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Note

6-Deoxy-α-L-sorbofuranose: anomeric disorder in a furanoid sugar crystal

S T RAO, PANCHANADAM SWAMINATHAN AND MUTTAIYA SUNDARALINGAM*
Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin–Madison, Madison, Wisconsin 53706 (U.S.A.)

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Further examination of the crystal structure of 6-deoxy-γ-L-sorbofuranose (space group $P2_12_12_1$, $a = 18.470$, $b = 7.636$, $c = 5.371$ Å), recently reported from this laboratory as existing exclusively in the γ-furanose form[1], has revealed the existence of 5% of the β anomer in admixture with 95% of the γ-furanose form. In solution, the γ:β ratio is 83:17.

Refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$, $\sigma = 4.0$ for $F_o < 40$ and $\sigma = 4.0 + 0.062(F_o - 40)$ for $F_o > 40$, starting with the earlier set of atomic coordinates followed by difference electron-density maps showed all of the hydrogen-atom densities with a 2:1 disorder in the position of H(O-1′). Moreover, there were three residual peaks around the anomeric carbon atom (C-2′) which suggested the presence of a minor proportion of the β-furanose form of the sugar. Inclusion of these minor sites in further refinement led to the final *R*-value ($= \sum||F_o| - |F_c||/\sum|F_o|$) of 0.033 for 560 observed reflections and 0.052 for all 744 reflections. The occupancy factor for the β-furanose form was 0.05(4). The final, residual density-map did not contain any peaks greater than 0.08 e Å^{-3}. The atomic parameters are given in Table I†.

The bond lengths, bond angles, and torsional parameters showed little change from the earlier values (Fig. 1). However, their e.s.d. values are now ~15% smaller. The O-1′* atom of the β anomer is at hydrogen-bonding distance to O-1′ of the γ anomer, translated along the *c* axis. H(O-4′) makes a bifurcated hydrogen-bond with O-3 and O-2′ of a symmetry-related molecule of the γ anomer. When the latter site is occupied by the β anomer, there appears to be a hydrogen bond to O-1* instead.

*To whom correspondence should be addressed.

†The anisotropic thermal parameters, the table of hydrogen bonds, and the table of observed and calculated structure-amplitudes are deposited with and can be obtained from Elsevier Scientific Publishing Co., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/162 *Carbohydr. Res.*, 89 (1981) 151–154.

TABLE I

POSITIONAL AND THERMAL PARAMETERS OF ATOMS IN 6-DEOXY-α-L-SORBOFURANOSE[a]

Atom	*Occupancy*	x	y	z	B_{iso}(Å^2)
O-1′	0 95	0 2198(2)	0 3011(5)	−0 2862(6)	3 62
O-2′	0 95	0 1436(2)	0 1874(5)	0 3177(5)	2 93
O-3′	1 00	0 0404(1)	0 1399(4)	−0 0180(6)	2 81
O-4′	1 00	−0 0204(1)	0 5096(4)	−0 0089(6)	2 82
O-5′	1 00	0 1679(1)	0 4671(3)	0 1544(5)	2 57
C-1′	0 95	0 2123(2)	0 2147(6)	−0 0520(9)	3 03
C-2	1 00	0 1507(2)	0 2915(6)	0 0951(8)	2 64
C-3′	1 00	0 0776(3)	0 3003(5)	−0 0331(8)	2 29
C-4′	1 00	0 0417(2)	0 4437(6)	0 1123(8)	2 36
C-5′	1 00	0 1025(2)	0 5767(6)	0 1447(8)	2 60
C-6	1 00	0 1105(3)	0 7081(6)	−0 0604(10)	3 62
O-1′*	0 05	0 175 (3)	0 096 (8)	0 300 (12)	4 07
O-2 *	0 05	0 168 (3)	0 325 (8)	−0 060 (11)	3 73
C-1′*	0 05	0 203 (4)	0 165 (9)	0 095 (14)	2 11
H(O-1′)1	0 66	0 200 (2)	0 394 (6)	−0 267 (9)	0 79
H(O-1′)2	0 33	0 262 (5)	0 393 (14)	−0 263 (20)	1 76
H(O-2′)	1 00	0 177 (3)	0 188 (7)	0 399 (13)	7 76
H(O-3′)	1 00	0 030 (3)	0 116 (7)	−0 132 (12)	8 24
H(O-4′)	1 00	−0 047 (2)	0 541 (6)	0 082 (9)	4 80
H(C-1′)A	1 00	0 263 (2)	0 214 (5)	0 050 (7)	3 33
H(C-1′)B	1 00	0 201 (2)	0 081 (6)	−0 074 (9)	6 02
H(C-3′)	1 00	0 081 (2)	0 332 (4)	−0 201 (7)	1 86
H(C-4′)	1 00	0 030 (2)	0 393 (5)	0 254 (8)	3 23
H(C-5′)	1 00	0 099 (2)	0 633 (6)	0 308 (10)	6 03
H(C-6′)A	1 00	0 067 (2)	0 781 (6)	−0 081 (10)	5 24
H(C-6′)B	1 00	0 108 (3)	0 626 (7)	−0 231 (11)	7 83
H(C-6′)C	1 00	0 157 (2)	0 771 (6)	−0 044 (10)	5 76

