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Structure of 4-Deoxy-4-fluoro-β-D-fructopyranose, $C_6H_{11}FO_5$

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Abstract. $M_r = 182\cdot15$, $P2_12_12_1$, $a = 7\cdot787\,(1)$, $b = 9\cdot272\,(2)$, $c = 10\cdot224\,(2)$ Å, $V = 738\cdot2\,(2)$ Å^3, $Z = 4$, $D_m = 1\cdot615\,(1)$, $D_x = 1\cdot64\,(1)$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot107$ mm^{-1}, $F(000) = 384$, $T = 296$ K, $R = 0\cdot043$ for 1254 unique reflexions. The material was prepared by specific dehydrogenation of 3-deoxy-3-fluoro-D-mannitol by *Gluconobacter oxydans* [Buděšínský, Černý, Doležalová, Kulhánek, Pacák & Tadra (1984). *Collect. Czech. Chem. Commun.* **49**, 267–274]. The molecular structure and conformation, $^2C_5$(D), are in accordance with literature data. The molecules are connected by hydrogen bonds, so that they form a three-dimensional network.

Introduction. The title compound is not a naturally occurring monosaccharide and was prepared for the study of its biochemical properties especially from the point of view of differences between the molecular structure in solution and in the crystalline state. The crystal structure of the parent β-D-fructopyranose has already been determined [X-ray data: Kanters, Roelofsen, Alblas & Meinders (1977), abbreviated X hereafter; neutron data: Takagi & Jeffrey (1977), abbreviated N].

Experimental. D_m measured by flotation. Clear colourless prismatic crystals with well developed faces. Spherical crystal, $R = 0\cdot19$ mm. Syntex $P2_1$ diffractometer, graphite monochromator. Unit cell: 25 reflexions in θ range 12–20°. Max. $(\sin\theta)/\lambda = 0\cdot68$ Å^{-1}. *hkl* octant with $h_{\max} = 10$, $k_{\max} = 12$, $l_{\max} = 14$. Two standard reflexions monitored every 100 reflexions. 1273 measured reflexions, 1254 unique, 186 with $I < 1\cdot96\sigma(I)$. No absorption correction. Direct methods. F magnitudes in full-matrix least-squares refinement in two blocks. All H atoms from ΔF synthesis. Positions, scale factor, anisotropic temperature factors of non-H atoms and isotropic temperature factors of H atoms refined. $R = 0\cdot043$, $wR = 0\cdot046$, $w = 0\cdot5003[\sigma^2(F) + 0\cdot002341F^2]^{-1}$. $(\Delta/\sigma)_{\max}$ for C, O, F 0·023, for H 0·031. Max. and min. height in final $\Delta\rho$ map 0·34 and $-0\cdot26$ e Å^{-3}. Standard tabulations of scattering factors for C, O, F (Cromer & Mann, 1968) and for H (Stewart, Davidson & Simpson, 1965). ICL4-72 computer. Programs *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Discussion. The final atomic parameters are given in Table 1.† The conformation of the molecule is depicted in Fig. 1. The intramolecular and some intermolecular bond distances and angles are given in Table 2. The title compound is isostructural with β-D-fructopyranose and corresponding bond parameters are in reasonable agreement (X,N). The mean value of the C—C distances in fluorofructopyranose is 1·52 (2) Å and in fructopyranose 1·52 (2) Å (X) and 1·53 (1) Å (N). The endocyclic C(2)—C(3) distance is longer than the mean value by 12σ (X: 5σ; N: 17σ). The distance C(5)—C(6) is very short [X: 1·494 (5); N: 1·511 (2) Å]. The anomeric C(2)—O(2) distance is also very short [X: 1·411 (4); N: 1·407 (2) Å] and differs by 8σ from the mean (X: 3σ; N: 6σ). The distance C—F is very similar to the mean value of 1·40 (2) Å of four deoxyfluoro derivatives of hexoses (Campbell, Dwek, Kent & Prout, 1969; Kothe, Luger & Paulsen, 1976, 1979).

