—C(4)—C(5)	109,0(7)	108,9(3)	107,1(6)
C(3)—C(4)—O(4)	113,1(7)	112,5(3)	111,7(7)
C(5)—C(4)—O(4)	111,4(8)	111,9(3)	108,3(7)
C(4)—C(5)—O(5)	110,5(7)	111,3(3)	111,9(6)
C(1)—O(5)—C(5)	113,5(6)	113,4(3)	112,7(6)
C(1)—O(1)—C(6)	113,7(7)		

TABLE 3. Conformational Angles (degrees) in Methyl β-L-Arabinopyranoside, β-DL-Arabinose, and β-D-Arabinose

Bond	Angle		
	Me β-L-arabipyranoside	β-DL-arabinose [3]	β-D-arabinose [2]
O(5)—C(1)—C(2)—C(3)	54,2	58,2	59,9
C(1)—C(2)—C(3)—C(4)	—53,7	—57,0	—58,4
C(2)—C(3)—C(4)—C(5)	56,7	55,4	55,4
C(3)—C(4)—C(5)—O(5)	—60,3	—55,8	—55,9
C(4)—C(5)—O(5)—C(1)	62,4	59,6	60,9
C(5)—O(5)—C(1)—C(2)	—58,7	—60,0	—61,3

the centrosymmetric crystals of β-DL-arabinose racemate [3]. Since β-L-arabinose is a component of many polysaccharides, definite interest is presented by the structure of its methyl glycoside — the simplest model containing a glycosidic bond. In the present paper we give the results of an x-ray structural investigation of methyl β-L-arabinopyranoside. The results on the geometry of the molecule so obtained with the geometric parameters of β-D-arabinose and β-DL-arabinose in order to demonstrate the differences due to the presence of the glycosidic bond in the molecule and the different natures of the hydrogen bonds in the crystals of these substances.

The form of the molecule of methyl β-L-arabinopyranoside is given in Fig. 1. The molecule is the β anomer with the pyranose ring in the chair form, the conformation of the molecule being $^4C_1$. The positions of the substituents in the ring are 1a2e3e4a.

TABLE 4. Torsion Angles (degrees) in Methyl β-L-Arabinopyranoside

Bond	Angle
O(1)—C(1)—C(2)—C(3)	—69,2
O(1)—C(1)—C(2)—O(2)	55,4
O(5)—C(1)—C(2)—O(2)	178,8
C(2)—C(1)—O(1)—C(6)	—1 6,3
O(5)—C(1)—O(1)—C(6)	71,5
O(1)—C(1)—O(5)—C(5)	61,9
C(1)—C(2)—C(3)—O(3)	—174,6
O(2)—C(2)—C(3)—C(4)	—178,3
O(2)—C(2)—C(3)—O(3)	60,8
C(2)—C(3)—C(4)—O(4)	—68,0
O(3)—C(3)—C(4)—C(5)	—179,0
O([illegible])—C(3)—C(4)—O(4)	54,4
O(4)—C(4)—C(5)—O(5)	65,2

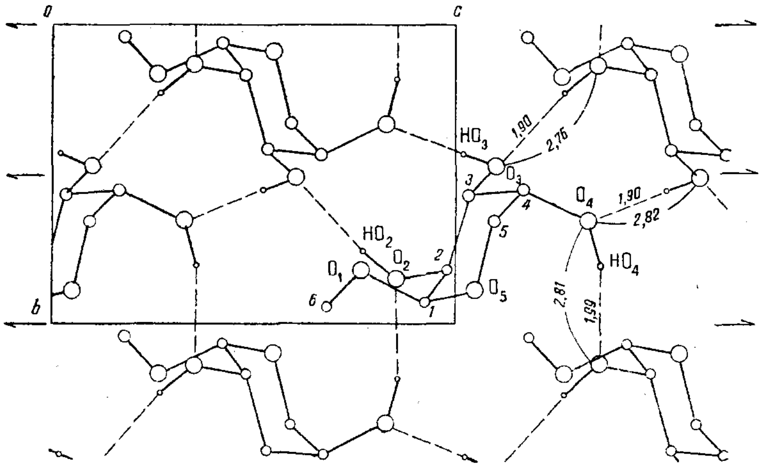

Fig. 2. Packing of the molecules of methyl β-L-arabinopyranoside in the crystal, and intermolecular H-bonds.

