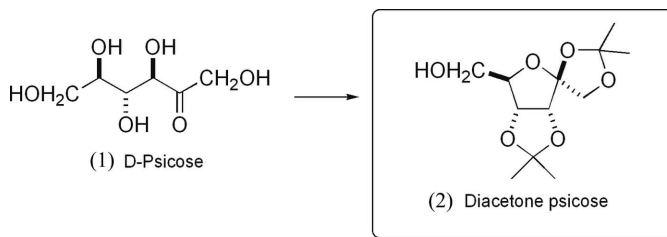


1,2:3,4-Di-O-isopropylidene- β -D-psicofuranoseDavid J Watkin,^{a*} Andreas F. G. Glawar,^a Raquel Soengas,^b Ken Izumori,^c Mark R. Wormald,^d Raymond A. Dwek^d and George W. J. Fleet^b^aDepartment of Chemical Crystallography, Chemical Research Laboratory, Oxford University, Mansfield Road, Oxford OX1 3TA, England, ^bDepartment of Organic Chemistry, Chemical Research Laboratory, Oxford University, Mansfield Road, Oxford OX1 3TA, England, ^cRare Sugar Research Centre, Kagawa University, Mikicho, Kagawa 761-0795 Japan, and ^dGlycobiology Institute, Department of Biochemistry, Oxford University, South Parks Road, Oxford OX1 3QU, EnglandCorrespondence e-mail:
david.watkin@chem.ox.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 190$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.041
 wR factor = 0.078
Data-to-parameter ratio = 10.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The crystal structure of the title diacetone psicose, $\text{C}_{12}\text{H}_{20}\text{O}_6$, establishes the stereochemistry of the anomeric spiroacetal 1,2:3,4-di-O-isopropylidene- β -D-psicofuranose. The structure consists of columns of molecules linked by hydrogen bonds into chains $[\text{O} \cdots \text{O} 2.962 (2) \text{ \AA}]$ lying parallel to the a axis.Received 5 August 2005
Accepted 10 August 2005
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Comment

Izumoring, a combination of enzymic epimerizations of ketohexoses combined with microbial oxidation–reduction procedures, can provide access to any hexose in substantial quantity *via* environmentally friendly procedures (Granstrom *et al.*, 2004; Izumori, 2002). The rare sugar D-psicose, (1), is now available for the first time in multi-kilogram quantities from the equilibration of D-fructose by D-tagatose 3-epimerase (Takeshita *et al.*, 2000; Itoh & Izumori, 1996; Itoh *et al.*, 1995). Although the main purpose of large-scale production of rare sugars such as D-psicose is for their use in food technology (Sun *et al.*, 2004, 2005), such studies will significantly increase the number of sugar chirons (Lichtenthaler & Peters, 2004; Soengas, Izumori *et al.*, 2005).Crystalline diacetone derivatives of carbohydrates are among the most common chiral building blocks in organic synthesis (Bols, 1996). The first report of the reaction of psicose with acetone was the formation of a furanose diacetone from L-psicose (Steiger & Reichstein, 1935); the reaction of D-psicose, (1), with acetone gave an enantiomeric diacetone, (2) (Steiger & Reichstein, 1936), with no indication of the chemistry at the anomeric position. All other syntheses of the furanose diacetone, (2), have been multi-step procedures starting from a pyranose diacetone of fructose. The original procedure for the preparation of (2) from D-fructose (James *et al.*, 1967) has been significantly improved (James *et al.*, 1967; Cree & Perlin, 1968; Tipson *et al.*, 1971). The diacetone, (2), has been used as a starting material for the synthesis of nucleosides (Prisbe *et al.*, 1976) and imino sugars (Joseph *et al.*, 2002). There is no report in any of the numerous previous papers of any attempt to determine the anomeric configuration of the spiro-acetal functionality in (2). In recent studies, it was found