The mean values of the C—C—C and C—C—O(H) angles are 111 (1) and 110 (2)° (X; N: the same values). A significant deviation from this mean is found for the C(1)—C(2)—O angle [X: 104·6 (2), N: 104·5°].

The conformational ring angles range from 50·3 to 60·9° (X: 52·2–58·0; N: 53·2–58·9°) and so are close to the range 55·8–61·7° reported for an ideal, strain-free pyranose ring (Kim & Jeffrey, 1967). The deviations from the three least-squares planes are in the range $-0\cdot654$ to 0·692 Å (X: $-0\cdot659$ to 0·661 Å). The exocyclic torsion angles are close to the ideal values of 60 and 180° respectively. The greatest deviations are found in the angles around the C(2)—C(3) bond, which is also the longest of the present C—C bonds.

In Table 2 intramolecular and intermolecular distances <3·1 Å are listed together with distance and angle parameters concerning hydrogen bonds. Five hydrogen bonds are intermolecular and one is intramolecular (Fig. 2). All hydroxyl groups act as H

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† Lists of strucutre factors, anisotropic thermal parameters, endocyclic and exocyclic torsion angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39353 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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donors: OH(1), OH(3) twice and OH(2), OH(5) once. All hydroxyl O atoms also act once as acceptor; the ring O atom is an acceptor twice, with intramolecular and very weak intermolecular interactions.

Table 1. *Atomic coordinates and isotropic thermal parameters* ($\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

For non-hydrogen atoms $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

	x	y	z	$U_{eq}/U(\text{Å}^2)$
F	3621 (2)	1579 (2)	2683 (1)	371 (6)
O	43 (2)	−1269 (2)	4055 (1)	245 (6)
O(1)	−2420 (2)	−87 (2)	2438 (2)	349 (7)
O(2)	−238 (2)	627 (2)	5531 (1)	269 (6)
O(3)	562 (2)	2655 (2)	3728 (2)	278 (7)
O(5)	2546 (2)	−1205 (2)	2106 (1)	325 (7)
C(1)	−2255 (2)	294 (2)	3771 (2)	265 (8)
C(2)	−392 (2)	200 (2)	4224 (2)	199 (7)
C(3)	786 (2)	1183 (2)	3400 (2)	204 (7)
C(4)	2657 (2)	810 (2)	3601 (2)	247 (8)
C(5)	2954 (2)	−790 (2)	3408 (2)	271 (9)
C(6)	1799 (3)	−1610 (2)	4315 (2)	296 (9)
H(O1)	−197 (5)	−84 (4)	234 (3)	59 (10)
H(O2)	−93 (4)	24 (3)	602 (2)	33 (7)
H(O3)	−33 (4)	293 (3)	342 (3)	37 (8)
H(O5)	336 (4)	−105 (3)	162 (3)	47 (9)
H(1*A*)	−293 (3)	−32 (3)	432 (2)	22 (6)
H(1*B*)	−269 (4)	121 (4)	395 (3)	41 (7)
H(3)	45 (3)	100 (2)	254 (2)	13 (5)
H(4)	299 (3)	111 (3)	448 (3)	27 (6)
H(5)	403 (4)	−104 (3)	357 (3)	34 (7)
H(6*A*)	208 (4)	−143 (3)	519 (3)	43 (8)
H(6*B*)	190 (3)	−253 (3)	413 (2)	26 (6)

Table 2. *Interatomic distances* (Å) *and angles* (°)

