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

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Key indicators

Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.002 Å
R factor = 0.041
wR factor = 0.078
Data-to-parameter ratio = 10.6

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

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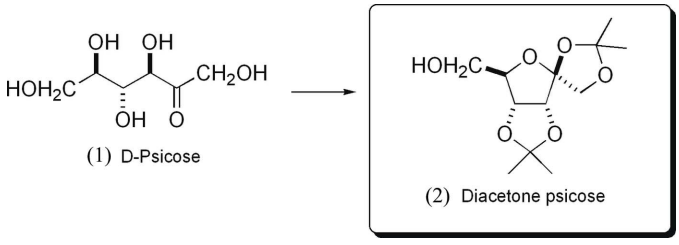
The crystal structure of the title diacetone psicose, $C_{12}H_{20}O_6$, establishes the stereochemistry of the anomeric spiroacetal 1,2:3,4-di-*O*-isopropylidene-β-D-psicofuranose. The structure consists of columns of molecules linked by hydrogen bonds into chains [O···O 2.962 (2) Å] lying parallel to the *a* axis.

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).



(1) D-Psicose

(2) Diacetone psicose

Crystalline diacetonides 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 diacetonide from L-psicose (Steiger & Reichstein, 1935); the reaction of D-psicose, (1), with acetone gave an enantiomeric diacetonide, (2) (Steiger & Reichstein, 1936), with no indication of the chemistry at the anomeric position. All other syntheses of the furanose diacetonide, (2), have been multi-step procedures starting from a pyranose diacetonide 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 diacetonide, (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

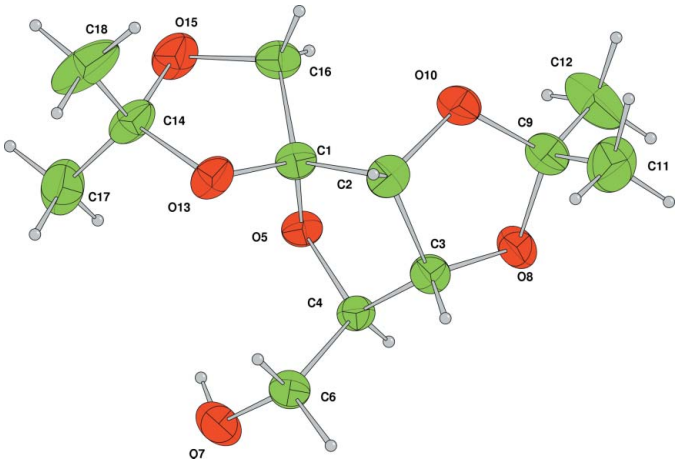


Figure 1
The molecule of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radii.

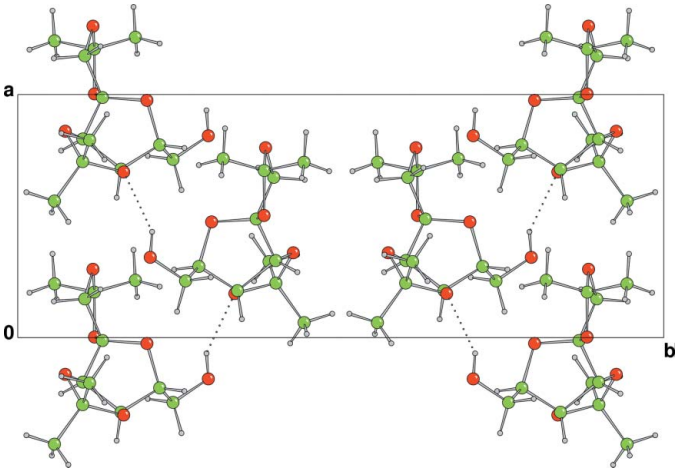


Figure 2
A projection along the *c* axis of the crystal structure of the title compound, showing chains of molecules lying parallel to the *a* axis. Hydrogen bonds are shown as dotted lines.

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 diacetonide, (3), as the β-form (Fig. 1).

The structure of (2) consists of columns of molecules linked by hydrogen bonds into chains [O···O = 2.962 (2) Å] 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) Å
b = 20.1407 (6) Å
c = 17.5607 (6) Å
V = 2685.00 (14) Å^3
Z = 8
D_x = 1.288 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1674 reflections
θ = 5–27°
μ = 0.10 mm^{-1}
T = 190 K
Prism, colourless
0.45 × 0.15 × 0.15 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_{int} = 0.030
θ_{max} = 27.5°
$h = -9 \rightarrow 9$
$k = -25 \rightarrow 25$
$l = -22 \rightarrow 22$

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 $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 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
O7—H1···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 0.93–98 Å and O—H = 0.82 Å, and U_{iso}(H) in the range 1.2–1.5U_{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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