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1-Deoxy-α-D-sorbopyranose

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Key indicators

Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.002 Å
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.

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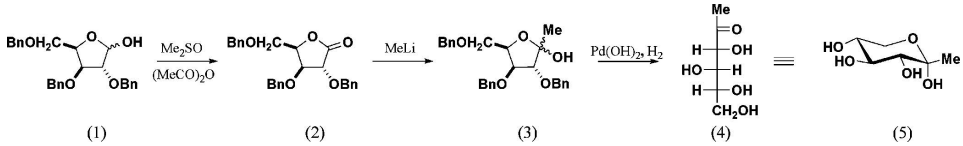
The crystalline form of 1-deoxy-D-sorbose, $C_6H_{12}O_5$, is shown to be 1-deoxy-α-D-sorbopyranose. This is the first reported crystal structure of a 1-deoxyketose. The absolute configuration was determined by the use of D-xylose as the starting material. The crystal structure has a three-dimensional hydrogen-bonded network.

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.



(1) (2) (3) (4) (5)

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

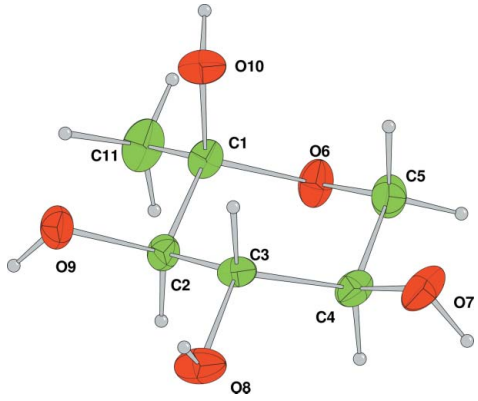


Figure 1
The molecular structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

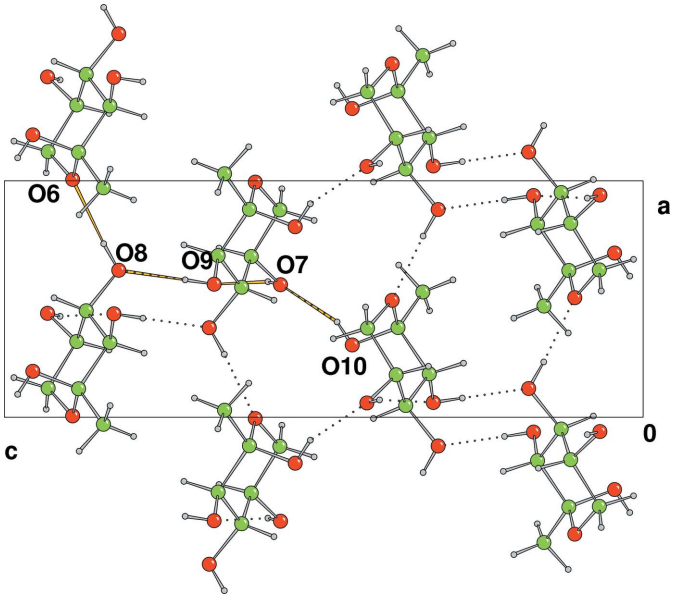


Figure 2
The crystal structure of (5), projected along the *b* axis, showing the three-dimensional hydrogen-bonding network (dotted lines). The hydrogen-bond chain involving atoms O6, O7, O8, O9 and O10 is highlighted in orange.

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). $[\alpha]_D^{20}$ 50.2 (*c* 1.0 in H_2O).