The bond lengths and valence angles in the molecules are given in Tables 1 and 2. With some exceptions, which are discussed below, their values agree to within the limits of the standard deviations with the values obtained for β-D-arabinose and β-DL arabinose (these are also given in Tables 1 and 2). The mean length of a C—C in the methyl β-L-arabinopyranoside molecule is 1.528 Å (1.537 Å in β-DL-arabinose).

With the exception of the bonds with the O(5) atom, the lengths of the C—O bonds agree, to within the limits of the standard deviations, with their values in β-DL-arabinose. The length of the C(5)—O(5) bond is less than the values for this bond observed in other pyranose sugars of 1.425-1.464 Å given by Arnott and Scott [4] and differ by more than 0.03 Å from the length of this bond in β-D- and β-DL-arabinose. The glycosidic bond of the molecule, O(1)—C(6), has the greatest length of the C—O in the molecule.

The valence angle at the glycosidic atom O(1) has a value close to that observed in other methyl glycosides. The mean value given for this angle by Arnott and Scott [4] is 113.2°.

The values of the cis-torsion angles in the pyranose ring of the molecule are given in Table 3. The conformational angles of the ring have values of from 53.7 to 62.4°, while the range of the corresponding values in β-DL-arabinose is 55.4-60.0°. One of the possible reasons both for the decrease in the length of the C(5)—O(5) bond in methyl β-L-arabinopyranoside and for the increase in the conformational angles is the absence of the intermolecular O(1)—H...O(5) hydrogen bond observed in crystals of β-DL-arabinose and of β-D-arabinose. A

TABLE 5. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) and Thermal Parameters ($\times 10^3$) of Methyl β-L-Arabinopyranoside

Atom	x/a	y/b	z/c	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{23} (Å^2)	U_{13} (Å^2)	U_{12} (Å^2)
C(1)	3046(11)	9275(13)	9227(13)	41(3)	16(3)	24(3)	—4(3)	—2(3)	10(2)
C(2)	4500(11)	8277(13)	9818(13)	35(3)	13(2)	15(3)	4(2)	0(2)	1(2)
C(3)	3880(10)	5726(14)	10331(13)	33(3)	30(3)	23(3)	4(3)	—2(3)	9(3)
C(4)	2499(10)	5541(15)	11677(14)	30(3)	33(3)	32(3)	3(3)	1(3)	12(3)
C(5)	1168(11)	6565(17)	10934(14)	30(3)	52(3)	38(3)	14(3)	3(3)	11(3)
C(6)	1385(12)	9454(17)	6806(15)	42(3)	45(3)	39(3)	12(3)	—2(3)	13(3)
O(1)	2475(8)	8228(11)	7656(11)	41(2)	34(2)	26(2)	—5(2)	-15(2)	19(2)
O(2)	5742(7)	8565(9)	8542(10)	31(2)	21(2)	24(2)	—1(2)	3(2)	2(2)
O(3)	5166(8)	4797(12)	11035(11)	37(2)	36(2)	27(2)	1(2)	0(2)	19(2)
O(4)	3074(8)	6591(11)	13288(11)	49(3)	40(3)	26(3)	—2(2)	—1(2)	19(2)
O(5)	1799(8)	8923(10)	10509	39(3)	32(2)	31	—1	5	17(2)

TABLE 6. Coordinates of the Hydrogen Atoms ($\times 10^4$) of Methyl β-L-Arabinopyranoside

Atom	x/a	y/b	z/c
H(C1)	3433	11135	9043
H(C2)	5050	9235	10938
H(C3)	3429	4733	9187
H(C4)	2006	3724	11958
H(C5—1)	189	6422	11865
H(C5—2)	685	5614	9778
H(C6—1)	888	8263	5775
H(C6—2)	2156	11017	6268
H(C6—3)	383	9884	7517
H(O2)	5108	7638	7694
H(O3)	5855	4401	10212
H(O4)	4404	8125	13586

comparison of all the geometric parameters of the methyl β-L-arabinopyranoside and β-DL-arabinose molecules shows that the fragment of the molecule from the C(2) atom to the C(5) atom scarcely changes its geometry on the formation of the methyl glycoside. The values of the remaining torsional angles are given in Table 4.

