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Note

Crystal structure of 2-deoxy-β-D-*arabino*-hexose (2-deoxy-β-D-glucose)

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The present study was undertaken as part of a programme[1-5] on the physicochemical properties of simple carbohydrates and their derivatives. Knowledge of the preferred conformations and hydrogen bonding in these molecules in the solid state can be utilized for the calculation of cohesive energies and for a better interpretation of their molecular interactions and properties in solution.

A perspective drawing of the molecule of 2-deoxy-β-D-*arabino*-hexose, with the thermal ellipsoids (30% probability) and the atomic numbering scheme used, is

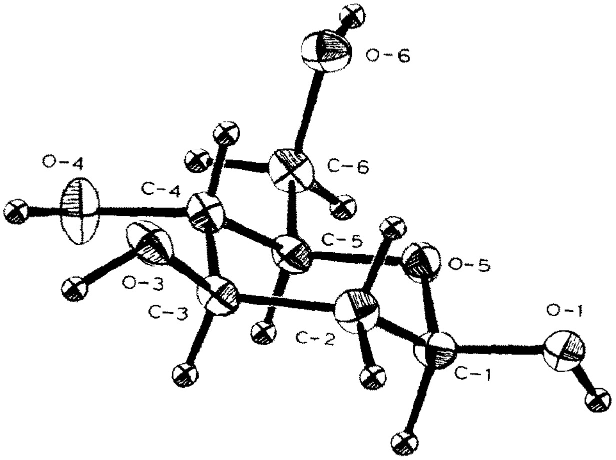

Fig. 1. View of the molecule with numbering scheme. Thermal ellipsoids at 30% probability.

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TABLE I

POSITIONAL PARAMETERS ($\times 10^4$ FOR NON-HYDROGEN ATOMS, $\times 10^3$ FOR HYDROGEN ATOMS) AND THERMAL PARAMETERS ($Å^2$)[a]

	x	y	z	$B_{eq}(B_{iso})$[b]
O-1	9126(3)	−403(2)	2855(2)	3.27(4)
O-3	4144(4)	2408(2)	1135(2)	3.28(4)
O-4	2211(4)	2484(2)	3529(2)	4.47(5)
O-5	6171(3)	55(2)	3860(2)	2.72(3)
O-6	2092(4)	−642(2)	4498(2)	3.32(4)
C-1	7774(5)	591(3)	3118(3)	3.01(5)
C-2	6829(5)	1098(3)	1966(3)	3.12(5)
C-3	5166(5)	2078(3)	2226(2)	2.67(5)
C-4	3607(5)	1539(3)	3107(2)	2.66(5)
C-5	4658(5)	993(3)	4216(2)	2.56(5)
C-6	3204(5)	361(3)	5079(2)	3.01(5)
HO-1	994(5)	−42(3)	352(3)	3.27
HO-3	406(5)	331(3)	105(2)	3.28
HO-4	181(6)	306(3)	290(3)	4.47
HO-6	164(5)	−116(3)	515(3)	3.32
H-1	859(5)	140(3)	365(2)	3.01
H′-2	807(5)	146(3)	155(2)	3.12
H″-2	620(5)	32(3)	151(3)	3.12
H-3	583(4)	283(3)	260(2)	2.67
H-4	285(5)	90(3)	271(2)	2.66
H-5	532(5)	168(3)	465(2)	2.56
H′-6	398(5)	10(3)	577(3)	3.01
H″-6	205(5)	101(3)	536(2)	3.01

[a]Standard deviations in parentheses. [b]$B_{eq} = 4/3\Sigma_i\Sigma_j b_{ij}a_i a_j$.

shown in Fig. 1. Final atomic parameters are listed in Table 1* and the intramolecular geometry concerning non-hydrogen atoms is given in Table II. Bond lengths involving hydrogen atoms lie in the range 0.91–1.04 Å.

The pyranose ring is close to the $^4C_1$ chair conformation, as shown by Cremer and Pople[6] puckering parameters, which are $\vartheta = 4.26°$, $Q = 0.5663$, $q_2 = 0.0420$, $q_3 = 0.5648$ Å, and $\phi_2 = 15.40°$ for the standard sequence O-5, C-1–C-5. There is a little distortion towards the twist-boat form ($\phi = 30°$) as frequently occurs in the β-anomers[7]. The primary alcohol group is in a *gauche–gauche* conformation with torsion angles O-5–C-5–C-6–O-6 = −64.6(4)° and C-4–C-5–C-6–O-6 = 57.3(4)°. The *gg* conformation for O-6 occurs very frequently in *gluco* derivatives[8,9], but it is highly disfavoured with respect to the *gt* conformation in the pyranosides in which O-4 is axial[2].