F—C(4)	1·397 (2)	O(1)—C(1)—C(2)	111·4 (2)
C(1)—O(1)	1·414 (3)	O(2)—C(2)—O	111·6 (1)
C(2)—O(2)	1·399 (2)	O(2)—C(2)—C(1)	110·8 (1)
C(3)—O(3)	1·416 (2)	O(2)—C(2)—C(3)	107·7 (1)
C(5)—O(5)	1·422 (3)	C(1)—C(2)—O	104·2 (1)
O—C(2)	1·413 (2)	C(1)—C(2)—C(3)	111·5 (1)
O—C(6)	1·429 (2)	C(3)—C(2)—O	111·1 (1)
C(1)—C(2)	1·526 (2)	O(3)—C(3)—C(4)	107·9 (1)
C(2)—C(3)	1·543 (2)	C(2)—C(3)—O(3)	111·5 (1)
C(3)—C(4)	1·512 (3)	C(2)—C(3)—C(4)	111·3 (1)
C(4)—C(5)	1·515 (3)	F—C(4)—C(5)	109·3 (2)
C(5)—C(6)	1·498 (3)	F—C(4)—C(3)	108·0 (1)
O(1)—H(O1)	0·79 (4)	C(3)—C(4)—C(5)	110·7 (2)
O(2)—H(O2)	0·82 (3)	O(5)—C(5)—C(4)	110·7 (2)
O(3)—H(O3)	0·80 (3)	O(5)—C(5)—C(6)	107·9 (2)
O(5)—H(O5)	0·82 (3)	C(4)—C(5)—C(6)	108·9 (2)
O—O(1)	2·759 (2)	O—C(6)—C(5)	110·3 (2)
O—H(O1)	2·38 (4)	C(2)—O—C(6)	114·8 (1)
		O(1)—H(O1)—O	111 (3)
O(1)—O(3^{i})	2·811 (3)	O(1)—H(O1)—O(3^{i})	152 (2)
O(2)—O(1^{ii})	2·716 (2)	O(2)—H(O2)—O(1^{ii})	155 (2)
O(3)—O^{iii}	3·052 (2)	O(3)—H(O3)—O^{iii}	114 (3)
O(3)—O(5^{iii})	2·775 (2)	O(3)—H(O3)—O(5^{iii})	171 (2)
O(5)—O(2^{iv})	2·698 (2)	O(5)—H(O5)—O(2^{iv})	175 (2)
H(O1)—O(3^{i})	2·09 (4)		
H(O2)—O(1^{ii})	1·95 (3)		
H(O3)—O^{iii}	2·64 (3)		
H(O3)—O(5^{iii})	1·98 (3)		
H(O5)—O(2^{iv})	1·88 (3)		

Symmetry code: (i) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-\frac{1}{2}-x, -y, \frac{1}{2}+z$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (v) $-\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (vi) $\frac{1}{2}-x, -y, \frac{1}{2}+z$.

Present results support the conclusions drawn from NMR measurements (Buděšínský *et al.*, 1984). The parent *β*-D-fructopyranose exists in deuterium oxide as a mixture of tautomeric forms (α-pyranose 2%, *β*-pyranose 70%, α-furanose 5%, *β*-furanose 23%; Horton & Wałaszek, 1982) and in the crystalline state as the *β*-D-fructopyranose. The 4-fluoro analogue exists in deuterium oxide practically in only one form, and that is the same as in the crystalline form; namely the *β*-pyranose is in the $^{2}C_{5}$(D) conformation. The replacement of the hydroxyl group by an F atom has only a very small influence on the geometry of the chair conformation. The value of the coupling constant $J_{3,4}$ is 9·75 Hz, in accordance with a torsion angle H(3)—C(3)—C(4)—H(4) = 173·8°, while the torsion angles

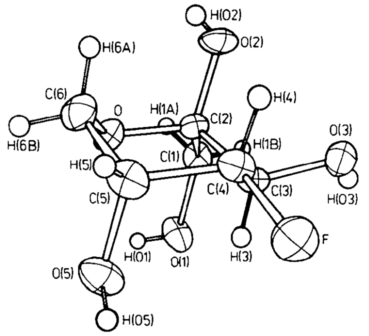

Fig. 1. A molecule of 4-deoxy-4-fluoro-*β*-D-fructopyranose. F, O and C atoms are represented by thermal ellipsoids at the 50% level (Johnson, 1965).

