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THE CRYSTAL STRUCTURE OF 2-DEOXY-β-D-*arabino*-HEXOPYRANOSE AT −150°

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ABSTRACT

2-Deoxy-β-D-*arabino*-hexopyranose, $C_6H_{12}O_5$, is orthorhombic, $P2_12_12_1$, with cell dimensions at −150° [20°], a = 6.484(2) [6.510(3)], b = 10.364(2) [10.427(4)], c = 11.134(3) [11.153(5)] Å, V = 748.2 [757.1] Å^3, Z = 4, D_x = 1.457 [1.440], and D_m = [1.455] g.cm^{-3}. The intensities of 1269 reflections were measured by using MoKα radiation. The structure was solved by direct methods, and refined by full-matrix least-squares, with anisotropic, thermal parameters for the carbon and oxygen atoms, and isotropic parameters for the hydrogen atoms. The pyranose has the $^4C_1$(D) conformation, with puckering parameters Q = 0.563 Å, θ = 3.9°, and φ = 350.3°. The departure from ideality is very small, and less than that in β-D-glucopyranose, Q = 0.584 Å and θ = 6.9°. The β-glycosidic, C–O bond is short, 1.383(4) Å, and the O–C–O–H torsion angle is −87°, consistent with the anomeric effect. The hydrogen-bonding scheme consists of infinite chains, with side chains terminating at a ring-oxygen atom.

EXPERIMENTAL

A sample of 2-deoxy-D-*arabino*-hexopyranose ("2-deoxy-D-glucopyranose"), $C_6H_{12}O_5$ (CAS Reg. No. 154–17–16) from Sigma Chemical Company was recrystallized from ethanol–water solution at room temperature. The crystals were twinned, except for those which were very thin plates, one of which was selected for data collection. A crystal 0.40 × 0.13 × 0.05 mm was used with graphite-monochromated, MoKα radiation (λ = 0.7107 Å) on a CAD-4 diffractometer at −150°. The unit-cell dimensions were measured at room temperature, and at −150°, from a least-squares analysis of the $\sin^2\theta$ values of 25 reflections with $12 < \theta < 19°$. Of the 1296 symmetry-independent reflections measured, 729 had $I > 2\sigma(I)$. No corrections were made for absorption ($\mu_{MoK\alpha}$ = 1.37 cm^{-1}) or extinction.

The structure was solved with the direct-method program, MULTAN[1], using 144 structure amplitudes with E > 1.53. All non-hydrogen atoms appeared in the E-maps, and all the hydrogen atoms were observed on subsequent, difference maps. There was no evidence of an α,β mixture in the crystal such as is observed in crystals of 6-deoxy-α-L-sorbopyranose[2], and, more commonly, in those of several disaccharides.

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TABLE I

FRACTIONAL ATOMIC COORDINATES[a] AND THERMAL PARAMETERS[b] FOR 2-DEOXY-β-D-*arabino*-HEXOPYRANOSE AT −150°

Atom	x	y	z	β_{11} *or* B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C-1	2226(6)	4414(4)	3115(3)	74(9)	28(4)	35(3)	−8(5)	−4(4)	4(3)
C-2	3141(6)	3887(3)	1956(3)	96(9)	33(4)	26(2)	3(5)	−18(4)	−4(3)
C-3	4834(6)	2910(3)	2223(3)	103(9)	22(3)	27(3)	−2(5)	0(5)	1(3)
C-4	6397(6)	3461(3)	3101(3)	101(10)	23(3)	26(3)	3(5)	−16(4)	5(3)
C-5	5331(5)	4000(3)	4219(3)	68(8)	18(3)	26(2)	−1(5)	−4(4)	3(2)
C-6	6793(6)	4644(4)	5090(3)	110(10)	33(4)	22(2)	12(6)	−3(4)	−3(3)
O-1	847(4)	5395(3)	2850(2)	100(7)	28(3)	52(2)	10(4)	6(3)	2(2)
O-3	5882(5)	2579(3)	1126(2)	163(8)	21(3)	31(2)	−4(4)	20(3)	−1(2)
O-4	7797(5)	2501(3)	3526(2)	181(8)	52(3)	38(2)	50(5)	−22(4)	−14(2)
O-5	3812(4)	4943(2)	3860(2)	83(6)	24(2)	34(2)	9(4)	2(3)	−6(2)
O-6	7911(4)	5651(3)	4495(2)	116(7)	36(3)	29(2)	−21(4)	−1(3)	−12(2)
H-C-1	144	365	359	2.5					
H-C-21	380	467	145	2.5					
H-C-22	195	343	144	2.5					
H-C-3	414	205	260	2.5					
H-C-4	726	422	266	2.5					
H-C-5	455	323	467	2.5					
H-C-61	787	393	543	2.5					
H-C-62	592	505	583	2.5					
H-O-1	−11(7)	540(5)	349(4)	4(1)					
H-O-3	590(10)	199(6)	108(5)	7(2)					
H-O-4	825(7)	214(4)	299(3)	3(1)					
H-O-6	820(5)	605(3)	504(3)	0(8)					