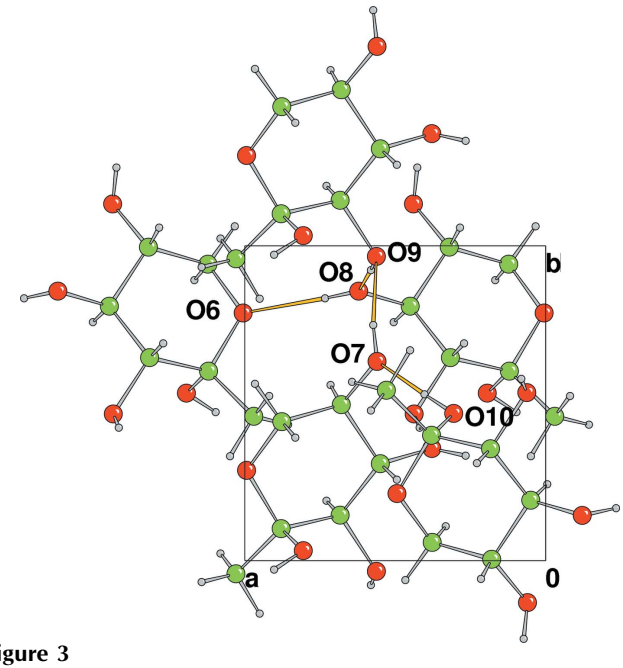


Figure 3
A projection of the crystal structure along the *c* axis, showing the five molecules linked by the discrete hydrogen-bond chain, in which the H···O hydrogen bonds are shown in orange.

Crystal data

$C_6H_{12}O_5$
M_r = 164.16
Orthorhombic, $P2_12_12_1$
a = 6.3661 (3) Å
b = 6.6684 (3) Å
c = 17.1873 (9) Å
V = 729.63 (6) Å^3
Z = 4
D_x = 1.494 Mg m^{-3}
Mo *Kα* 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 $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 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 $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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_{iso}(H) in the range 1.2–1.5U_{eq}(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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supporting information

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$c = 17.1873$ (9) Å
$V = 729.63$ (6) Å^3
$Z = 4$
$F(000) = 352$
$D_x = 1.494$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 926 reflections
$\theta = 5$–27°
$\mu = 0.13$ mm^{-1}
$T = 190$ K
Plate, colourless
0.60 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Graphite monochromator
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 $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 27.5°$, $\theta_{min} = 5.7°$
$h = -8\rightarrow8$
$k = -8\rightarrow8$
$l = -22\rightarrow22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.063$
$S = 1.01$
981 reflections
100 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.02P)^2 + 0.17P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.000444$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8793 (3)	0.1019 (2)	0.61632 (9)	0.0222
C2	0.6834 (2)	0.1446 (2)	0.66525 (8)	0.0199
C3	0.5498 (2)	0.3081 (2)	0.62834 (8)	0.0201
C4	0.6796 (2)	0.4956 (2)	0.61343 (8)	0.0220
C5	0.8770 (3)	0.4417 (2)	0.56865 (9)	0.0274