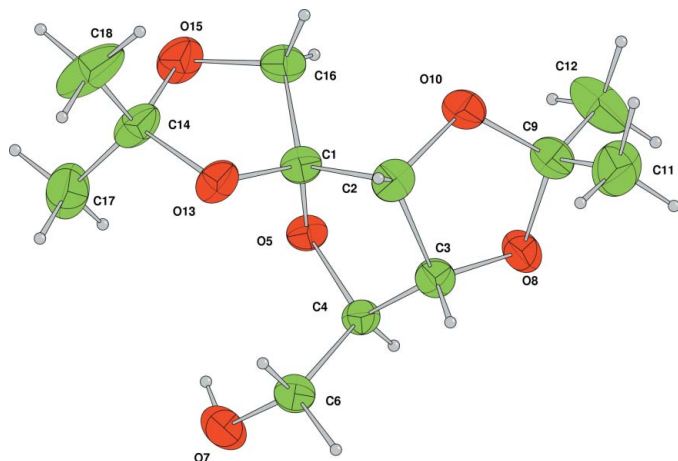


Figure 1
The molecule of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

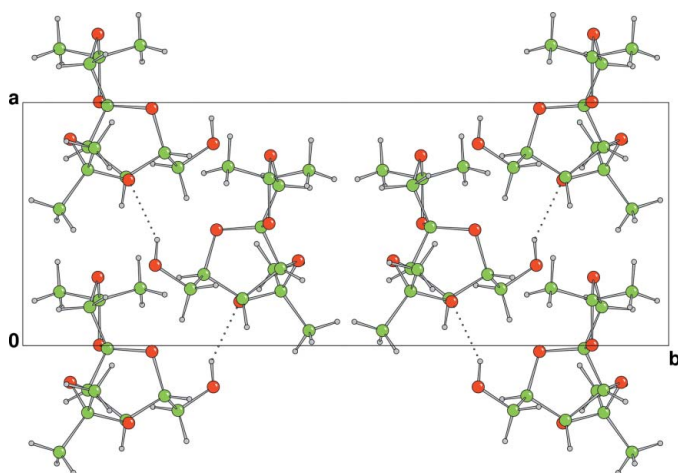


Figure 2
A projection along the *c* axis of the crystal structure of the title compound, showing chains of molecules lying parallel to the *a* axis. Hydrogen bonds are shown as dotted lines.

that treatment of psicose (1) with acetone in the presence of acid afforded the easily crystallized diacetone psicose, (2) (Soengas, Wormald *et al.*, 2005), in good yield. The present report of the crystal structure of (2) unequivocally establishes the anomeric configuration of the diacetone, (3), as the β -form (Fig. 1).

The structure of (2) consists of columns of molecules linked by hydrogen bonds into chains [$O \cdots O = 2.962(2) \text{ \AA}$] lying parallel to the *a* axis (Fig. 2). Contacts between the chains are determined largely by the methyl groups.

Experimental

The title material, (2) (Soengas, Wormald *et al.*, 2005), was crystallized from 333–353 K petroleum ether.

Crystal data

$C_{12}H_{20}O_6$
 $M_r = 260.29$
Orthorhombic, $C222_1$
 $a = 7.5915(2) \text{ \AA}$
 $b = 20.1407(6) \text{ \AA}$
 $c = 17.5607(6) \text{ \AA}$
 $V = 2685.00(14) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.288 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 1674 reflections
 $\theta = 5\text{--}27^\circ$
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 190 \text{ K}$
Prism, colourless
 $0.45 \times 0.15 \times 0.15 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
 $T_{\min} = 0.86$, $T_{\max} = 0.98$
9365 measured reflections

1721 independent reflections
1721 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -25 \rightarrow 25$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.078$
 $S = 0.94$
1721 reflections
163 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.76P]$
where $P = (\max(F_o^2, 0) + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O7-H1 \cdots O8^i$	0.84	2.19	2.962 (2)	152

Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

Because the data were collected with molybdenum radiation, there were no measurable anomalous differences, as a consequence of which it was admissible to merge Friedel pairs of reflections. 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 in order to regularize their geometry [C–H distances in the range 0.93–0.98 \AA and $O-H = 0.82 \text{ \AA}$, and $U_{\text{iso}}(\text{H})$ in the range 1.2–1.5 U_{eq} of the adjacent atom], after which they were refined with riding constraints.