[a]Values are $\times 10^4$ for non-hydrogen atoms, $\times 10^3$ for hydrogen atoms. Estimated, standard deviations, given in parentheses, refer to the least-significant digit. [b]Values are $\times 10^4$ for non-hydrogen atoms. The anisotropic-temperature expression is $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The isotropic-temperature expression is: $T = \exp[-(B\sin^2\theta/\lambda^2)]$.

The atomic parameters were refined by using full-matrix least-squares[3], minimizing $\Sigma\omega||F_o| - k|F_c||^2$, with $\omega^{-1} = \sigma_c^2$, where σ_c is from counting statistics. Anisotropic temperature-factors were used for carbon and oxygen atoms, and isotropic temperature-factors for hydrogen atoms. The methylene hydrogen-atom coordinates were fixed at calculated positions, with tetrahedral-carbon geometry and C–H = 1.08 Å. The hydroxyl hydrogen-atom positions cannot be deduced in this way, and were refined in the analysis. The standard, atomic scattering-factors were used[4,5]. The final agreement-factors are R = 0.058, R_ω = 0.045 for the 729 observed reflections*, and S = 1.02 for all 1269 measured reflections. The atomic parameters are given in Table I. The atomic notation and thermal ellipsoids are given in Fig. 1,

*Tables of observed and calculated structure factors have been deposited with, and can be obtained from: Elsevier Scientific Publishing Company, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/208/*Carbohydr. Res.*, 97 (1981) 199–204.

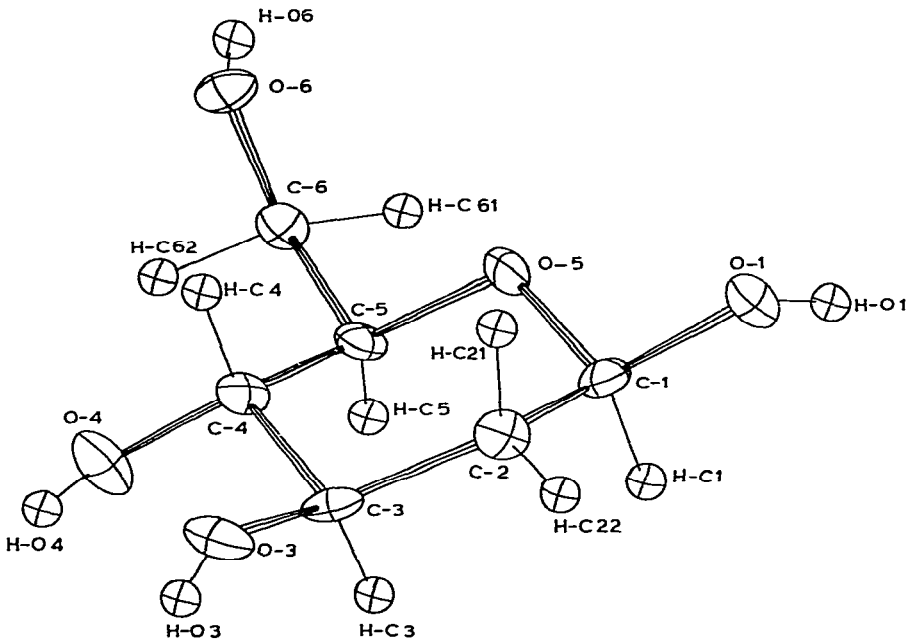

Fig. 1. 2-Deoxy-β-D-*arabino*-hexopyranose at −150°. [Atomic notation and thermal ellipsoids at 50% probability[13].]

the molecular dimensions in Fig. 2, and the hydrogen-bonding scheme and geometry in Fig. 3.

