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Key indicators

Single-crystal X-ray study
T = 190 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.027
wR factor = 0.063
Data-to-parameter ratio = 9.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

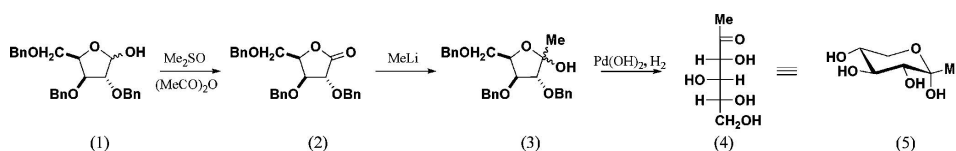
1-Deoxy- α -D-sorbopyranose

The crystalline form of 1-deoxy-D-sorbose, $\text{C}_6\text{H}_{12}\text{O}_5$, is shown to be 1-deoxy- α -D-sorbopyranose. This is the first reported crystal structure of a 1-deoxyketose. The absolute configuration was determined by the use of D-xylose as the starting material. The crystal structure has a three-dimensional hydrogen-bonded network.

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Comment

Although the driving force for the large-scale production of rare sugars by biotechnological (Izumori, 2002; Granström *et al.*, 2004) and chemical (Beadle *et al.*, 1992) methods is driven by the demand for alternative foodstuffs (Skytte, 2002), rare monosaccharides such as D-psicose (Takata *et al.*, 2005; Matsuo *et al.*, 2006) and D-allose (Sui *et al.*, 2005; Hossain *et al.*, 2006) have significant chemotherapeutic properties. As well as being useful for their potential biological properties, the 1-deoxyketoses are likely to provide a new set of building blocks for the synthesis of a wide variety of complex biomolecules. However, the properties of 1-deoxyketoses have been little studied to date; there are no reports of the crystal structure of any of the four diastereomers. As part of our work to extend the range of simple monosaccharide derivatives, 1-deoxy-D-sorbose, (4), was synthesized. Although the compound has been prepared previously (James & Angyal, 1972; Dills & Meyer, 1976), a solution of the compound contains a mixture of equilibrating structures (Angyal *et al.*, 1976). 1-Deoxy-D-sorbose was readily crystallized and this paper firmly establishes that it exists in the crystalline state as the α -anomer of the pyranose ring form, (5), in a chair conformation.



In summary, 1-deoxy-D-sorbose, (4), exists in the crystalline state as 1-deoxy- α -D-sorbopyranose, (5). The absolute configuration was determined by the use of D-xylose as the starting material. A D-sugar is defined by the absolute stereochemistry at C-5 (relative to D-glyceraldehyde); see <http://www.chem.qmw.ac.uk/iupac/2carb/> for an explanation of carbohydrate nomenclature (IUPAC-IUBMB, 1996). The present X-ray crystal structure determined the stereochemistry at the anomeric position (C1) as being α , with the hydroxyl group in the axial position.

The crystal structure of (5) has a three-dimensional hydrogen-bonded network, with each molecule interacting

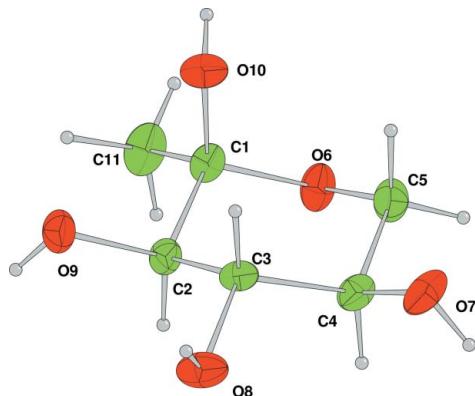


Figure 1
The molecular structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

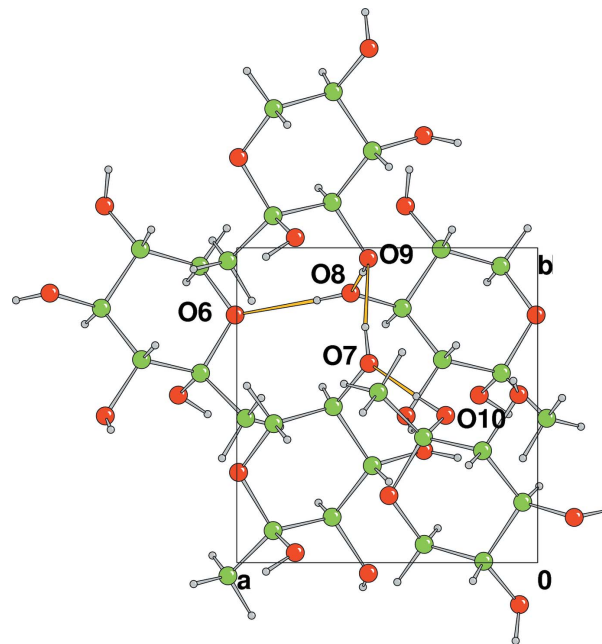


Figure 3
A projection of the crystal structure along the *c* axis, showing the five molecules linked by the discrete hydrogen-bond chain, in which the H...O hydrogen bonds are shown in orange.