Data collection: *COLLECT*. (Nonius, 1997–2001); 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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1,2:3,4-Di-O-isopropylidene- β -D-psicofuranose

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1,2:3,4-Di-O-isopropylidene- β -D-psicofuranose*Crystal data*

$C_{12}H_{20}O_6$

$M_r = 260.29$

Orthorhombic, $C222_1$

Hall symbol: $C\ 2c\ 2$

$a = 7.5915\ (2)\ \text{\AA}$

$b = 20.1407\ (6)\ \text{\AA}$

$c = 17.5607\ (6)\ \text{\AA}$

$V = 2685.00\ (14)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1120$

$D_x = 1.288\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1674 reflections

$\theta = 5\text{--}27^\circ$

$\mu = 0.10\ \text{mm}^{-1}$

$T = 190\ \text{K}$

Prism, colourless

$0.45 \times 0.15 \times 0.15\ \text{mm}$

Data collection

Nonius KappaCCD area-detector
diffractometer

Graphite monochromator

ω scans

Absorption correction: multi-scan

(DENZO/SCALEPACK; Otwinowski & Minor,
1997)

$T_{\min} = 0.86$, $T_{\max} = 0.98$

9365 measured reflections

1721 independent reflections

1721 reflections with $I > -3\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 5.3^\circ$

$h = -9 \rightarrow 9$

$k = -25 \rightarrow 25$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.078$

$S = 0.94$

1721 reflections

163 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.76P]$

where $P = (\max(F_o^2, 0) + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.000268$

$\Delta\rho_{\max} = 0.18\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.17\ \text{e \AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.9879 (2)	0.86900 (8)	0.45535 (9)	0.0289
C2	0.8171 (2)	0.89925 (9)	0.48595 (11)	0.0326
C3	0.6934 (2)	0.84018 (8)	0.49965 (10)	0.0306