DISCUSSION

The molecule has the expected $^4C_1$(D) conformation, which is very close to ideal, with puckering parameters[6] of Q = 0.563 Å, θ = 3.9°, and φ = 350.3°. This is compared with Q = 0.549, 0.584 Å, θ = 3.5, 6.9° for α- and β-D-glucopyranose, respectively. (At small values of θ, differences in φ are not significant[7].) The degree of ring puckering, Q, is mid-way between that of α- and β-D-glucose. The shape of the ring is unusually symmetrical with respect to a mirror plane through C-3 and O-5. As shown in Fig. 2, the corresponding bond-lengths across the ring differ by less than 0.015 Å, and the ring torsion-angles by less than 1°. The O-1–O-4 "virtual bond" distance is 5.465 Å, which is 0.01 Å longer than in β-D-glucose, but very close to the Arnott–Scott[8] mean value of 5.468 Å. The orientation of the primary alcoholic group is *gauche*/*gauche* with O-5–C-5–C-6–O-6 = −65°.

The stereochemistry about the β-anomeric carbon atom is characteristic for a β-pyranose molecule; C-1–O-1 = 1.386(4) Å, and the O-5–C-1–O-1 valence-angle is 107.8(3)°. The glycosidic torsion angle O-5–C-1–O-1–H is −87(3)°. This is greater than in other β-pyranoses, the values for which range[9] from −72 to −80°. This angle is very dependent on the hydrogen-bonding requirements in the crystal structure.

