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Methyl β-D-fructopyranoside

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In methyl β-D-fructopyranoside, $C_7H_{14}O_6$, the thermodynamically most stable methyl glycoside of the ketose D-fructose, the pyranose ring is close to being an ideal $^2C_5$ chair. The compound forms bilayers involving a complex hydrogen-bonding pattern of five independent hydrogen bonds. Graph-set analysis was applied to distinguish the hydrogen-bond patterns at unary and higher level graph sets.

Comment

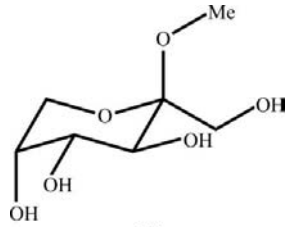
Fructose is a hexose of increasing importance and is produced commercially by enzyme-catalysed epimerization of glucose. For nutritional application, it is often not separated from the residual glucose, but is used as a syrup that approximates the composition of invert sugar syrups, so-called 'high-fructose syrups'. Fructose can also be crystallized from essentially pure fructose syrups.

As distinct from the aldehyde sugars, the ketoses favour different conformational structures. The hexuloses all involve a $-CH_2OH$ residue at C1 and C6 which, especially in the neighbourhood of an anomeric C atom, tends to adopt an equatorial position. Consequently, the anomeric hydroxy group is axial. Thus, sorbose and tagatose form stable pyranoid ring structures, while fructose does not.

For this reason, fructose shows the following distribution of species in aqueous solution: β-D-fructopyranose 64.80%, β-D-fructofuranose 25.25%, α-D-fructofuranose 6.50% and α-D-fructopyranose 2.65% (Wolff & Breitmaier, 1979). Now, to investigate the individual configurations of fructose, we have prepared the compounds methyl β-D-fructopyranoside, methyl α-D-fructofuranoside and methyl β-D-fructofuranoside according to a published procedure (Voss, 1980).

We report here the crystal structure of methyl β-D-fructopyranoside, (I). Our interest lies in the geometry, molecular conformation and hydrogen-bond pattern of the compound. For this network of hydrogen bonds, graph-set analysis according to Etter *et al.* (1990) and Bernstein *et al.* (1995) was applied, taking into account unary, binary and ternary graph sets.

The pyranose ring of (I) is close to being an ideal $^2C_5$ chair, as shown by the Cremer & Pople (1975) puckering parameters, q_2 = 0.0327 (19) Å, q_3 = −0.580 (2) Å, Q = 0.580 (2) Å, φ_2 = 332 (4)° and θ = 177.13 (19)°. The small distortion is in the direction of a twist-boat (φ_2 = 330°). The conformation of the molecule and the numbering of the atoms are shown in Fig. 1. The puckering parameters are close to those of β-D-fructopyranose (q_2 = 0.026 Å, q_3 = −0.555 Å, Q = 0.556 Å, φ_2 = 47.9° and θ = 177.3°; Takagi & Jeffrey, 1977, 1978). For the crystal structure of the related β-D-fructopyranoside, see Kanters *et al.* (1977) and Takagi & Jeffrey (1977, 1978).



(I)

In contrast with the conformation of the compound, the hydrogen-bond pattern differs from that of β-D-fructopyranose. The five independent hydrogen bonds, labelled (*a*)–(*e*) in Table 1, play a major part in controlling the supramolecular assembly of the molecules. As depicted in Fig. 2, the structure is composed of bilayers along [010] that are held together by van der Waals attraction. No classical hydrogen bonds are found between the bilayers. In contrast, within each bilayer an $R_2^2(10)$ ring motif and two opposite homodromic $C(8)$ chains are detected on the unary level. On the binary level, these two patterns result in a basic $C_2^2(13)$ descriptor [hydrogen bonds (*c*) and (*e*)], whereas a complex $R_4^4(22)$ descriptor better fits the situation.

Patterns for hydrogen bonds (*a*), (*b*), (*d*) and (*e*) in one half of the bilayer perpendicular to [001] are shown in Fig. 3. On