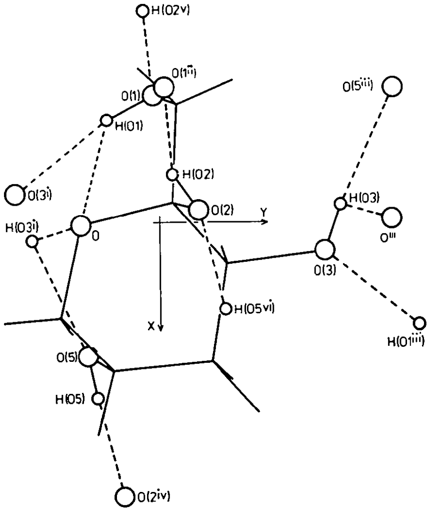

Fig. 2. A view of the structure of 4-deoxy-4-fluoro-*β*-D-fructopyranose down *Z* with hydrogen bonds indicated by dashed lines. For symmetry code see Table 2.

H(4)—C(4)—C(5)—H(5) = −55·7, H(5)—C(5)—C(6)—H(6A) = 57·9 and H(5)—C(5)—C(6)—H(6B) = −63·9° have constants $J_{4,5} = 3{\cdot}5$, $J_{5,6A} = 1{\cdot}6$ and $J_{5,6B} = 2{\cdot}0$ Hz. Restricted rotation around the C(1)—C(2) bond, investigated by ^{1}H NMR measurements, gives evidence for the intramolecular hydrogen bond O(1)—H(O1)···O. The F atom does not take part in any hydrogen bonds.

The molecular conformations of β-D-frutopyranose and the 4-fluoro analogue then only differ in the change O(4)—H(O4) for F. It may be concluded that the hydrogen bond O(4)—H(O4)···O(2$^{\rm i}$) in β-D-fructopyranose is not of crucial importance to the structural packing.

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(*R*,*S*)-2,3-Dihydroxy-2,3-dimethylbutanedioic Acid Monohydrate (*meso*-Dimethyltartaric Acid), $C_6H_{10}O_6.H_2O$

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Abstract. $M_r = 196{\cdot}2$, $C2/c$, $a = 12{\cdot}199\,(3)$, $b = 9{\cdot}177\,(2)$, $c = 7{\cdot}589\,(2)$ Å, $\beta = 98{\cdot}57\,(2)°$, $V = 840{\cdot}2\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}55$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}16$ mm^{-1}, $F(000) = 416$, $T = 293\,(2)$ K, $R = 0{\cdot}041$ for 1013 observed, unique reflections. The molecule has a centrosymmetric antiperiplanar conformation and exhibits C—C bond lengths [C(1)—C(2) 1·543 (2), C(2)—C(2′) 1·572 (2) Å] significantly longer than those found for the non-methyl-substituted parent compound (tartaric acid). The organic molecules pack into sheets parallel to the *ac* plane with the sheets separated by water molecules.

Introduction. Probably no compounds have played so great a role in the founding of organic stereochemistry as tartaric acid, which can exist as a *meso* or *R,S* isomer and as the *R,R* and *S,S* enantiomers. In view of this, it is not surprising that in excess of sixty crystal structures of tartaric acid isomers and their salts and complexes have been reported (Tapscott, 1982). However, it is surprising that to date only three structures of alkyl-substituted tartrates have been published and that all of these have been for coordination compounds (Marcovich, Duesler, Tapscott & Them, 1982; Hahs, Ortega, Tapscott, Campana & Morosin, 1982; Ortega, Tapscott & Campana, 1982). Here we report the structure of $HOOCC(CH_3)(OH)C(CH_3)(OH)COOH$ as the monohydrate. This is the first structure reported for a *meso*-dimethyltartrate in any form and the first reported for any alkyl-substituted tartrate as the free acid.

Experimental. Dimethyltartaric acid was prepared and its isomers were separated by literature methods (Leermakers & Vesley, 1963; Tatsumi, Izumi, Imaida, Fukuda & Akabori, 1966). Crystal obtained by evaporation of ethyl acetate solution, 0·21 × 0·35 × 0·41 mm. D_m not determined. Syntex *P*3/*F* diffractometer, graphite monochromator. Lattice parameters from 25 reflections ($10 < 2\theta < 42°$). Empirical absorption correction based on ψ scans; min. and max. transmission coefficients 0·830 and 0·881. θ–2θ scan, $(\sin\theta)/\lambda = 0{\cdot}01$ to $0{\cdot}70$ Å^{-1} ($1 \le 2\theta \le 60°$, $\pm h$, $\pm k$,

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