C4	0.7929 (2)	0.78036 (8)	0.47003 (10)	0.0275
O5	0.97603 (15)	0.79999 (5)	0.47083 (6)	0.0275
C6	0.7334 (2)	0.75971 (9)	0.39077 (10)	0.0337
O7	0.8303 (2)	0.70508 (7)	0.36253 (8)	0.0469
O8	0.68145 (18)	0.83598 (6)	0.58096 (7)	0.0376
C9	0.7244 (3)	0.89956 (10)	0.61173 (12)	0.0420
O10	0.84906 (18)	0.92652 (7)	0.55968 (8)	0.0444
C11	0.5620 (3)	0.94323 (12)	0.61528 (16)	0.0624
C12	0.8129 (5)	0.88883 (13)	0.68779 (13)	0.0715
O13	1.00256 (16)	0.88126 (6)	0.37606 (7)	0.0345
C14	1.1874 (2)	0.88150 (11)	0.35570 (11)	0.0394
O15	1.28119 (17)	0.88358 (7)	0.42634 (8)	0.0435
C16	1.1595 (2)	0.89624 (9)	0.48621 (11)	0.0339
C17	1.2359 (3)	0.81797 (12)	0.31560 (12)	0.0549
C18	1.2212 (3)	0.94316 (13)	0.30907 (15)	0.0683
H21	0.7694	0.9328	0.4502	0.0469*
H31	0.5761	0.8468	0.4764	0.0423*
H41	0.7800	0.7421	0.5053	0.0377*
H61	0.6070	0.7465	0.3941	0.0480*
H62	0.7479	0.7987	0.3569	0.0483*
H111	0.5982	0.9867	0.6347	0.1113*
H112	0.5147	0.9473	0.5645	0.1113*
H113	0.4766	0.9217	0.6485	0.1119*
H121	0.8409	0.9325	0.7088	0.1258*
H122	0.7326	0.8657	0.7212	0.1269*
H123	0.9185	0.8621	0.6796	0.1264*
H161	1.1489	0.9442	0.4944	0.0481*
H162	1.1984	0.8720	0.5333	0.0472*
H171	1.3606	0.8208	0.3027	0.0983*
H172	1.1677	0.8152	0.2679	0.0984*
H173	1.2098	0.7803	0.3489	0.0988*
H181	1.3447	0.9462	0.2985	0.1209*
H182	1.1572	0.9398	0.2621	0.1211*
H183	1.1845	0.9819	0.3380	0.1212*
H1	0.9352	0.7080	0.3775	0.0833*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0298 (8)	0.0252 (8)	0.0317 (9)	-0.0004 (7)	-0.0024 (7)	0.0033 (7)
C2	0.0307 (9)	0.0282 (9)	0.0390 (10)	0.0043 (8)	-0.0006 (8)	0.0047 (8)
C3	0.0288 (8)	0.0322 (9)	0.0307 (8)	0.0018 (8)	-0.0027 (8)	-0.0006 (7)
C4	0.0269 (8)	0.0287 (8)	0.0270 (8)	-0.0032 (7)	-0.0016 (7)	0.0003 (7)
O5	0.0266 (6)	0.0228 (5)	0.0331 (6)	0.0004 (5)	-0.0027 (5)	0.0015 (5)
C6	0.0309 (9)	0.0389 (10)	0.0314 (9)	-0.0032 (8)	-0.0027 (7)	-0.0031 (8)
O7	0.0438 (8)	0.0537 (8)	0.0432 (8)	0.0008 (7)	-0.0022 (7)	-0.0204 (6)
O8	0.0509 (8)	0.0301 (6)	0.0317 (6)	-0.0030 (6)	0.0066 (6)	-0.0054 (5)
C9	0.0460 (11)	0.0347 (10)	0.0453 (11)	-0.0019 (9)	0.0049 (9)	-0.0112 (9)

O10	0.0441 (8)	0.0368 (7)	0.0524 (8)	-0.0069 (6)	0.0084 (7)	-0.0168 (6)
C11	0.0559 (14)	0.0432 (12)	0.0881 (19)	0.0039 (11)	0.0269 (13)	-0.0142 (12)
C12	0.099 (2)	0.0689 (15)	0.0468 (13)	0.0017 (18)	-0.0115 (15)	-0.0215 (12)
O13	0.0267 (6)	0.0445 (7)	0.0323 (6)	-0.0030 (7)	-0.0031 (5)	0.0103 (5)
C14	0.0252 (9)	0.0569 (12)	0.0360 (10)	-0.0085 (9)	-0.0049 (8)	0.0145 (9)
O15	0.0268 (6)	0.0635 (9)	0.0400 (7)	-0.0028 (6)	-0.0055 (6)	0.0040 (7)
C16	0.0345 (9)	0.0272 (9)	0.0399 (11)	-0.0008 (8)	-0.0039 (8)	-0.0005 (8)
C17	0.0400 (11)	0.0813 (16)	0.0433 (12)	0.0001 (12)	0.0055 (9)	-0.0016 (11)
C18	0.0451 (13)	0.0847 (18)	0.0752 (17)	-0.0270 (13)	-0.0131 (12)	0.0452 (15)

Geometric parameters (Å, °)