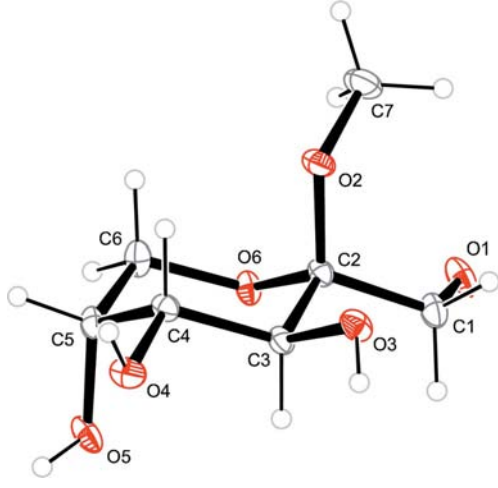


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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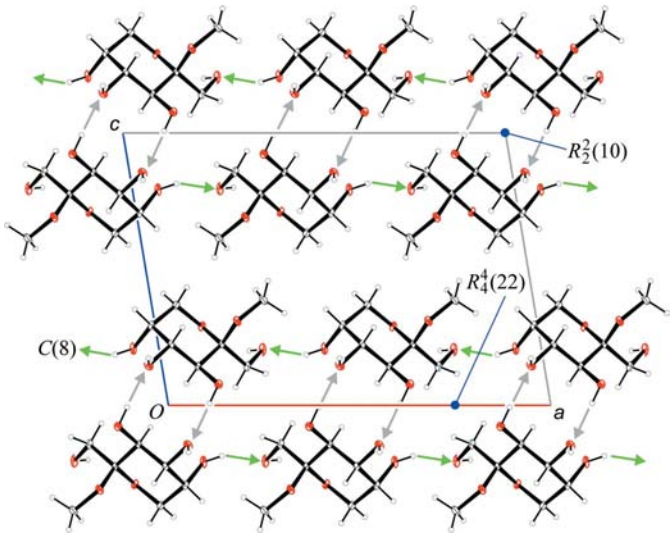

Figure 2
The crystalline packing of (I), viewed along [010]. Note the homodromic hydrogen-bonded $C(8)$ chains along [100] and the $R_2^2(10)$ ring motif formed by hydrogen bond (*c*). The combination of hydrogen bonds (*c*) and (*e*) builds the $C_2^2(13)$ chain. [Colour code in the electronic version of the paper: hydrogen bond (*c*), O3—H···O4, grey; hydrogen bond (*e*), O5—H···O1, green.]

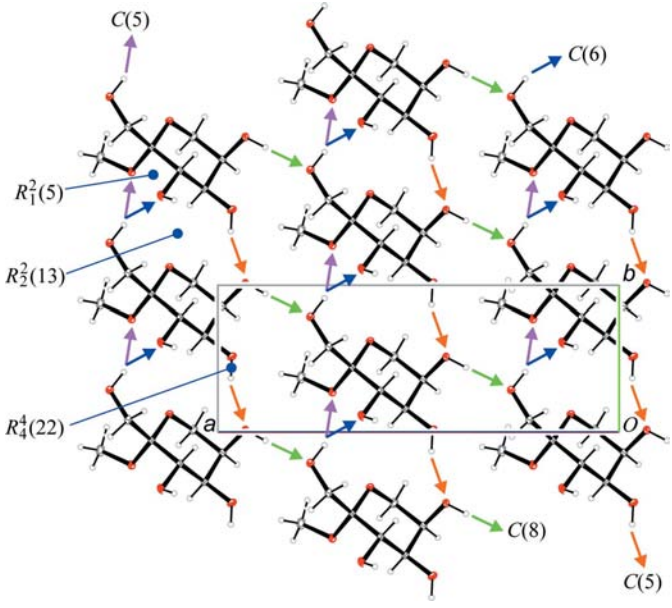

Figure 3
The crystalline packing of (I), viewed along [001], showing four chain motifs (*a*,*b*,*d*,*e*) on the unary level. The combination of alternating hydrogen bonds (*a*,*d*) and (*b*,*d*) can be described as heterodromic $C_2^2(14)$ and $C_2^2(13)$ chains or as homodromic $R_2^2(14)$ and $R_2^2(13)$ rings. Other combinations on the binary level are $C_2^2(13)$ for hydrogen bonds (*a*) and (*e*), $C_2^2(8)$ for (*b*) and (*e*), and $C_2^2(9)$ for (*d*) and (*e*). [Colour code in the electronic version of the paper: hydrogen bond (*a*), O1—H···O2, lilac; hydrogen bond (*b*), O1—H···O3, blue; hydrogen bond (*d*), O4—H···O5, orange; hydrogen bond (*e*), O5—H···O1, green.]

the unary level, these hydrogen bonds all form homodromic chains, so the complete graph-set notation for N_1 is $C(5)C(6)R_2^2(10)C(5)C(8)$. The basic graph set N_2 = $R_1^2(5)C_2^2(14)[R_2^2(14)]C_2^2(13)C_2^2(13)[R_2^2(13)]C_2^2(8)C_2^2(13)C_2^2(9)$ at the binary level indicates the high connectivity of the hydrogen-bonded network. The sets of alternating hydrogen bonds (*a*,*d*) and (*b*,*d*) can be described as heterodromic $C_2^2(14)$ and $C_2^2(13)$ chains or as homodromic $R_2^2(14)$ and $R_2^2(13)$ rings, which connect two molecules of the compound. Furthermore, the $R_1^2(5)$ ring describing a bifurcated hydrogen bond from O1—H81 to the two acceptors O2/O3 is noteworthy. Complex $R_4^4(22)$ descriptors for homodromic combinations of hydrogen bonds (*a*,*e*,*a*,*e*), (*b*,*e*,*b*,*e*) or (*c*,*e*,*c*,*e*) show that the structure is linked in the [001] and [010] directions along the $C(8)$ chain of (*e*) by these rings.