O6	0.99453 (17)	0.28675 (16)	0.60708 (7)	0.0270
O7	0.56049 (19)	0.63292 (16)	0.56760 (6)	0.0310
O8	0.37853 (18)	0.35613 (19)	0.67922 (6)	0.0297
O9	0.56267 (18)	−0.03378 (17)	0.67154 (6)	0.0262
O10	0.80574 (17)	0.03214 (17)	0.54462 (6)	0.0277
C11	1.0298 (3)	−0.0414 (3)	0.65528 (11)	0.0323
H21	0.7287	0.1902	0.7188	0.0209*
H31	0.4948	0.2574	0.5779	0.0227*
H41	0.7152	0.5578	0.6639	0.0246*
H51	0.9664	0.5617	0.5656	0.0327*
H52	0.8323	0.3907	0.5150	0.0327*
H111	1.1438	−0.0680	0.6173	0.0481*
H112	1.0808	0.0230	0.7024	0.0484*
H113	0.9509	−0.1681	0.6657	0.0470*
H5	0.9030	−0.0283	0.5210	0.0428*
H9	0.5732	0.7483	0.5874	0.0468*
H10	0.2664	0.3333	0.6556	0.0451*
H12	0.5811	−0.0775	0.7170	0.0406*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0220 (7)	0.0182 (7)	0.0262 (7)	−0.0013 (7)	−0.0013 (6)	−0.0004 (6)
C2	0.0211 (7)	0.0185 (7)	0.0203 (6)	−0.0050 (7)	−0.0012 (6)	−0.0004 (6)
C3	0.0196 (7)	0.0214 (7)	0.0193 (6)	0.0008 (7)	0.0007 (6)	−0.0053 (6)
C4	0.0250 (8)	0.0184 (7)	0.0227 (6)	0.0005 (7)	−0.0049 (6)	−0.0023 (6)
C5	0.0301 (8)	0.0206 (7)	0.0316 (8)	−0.0008 (8)	0.0042 (7)	0.0037 (7)
O6	0.0207 (5)	0.0216 (5)	0.0386 (6)	−0.0027 (5)	−0.0003 (5)	0.0045 (5)
O7	0.0413 (7)	0.0167 (5)	0.0350 (6)	0.0028 (6)	−0.0140 (6)	−0.0032 (5)
O8	0.0195 (5)	0.0380 (7)	0.0315 (6)	0.0008 (6)	0.0027 (5)	−0.0124 (5)
O9	0.0293 (6)	0.0222 (5)	0.0271 (5)	−0.0083 (6)	−0.0001 (5)	0.0026 (5)
O10	0.0266 (6)	0.0308 (6)	0.0257 (5)	0.0039 (6)	0.0016 (5)	−0.0078 (5)
C11	0.0251 (8)	0.0264 (8)	0.0455 (9)	0.0004 (8)	−0.0062 (8)	0.0040 (8)

Geometric parameters (Å, º)

C1—C2	1.531 (2)	C4—H41	0.988
C1—O6	1.4431 (19)	C5—O6	1.4365 (19)
C1—O10	1.3981 (18)	C5—H51	0.983
C1—C11	1.510 (2)	C5—H52	1.024
C2—C3	1.522 (2)	O7—H9	0.845
C2—O9	1.4204 (18)	O8—H10	0.835
C2—H21	1.011	O9—H12	0.843
C3—C4	1.520 (2)	O10—H5	0.843
C3—O8	1.4339 (18)	C11—H111	0.992
C3—H31	0.995	C11—H112	0.972
C4—C5	1.517 (2)	C11—H113	0.999
C4—O7	1.4263 (18)		

C2—C1—O6	108.39 (12)	C3—C4—H41	108.8
C2—C1—O10	105.85 (12)	C5—C4—H41	110.8
O6—C1—O10	110.94 (12)	O7—C4—H41	109.7
C2—C1—C11	113.02 (13)	C4—C5—O6	111.62 (12)
O6—C1—C11	105.50 (13)	C4—C5—H51	108.3
O10—C1—C11	113.15 (13)	O6—C5—H51	108.0
C1—C2—C3	111.08 (12)	C4—C5—H52	107.8
C1—C2—O9	109.08 (12)	O6—C5—H52	108.7
C3—C2—O9	109.23 (11)	H51—C5—H52	112.5
C1—C2—H21	108.9	C1—O6—C5	113.61 (11)
C3—C2—H21	108.9	C4—O7—H9	108.1
O9—C2—H21	109.7	C3—O8—H10	108.3
C2—C3—C4	110.84 (12)	C2—O9—H12	106.6
C2—C3—O8	109.31 (12)	C1—O10—H5	109.8
C4—C3—O8	109.42 (12)	C1—C11—H111	106.6
C2—C3—H31	108.5	C1—C11—H112	107.6
C4—C3—H31	108.9	H111—C11—H112	112.4
O8—C3—H31	109.9	C1—C11—H113	107.2
C3—C4—C5	109.95 (12)	H111—C11—H113	109.6
C3—C4—O7	109.41 (11)	H112—C11—H113	113.1
C5—C4—O7	108.19 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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
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Symmetry codes: (i) $x+1/2, -y+1/2, -z+1$; (ii) $x, y+1, z$; (iii) $-x+1, y-1/2, -z+3/2$; (iv) $x-1, y, z$.