Figure 1 gives the distances between the non-valence-bound oxygen atoms and the O...H distances in the molecules that are less than 3 Å. The observed values of the geometric parameters show the existence of a O(2)—H...O(1) intramolecular hydrogen bond. The packing of the molecules in the crystal is shown in Fig. 2. Only the hydroxy groups of the molecules participate in the formation of intermolecular hydrogen bonds in the crystal, each hydroxy group taking part in the formation of two intermolecular hydrogen bonds. The molecules bound by hydrogen bonds form layers parallel to the (100) plane of the crystal.

EXPERIMENTAL

Crystals of methyl β-L-arabinopyranoside ($C_6H_{12}O_5$, mol. wt. = 164) obtained from solution in ethanol belong to the monoclinic system, space group $P2_1$, Z = 2. The parameters of the elementary cell were determined and refined on a Syntex PI diffractometer, and their values are given below together with other crystallographic characteristics:

$a = 8.347$ (3) Å $\gamma = 103.62$ (2)°
$b = 5.918$ (1) Å $V = 372.1$ (2) Å^3
$c = 7.750$(1) Å $\rho_{calc} = 1.46$ g/cm^3

The integral intensities of 678 independent reflections with $I \geq 3\sigma$ (I) were measured on the Syntex PI diffractometer (Mo, K_α radiation, graphite monochromator, θ/2θ method of scanning, $\sin\theta/\lambda \leqslant 0.6$ Å^{-1}). In the recalculation of the intensities to structure factors, corrections were introduced for the Lorentz and polarization factors.

The structure was determined by the direct method using the MULTAN-78 programs [5] and was refined by the method of least squares in the full-matrix anisotropic approximation to R = 0.09. The positions of the hydrogen atoms in the molecule were determined from difference syntheses. The coordinates of the C and O atoms and their anisotropic thermal parameters are given in Table 5, while Table 6 gives the coordinates of the hydrogen atoms.

SUMMARY

The crystal and molecular structure of methyl β-L-arabinopyranoside has been determined. The geometric parameters of the glycosidic bond have been found and the presence of a O(2)—H...O(1) intramolecular hydrogen bond in the molecule has been established. Differences are observed in the geometric parameters of the molecules of methyl β-L-arabinopyranoside, β-D-arabinose, and β-DL-arabinose which are expressed in smaller values of the lengths of the C(4)—C(5) and C(5)—O(6) bonds and in changes in the conformational angles of the molecule except for the angle at the C(3)—C(4) bond.

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^{13}C NMR SPECTRA OF BIOLOGICALLY ACTIVE COMPOUNDS.

II. 11-DEOXY-16- AND 17-ARYLOXYPROSTAGLANDINS

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UDC: 543.422.25+547.915

The ^{13}C NMR spectra of the initial ω-aryloxy chains and the final 16- and 17-aryloxyprostaglandins of the 11-deoxy series have been investigated, and stereochemical assignments have been made for the diastereomeric pairs. A weakening of the diastereotopic effects in the spectra of the 15- and 16-methyl-substituted 16- and 17-phenoxypropstaglandins to 0.1 ppm has been shown.

Aromatic fragments in the molecules of synthetic prostaglandins impart new properties to them: resistance to biological breakdown, and increased activity and selectivity of biological action [1]. With the aim of the stereochemical monitoring and study of diastereotopic effects in aryloxyprostaglandin derivatives we have as before [2], used the method of ^{13}C NMR spectroscopy. In the literature on aryloxyprostaglandins only the ^{13}C NMR spectrum of 16-phenoxy-11-deoxyprostaglandin has been described [3]. In this paper, erroneous assignments of some stereochemically important C_{13}—C_{16} signals of the ω-chain are given. In this connection, we have made a detailed study of ^{13}C NMR spectra of the final 16- and 17-aryloxy-11-deoxy-PGE$_1$'s and their initial ω-chains, have made spectral and stereochemical assignments, and have estimated the diastereotopic effects according to the types of chiral centers and the distance between them.

Table 1 gives the chemical shifts (CSs) and multiplicities of some signals and (in the case of the fluorine-substituted derivatives) the $J_{^{13}C-^{19}F}$ spin-spin coupling constants

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