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* The structure factors and anisotropic thermal parameters have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., B.B.A. Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/400/*Carbohydr. Res.*, 182 (1988) 148–152.

TABLE II

BOND LENGTHS, BOND ANGLES, AND TORSION ANGLES[a]

Bonds			
O-1–C-1	1.387(3)	C-1–C-2	1.517(4)
O-3–C-3	1.426(3)	C-2–C-3	1.513(4)
O-4–C-4	1.417(3)	C-3–C-4	1.517(4)
O-5–C-1	1.441(3)	C-4–C-5	1.520(3)
O-5–C-5	1.439(3)	C-5–C-6	1.499(3)
O-6–C-6	1.423(3)		
Angles			
C-1–O-5–C-5	112.9(2)	O-4–C-4–C-3	112.6(2)
O-1–C-1–O-5	106.9(2)	O-4–C-4–C-5	106.1(2)
O-1–C-1–C-2	109.6(2)	C-3–C-4–C-5	111.3(2)
O-5–C-1–C-2	109.1(2)	O-5–C-5–C-4	109.6(2)
C-1–C-2–C-3	111.1(2)	O-5–C-5–C-6	108.0(2)
O-3–C-3–C-2	109.3(2)	C-4–C-5–C-6	113.6(2)
O-3–C-3–C-4	109.2(2)	O-6–C-6–C-5	110.4(2)
C-2–C-3–C-4	110.6(2)		
Torsion angles			
C-5–O-5–C-1–O-1	179.3(4)	O-3–C-3–C-4–C-5	171.8(4)
C-5–O-5–C-1–C-2	−62.2(4)	C-2–C-3–C-4–O-4	170.4(5)
C-1–O-5–C-5–C-4	61.3(4)	C-2–C-3–C-4–C-5	51.5(4)
C-1–O-5–C-5–C-6	−174.4(5)	O-4–C-4–C-5–O-5	−177.7(4)
O-1–C-1–C-2–C-3	173.5(5)	O-4–C-4–C-5–C-6	61.3(4)
O-5–C-1–C-2–C-3	56.7(4)	C-3–C-4–C-5–O-5	−54.9(4)
C-1–C-2–C-3–O-3	−172.7(5)	C-3–C-4–C-5–C-6	−175.9(5)
C-1–C-2–C-3–C-4	−52.5(4)	O-5–C-5–C-6–O-6	−64.6(4)
O-3–C-3–C-4–O-4	−69.3(4)	C-4–C-5–C-6–O-6	57.3(4)

[a] Bond lengths in Å; bond and torsion angles in degrees; standard deviations in parentheses.

Bond lengths and bond angles are in good agreement with the values expected for β-pyranosides[10,11]. The average C–C bond is 1.517 Å with the C-5–C-6 distance slightly but significantly shorter [1.499(3) Å]. The C-1–O-1 bond has a length [1.387(3) Å] which is much shorter than those of the other C–O bonds (on average 1.43 Å). Furthermore, the two bond distances involving the ring oxygen are equal within experimental error. This pattern of bond lengths is a common feature of carbohydrates and has been correlated with the anomeric effect[12,13]. The geometrical parameters involving C-1 (see Table II) are close to the values (C-1–O-1 = 1.389 Å, C-1–O-5 = 1.430 Å, C-1–O-5–C-5 = 112.0°, and O-5–C-1–O-1 = 107.3°) given[11] for an equatorial O-1. For comparison, the corresponding values when O-1 is axial are 1.415 Å, 1.414 Å, 114.0°, and 111.6°, respectively.

A stereoview of the molecular packing is shown in Fig 2, in which the thinner lines indicate the intermolecular H-bonds. The H-bond geometry is reported in Table III. In the present structure, the H-bond pattern involves also the ring oxygen and can be included in the type II classification given by Jeffrey and Mitra[14] for the