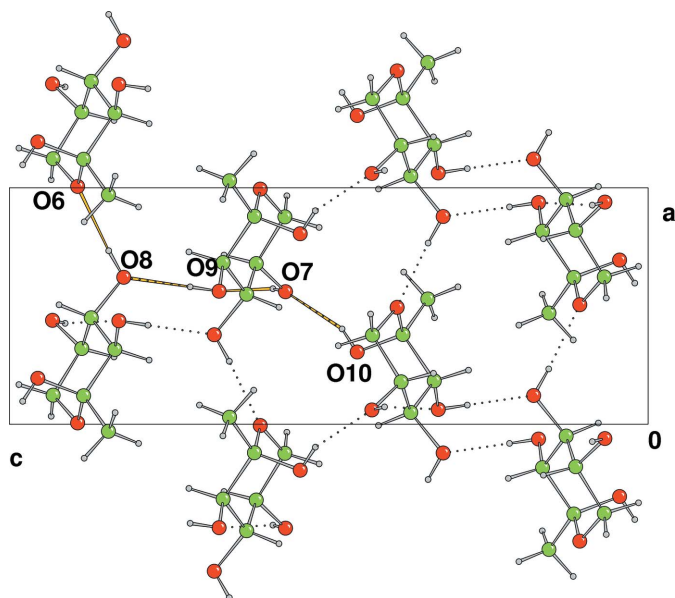


Figure 2
The crystal structure of (5), projected along the *b* axis, showing the three-dimensional hydrogen-bonding network (dotted lines). The hydrogen-bond chain involving atoms O6, O7, O8, O9 and O10 is highlighted in orange.

with six neighbours (Fig. 2). The hydrogen bonds themselves form a discrete continuous chain: O10...O7, O7...O9, O9...O8 and O8...O6, with O10 at the head of the chain as a donor and O6 at the tail as an acceptor (Fig. 3).

Experimental

For the synthesis of 1-deoxy-D-sorbose, the tribenzylated derivative of D-xylose, (1) (Barker & Fletcher, 1961; Postema *et al.*, 2000), was oxidized to the lactone, (2), with acetic anhydride and dimethyl sulfoxide (Calzada *et al.*, 1995). Addition of methyl lithium to the protected lactone, (2), afforded the lactol, (3). Subsequent hydrogenation yielded 1-deoxy-D-sorbose, (4) (Jones *et al.*, in preparation). The title compound, (5), was recrystallized from a mixture of ethyl acetate and methanol (3:1) to give colourless crystals (m.p. 425–427 K). $[\alpha]_{\text{D}}^{20}$ 50.2 (*c* 1.0 in H₂O).

Crystal data

C₆H₁₂O₅
M_r = 164.16
 Orthorhombic, *P*2₁2₁2₁
a = 6.3661 (3) Å
b = 6.6684 (3) Å
c = 17.1873 (9) Å
V = 729.63 (6) Å³

Z = 4
D_x = 1.494 Mg m⁻³
 Mo *K*α radiation
 μ = 0.13 mm⁻¹
T = 190 K
 Needle, colourless
 0.60 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.88, *T_{max}* = 0.97

1613 measured reflections
 981 independent reflections
 894 reflections with *I* > 2σ(*I*)
R_{int} = 0.012
 θ_{max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.027
wR (*F*²) = 0.063
S = 1.01
 981 reflections
 100 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.02P)^2 + 0.17P]$,
 where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.17 e Å⁻³
 Δρ_{min} = -0.17 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O10—H5...O7 ⁱ	0.84	1.95	2.750 (2)	158
O7—H9...O9 ⁱⁱ	0.85	2.05	2.852 (2)	158
O9—H12...O8 ⁱⁱⁱ	0.84	1.86	2.694 (2)	174
O8—H10...O6 ^{iv}	0.84	1.95	2.780 (2)	176

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $x, y + 1, z$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $x - 1, y, z$.

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from the known starting materials. The H atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry [C–H in the range 0.93–0.98 Å and O–H = 0.82 Å and $U_{\text{iso}}(\text{H})$ in the range 1.2–1.5 $U_{\text{eq}}(\text{C,O})$], after which they were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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