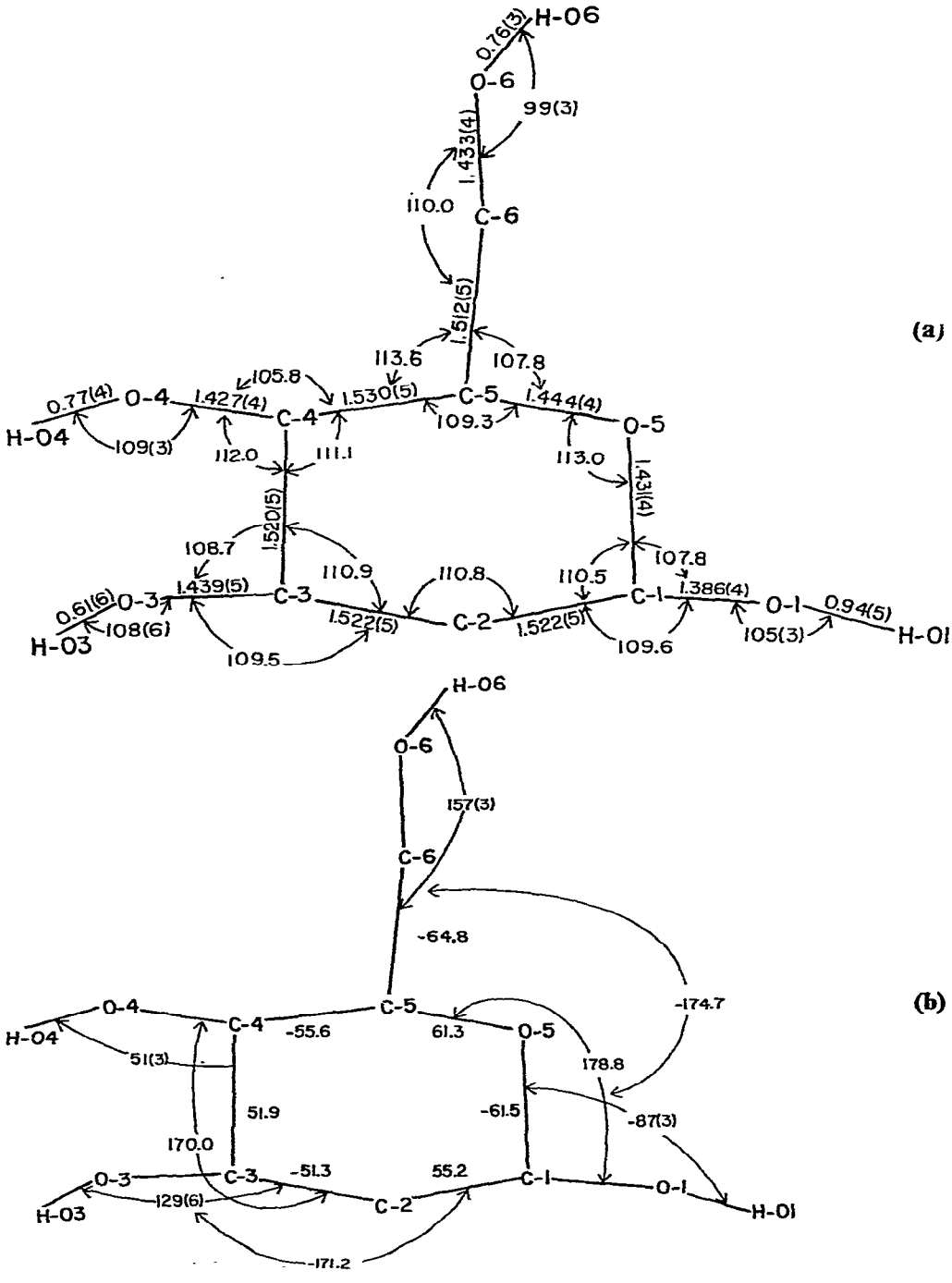

Fig. 2. (a) Bond lengths (Å) and valence angles (°) in 2-deoxy-β-D-*arabino*-hexopyranose. [The standard deviations of the angles are (0.3°), except where indicated otherwise.] (b) Torsion angles (°) in 2-deoxy-β-D-*arabino*-hexopyranose. [The standard deviations are (0.3–0.4°), except where indicated otherwise.]

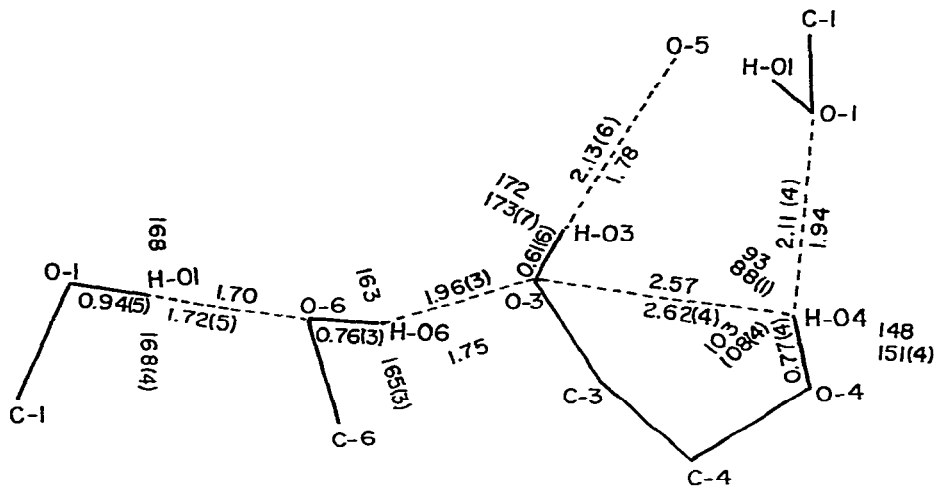

Fig. 3. Hydrogen bonding in the crystal structure of 2-deoxy-β-D-*arabino*-hexopyranose. [The values lacking standard deviations in parentheses were obtained with normalized, O–H covalent-bond distances of 0.97 Å].

The hydrogen bonding, shown in Fig. 3, consists of infinite chains, where the weak intramolecular-component of the bifurcated bond from O-4–H is included. The ring-oxygen atom, O-5, is hydrogen-bonded through a side-chain from O-3-H. This scheme therefore includes all of the oxygen atoms in the structure, and has the maximum cooperative energy. It is consistent with the hydrogen-bonding patterns observed in other monosaccharide structures[10].

Using normalized, O-H covalent bond-lengths of 0.97 Å, the O-1-H–O-6 hydrogen bond is the shortest in the crystal structure, as predicted from the charge distribution associated with the anomeric effect[12]. Excluding the weak intramolecular-bond, the mean H–O bond length is 1.793 Å, which is shorter than the mean value of 1.818 Å obtained from an analysis of the data from 24 neutron-diffraction crystal-structures. This is not surprising, in view of the scheme of infinite chains which includes the ring-oxygen atoms, and thereby optimizes the total, hydrogen-bonding component to the lattice energy of the crystal.

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