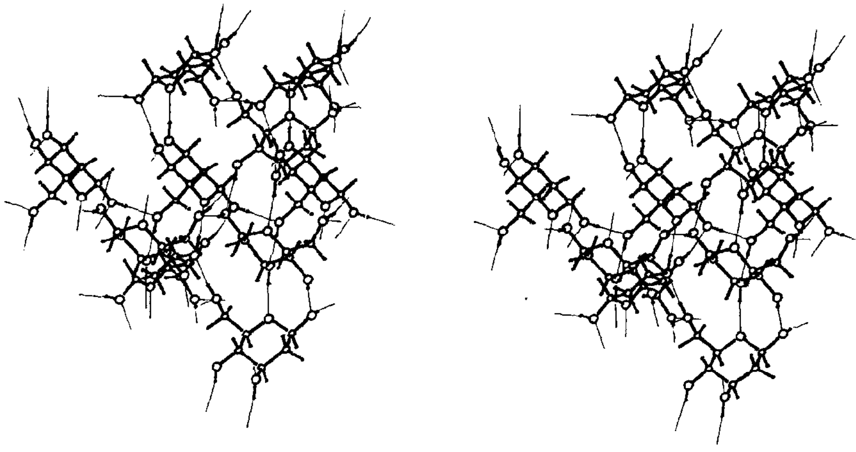

Fig. 2. Stereoview of crystal packing.

crystal structures of pyranosides. The extensive H-bond system consists of finite chains which originate at O-4 (single donor) and terminate at O-5 (single acceptor), whereas each of the remaining hydroxyl oxygens acts as both donor and acceptor in the intermolecular sequence: O-4-H→O-1-H→O-6-H→O-3-H→O-5. The H-bond distances involving the anomeric oxygen [O-1·····O-6 = 2.669(3) Å and O-4·····O-1 = 2.819(3) Å] reflect the nature of O-1, acting usually as a strong donor and weak acceptor[15].

EXPERIMENTAL

Single crystals of 2-deoxy-β-D-*arabino*-hexose, obtained by crystallization from ethanol, are normally lanceolate prismatic in shape and give an X-ray diffraction pattern with a very high ω spread. The large errors associated with the intensity data have, in the past, prevented a good refinement of the structure[16]. By very slow crystallization from ethanol, more-ordered crystals were obtained and new data have been collected on a single crystal of dimensions 0.09 x 0.25 x 0.38 mm. Accu-

TABLE III

H-BOND GEOMETRY[a]

D—H·····A	*D·····A (Å)*	*D—H (Å)*	*H·····A (Å)*	*D—H·····A (°)*
O-1—H·····O-6[a]	2.669(3)	0.91(3)	1.79(3)	162(2)
O-3—H·····O-5[b]	2.759(2)	0.95(3)	1.82(3)	171(2)
O-4—H·····O-1[b]	2.819(3)	0.96(3)	1.90(3)	159(2)
O-6—H·····O-3[c]	2.709(3)	0.95(3)	1.77(3)	167(2)

[a] Symmetry code: a = $1+x,y,z$; b = $1-x$, $1/2+y,1/2-z$; c = $1/2-x$, $-y,1/2+z$.

rate cell parameters were obtained by least-squares refinement of the setting angles of 24 reflections ($19° \leqq \vartheta \leqq 26°$) carefully centered, using Cu-K_α filtered radiation and an Enraf-Nonius CAD-4F diffractometer on line with a PDP11/34 Digital computer. Crystal data: $C_6H_{12}O_5$, $M_r = 164.16$, or thorombic, space group $P2_12_12_1$ with $a = 6.494(1)$, $b = 10.392(2)$, Å, $V = 751.6(4)$ Å^3, $Z = 4$, $D_x = 1.451$ g $D_x = 1.451$ g cm^{-3}. Intensities of 917 independent reflections with $\vartheta \leqq 75°$ were collected at room temperature, using the $\omega - \vartheta$ scan mode. The equipment and crystal stability were checked by four standard reflections monitored at intervals of 5 h (3% variation) during the data collection; 782 reflections with $I \geqq 3\sigma(I)$ were considered observed. Intensities were corrected for Lp factors, absorption ignored (μ = 1.05 mm^{-1}). The structure was solved using MULTAN-79[17]. The refinement of positional and anisotropic parameters for all non-hydrogen atoms was carried out by full-matrix (on F) least-squares method, yielding a conventional R value of 0.072. At this point, all the H-atoms were unambiguously located from a difference electron-density map and included in the last refinement cycles with isotropic thermal parameters fixed equal to the B_{eq} of the parent atoms (only positional parameters refined for H-atoms). At convergence, the final discrepancy index $R = \Sigma||F_o - F_c||/\Sigma|F_o|$ was 0.037, $R_w = 0.053$ with $w^{-1} = \sigma^2(F_o)$, and σ from counting statistics. During the crystallographic work, the equipment of the "Centro di Metodologie Chimico-fisiche dell'Università di Napoli" and the SDP package were used. Atomic scattering factors were taken from Cromer and Waber[18].

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