C1—C2	1.530 (2)	C9—C12	1.511 (3)
C1—O5	1.419 (2)	C11—H111	0.980
C1—O13	1.418 (2)	C11—H112	0.965
C1—C16	1.514 (2)	C11—H113	0.973
C2—C3	1.535 (2)	C12—H121	0.977
C2—O10	1.427 (2)	C12—H122	0.966
C2—H21	0.991	C12—H123	0.977
C3—C4	1.514 (2)	O13—C14	1.448 (2)
C3—O8	1.433 (2)	C14—O15	1.431 (2)
C3—H31	0.989	C14—C17	1.506 (3)
C4—O5	1.446 (2)	C14—C18	1.510 (3)
C4—C6	1.521 (2)	O15—C16	1.423 (2)
C4—H41	0.993	C16—H161	0.979
C6—O7	1.413 (2)	C16—H162	1.005
C6—H61	0.997	C17—H171	0.975
C6—H62	0.992	C17—H172	0.986
O7—H1	0.841	C17—H173	0.978
O8—C9	1.428 (2)	C18—H181	0.958
C9—O10	1.424 (2)	C18—H182	0.960
C9—C11	1.516 (3)	C18—H183	0.973
C2—C1—O5	105.60 (14)	C2—O10—C9	108.83 (14)
C2—C1—O13	110.00 (14)	C9—C11—H111	107.8
O5—C1—O13	111.31 (13)	C9—C11—H112	108.3
C2—C1—C16	117.33 (13)	H111—C11—H112	110.5
O5—C1—C16	109.94 (15)	C9—C11—H113	108.0
O13—C1—C16	102.76 (14)	H111—C11—H113	112.1
C1—C2—C3	105.37 (14)	H112—C11—H113	110.1
C1—C2—O10	109.14 (15)	C9—C12—H121	107.6
C3—C2—O10	105.08 (14)	C9—C12—H122	109.0
C1—C2—H21	111.1	H121—C12—H122	109.9
C3—C2—H21	113.8	C9—C12—H123	108.3
O10—C2—H21	111.9	H121—C12—H123	111.9
C2—C3—C4	104.93 (14)	H122—C12—H123	110.0
C2—C3—O8	103.91 (14)	C1—O13—C14	108.60 (14)
C4—C3—O8	109.08 (14)	O13—C14—O15	105.56 (15)

C2—C3—H31	112.4	O13—C14—C17	110.45 (17)
C4—C3—H31	114.6	O15—C14—C17	107.98 (17)
O8—C3—H31	111.2	O13—C14—C18	107.55 (17)
C3—C4—O5	105.01 (13)	O15—C14—C18	111.19 (18)
C3—C4—C6	112.58 (15)	C17—C14—C18	113.81 (19)
O5—C4—C6	111.65 (14)	C14—O15—C16	108.83 (13)
C3—C4—H41	110.7	C1—C16—O15	103.25 (14)
O5—C4—H41	107.5	C1—C16—H161	109.8
C6—C4—H41	109.2	O15—C16—H161	109.8
C4—O5—C1	109.09 (13)	C1—C16—H162	111.8
C4—C6—O7	112.30 (15)	O15—C16—H162	109.3
C4—C6—H61	107.7	H161—C16—H162	112.5
O7—C6—H61	108.3	C14—C17—H171	107.2
C4—C6—H62	107.4	C14—C17—H172	108.5
O7—C6—H62	110.4	H171—C17—H172	108.4
H61—C6—H62	110.6	C14—C17—H173	109.3
C6—O7—H1	109.2	H171—C17—H173	112.4
C3—O8—C9	108.05 (14)	H172—C17—H173	111.0
O8—C9—O10	104.52 (15)	C14—C18—H181	108.9
O8—C9—C11	110.51 (17)	C14—C18—H182	108.8
O10—C9—C11	110.24 (17)	H181—C18—H182	109.5
O8—C9—C12	107.93 (17)	C14—C18—H183	109.2
O10—C9—C12	109.1 (2)	H181—C18—H183	109.2
C11—C9—C12	114.1 (2)	H182—C18—H183	111.1

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O7—H1 \cdots O8 ⁱ	0.84	2.19	2.962 (2)	152

Symmetry code: (i) $x+1/2, -y+3/2, -z+1$.