Higher level graph sets, not marked in the figures, can also be defined. On the ternary level there are two chains, $C_3^3(10)$ (*d*,*e*,*a*) and $C_3^3(9)$ (*d*,*e*,*b*), which form a $C_3^3(9)[R_1^2(5)]$ pattern on the quaternary level. Further, a basic $R_2^2(14)[R_1^2(5)]$ descriptor and a complex $R_4^4(23)[R_1^2(5)]$ descriptor can be found on the ternary level, with the latter being the combination of two $R_4^4(22)$ descriptors on the binary level. Besides these hydrogen bonds, the C4—H4···O6 contact, with H···O = 2.43 Å, should be mentioned, although this type of contact is unlikely to be very important in the presence of classical hydrogen bonds.

In conclusion, the most important description of the structure of (I) seems to be that of the unary graph set as, in general, assembling these graph sets provides patterns consisting of a few hydrogen-bond types which are then described by higher level graph sets.

Experimental

The title compound was prepared according to a published procedure (Voss, 1980). D-Fructose (10.5 g) was dissolved in dry methanol (250 ml), concentrated H_2SO_4 (0.9 ml) was added and the reaction mixture stirred for 48 h at room temperature. The reaction was stopped by adding anion-exchange resin (Ionentauscher III, Merck; 15–20 g) and stirring until the pH value was neutral. The resin was filtered off and the methanolic solution reduced *in vacuo*. The resulting syrup was dissolved in water (100 ml), $NaBH_4$ (0.5 g) was added and the mixture stirred for 4–5 h. After adding 2 *M* acetic acid (about 6 ml), the solution was reduced *in vacuo*. To remove the boric acid, methanol was added and removed *in vacuo* several times. For the separation of the three reaction products, ion-exchange chromatography was performed using Dowex 1X2 16–100 mesh chloride anion-exchange resin, and the three fractions were reduced *in vacuo*. Crystals of (I) suitable for X-ray analysis were obtained directly from the crystallized syrup of the first reaction.

Crystal data

$C_7H_{14}O_6$
M_r = 194.18
Monoclinic, *C*2
a = 14.9990 (8) Å
b = 5.4114 (3) Å
c = 10.8287 (6) Å
β = 99.477 (5)°
V = 866.92 (8) Å^3
Z = 4
Mo *Kα* radiation
μ = 0.13 mm^{-1}
T = 200 K
0.51 × 0.49 × 0.15 mm

Data collection

Oxford XCalibur CCD diffractometer
2704 measured reflections
976 independent reflections
914 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Table 1
Hydrogen-bond geometry (Å, °).

Label	D—H···A	D—H	H···A	D···A	D—H···A
(*a*)	O1—H81···O2^{i}	0.84	2.34	3.029 (2)	140
(*b*)	O1—H81···O3^{i}	0.84	2.09	2.802 (2)	142
(*c*)	O3—H83···O4^{ii}	0.84	1.89	2.731 (2)	177
(*d*)	O4—H84···O5^{iii}	0.84	2.05	2.868 (2)	163
(*e*)	O5—H85···O1^{iv}	0.84	1.91	2.718 (2)	162
	C4—H4···O6^{iii}	1.00	2.43	3.226 (2)	136

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.092$
$S = 1.08$
976 reflections
123 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

In the absence of any strong anomalous scatterers, the absolute structure parameter, −0.2 (12), is meaningless. Thus, the 520 Friedel opposites were merged. The absolute configuration was assigned to match that of the parent compound D-fructose. C- and O-bound H atoms were placed in calculated positions, with C—H = 1.00 Å for CH groups, 0.99 Å for CH_2 groups and 0.98 Å for methyl groups, and O—H = 0.84 Å for hydroxy groups, with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH and CH_2 groups, $1.5U_{eq}(C)$ for methyl groups and $1.5U_{eq}(O)$ for hydroxy groups. The H atoms of the CH and CH_2 groups were included in the refinement in the riding-model approximation, and electron-density supported rigid-group refinement was used for the methyl group and for the hydroxy groups [AFIX137 for CH_3 groups and AFIX147 for O—H groups; *SHELXL97* (Sheldrick, 2008)].

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *PLATON* (Spek, 2009)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3186). Services for accessing these data are described at the back of the journal.

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