[a]Standard deviations refer to the least-significant digits For the first eleven anisotropic atoms, B_{iso} is calculated from $\frac{4}{3}\sum_i\sum_j \beta_{ij}\,(a_i \cdot a_j)$

of to O-2′ There is no hydrogen bond involving O-2′* of the β anomer The hydrogen atom H(O-1′) of the α anomer is distributed over two sites, with occupancies 0 66 and 0 33 The higher-occupied H(O-1′) site is too far to make a good intramolecular hydrogen-bond to O-5′ (the ring-oxygen atom) The lower-occupied site H(O-1′) forms a normal hydrogen-bond with O-5′ of a symmetry-related molecule

The co-existence of α and β anomers in the crystalline state is always a possibility where an anomeric mixture exists in solution It is common in reducing disaccharides[3−9], but has rarely been observed by crystallography in monosaccharides — the only exception being 2-acetamido-2-deoxy-D-glucose[2,10] Interestingly, in all known cases of anomeric disorder, the major component is the α anomer 6-Deoxy-α-L-sorbofuranose is the first instance of anomeric disorder to be observed in a furanoid-sugar crystal, and the anomerization occurs between the OH group and a bulky

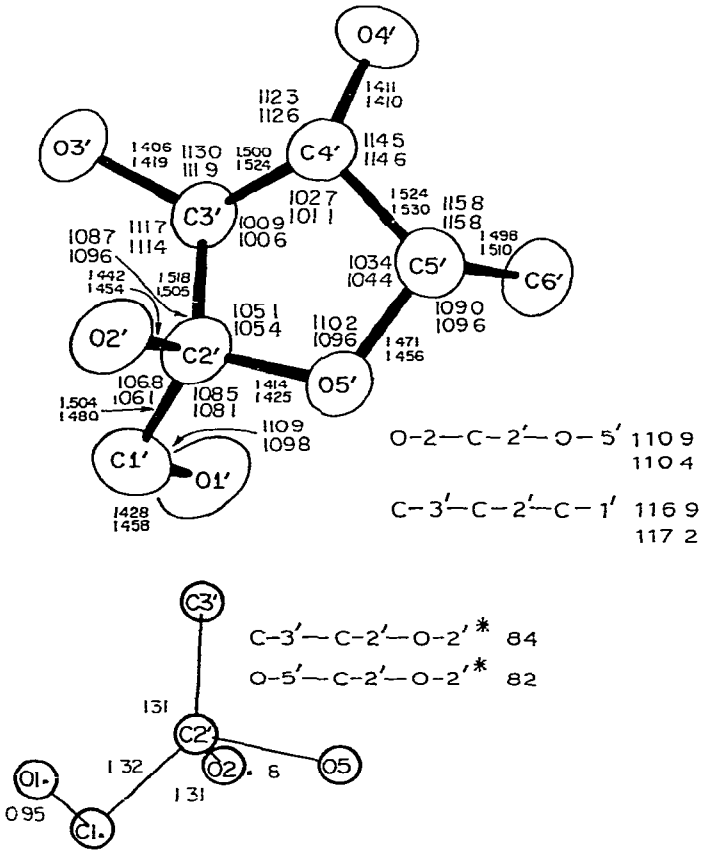

Fig 1 Bond lengths and bond angles in 6-deoxy-α-L-sorbofuranose shown on an ORTEP[11] diagram The boundaries of the 50%-probability ellipsoids are shown The values from the present refinement are given and, below each number, the corresponding values from the earlier study are shown The mean standard-deviations in the bond lengths and bond angles are 0 005Å and 0 35°, respectively, for the α anomer The bond lengths and bond angles involving the β anomer are shown in the lower part of the figure The standard deviations in the bond lengths and bond angles are 0 08 Å and 6°, respectively

CH_2OH group rather than between OH and H When anomeric crystallization occurs, the α,β proportions in the crystal depend on a number of non-equilibrium conditions, such as the rate of crystallization In the case of α,β-maltose, three different investigators have reported three different ratios of α and β in the crystal[3–5] Thus, the 5% population of the β form we have found is a property of this particular crystal another crystallization may well result in only one anomer's being present, or both anomers with a different α,β ratio

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