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1,2:3,4-Di-*O*-isopropylidene-*α*-D-tagatofuranose

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Key indicators

Single-crystal X-ray study
T = 190 K
Mean *σ*(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.087
Data-to-parameter ratio = 13.7

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

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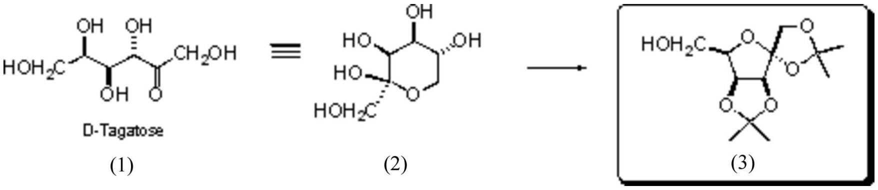
The crystal structure of diacetone tagatose, $C_{12}H_{20}O_6$, establishes the stereochemistry of the anomeric spiroacetal as 1,2:3,4-di-*O*-isopropylidene-*α*-D-tagatofuranose. Molecules are linked by O—H···O hydrogen bonds [O···O = 2.862 (2) Å] to form chains running parallel to the *b* axis.

Comment

Carbohydrates provide a rich source of chirons (Lichtenthaler & Peters, 2004). D-Tagatose, (1), is the first example for more than 50 years of a sugar that has changed its status from rare ($5,000 per lb) to common ($2.5 per lb). The driving force for the production of large quantities of hitherto scarce carbohydrates is their potential as enhanced dietary targets. D-Tagatose is a healthy sweetener prepared cheaply from galactose (Beadle *et al.*, 1992). Its use as a dietary substitute in soft drinks and ready-to-eat cereals (Skytte, 2002) is rapidly increasing. So far, there has been little exploitation of tagatose as a chiral building block, although recently the easy preparation of branched sugar lactones by the Kiliani cyanohydrin reaction on D-tagatose has been reported (Soengas, Izumori *et al.*, 2005); the structures of the diacetonide products could only be firmly established by X-ray crystallographic analysis (Harding *et al.*, 2005; Shallard-Brown *et al.*, 2004). For a sugar to be used as a chiral starting material in organic synthesis, it must not only be cheap but also efficiently protected (Bols, 1996).



(1) (2) (3)

The first reports of the protection of tagatose, (1), with acetone (Reichstein & Bosshard, 1934; Barnett & Reichstein, 1937) gave no indication of the chemistry at the anomeric position of the diacetonide, (3). Otherwise, compound (3) has only been prepared by lengthy synthesis from D-fructose (Cubero *et al.*, 1988); the enantiomer of (3) was derived from a multi-step procedure from L-sorbose (Furneaux *et al.*, 1993). No previous publication has provided any evidence for the anomeric configuration of the diacetonide, (3). In recent studies, treatment of tagatose, (1), which exists in both its crystalline form and in solution in the pyranose form, (2), with acetone produces high yields of crystalline (3) (Soengas, Wormald *et al.*, 2005). The present report of the crystal structure of (3) unequivocally establishes the anomeric configuration of the diacetonide, (3), as the β-form.

The crystal structure of (3) consists of O—H···O hydrogen-bonded chains running parallel to the *b* axis (Table 1 and Fig. 2). There are no other short intermolecular contacts. Atoms C17 and C18 refined to have very anisotropic displacement parameters. A difference electron-density map phased on all the structure except for atoms C17 and C18 showed only a single elongated peak at these sites, indicating that the anisotropic displacement parameter model would be appropriate. The large anisotropic displacement parameters for these atoms are due to disorder of these atoms arising from out-of-plane displacements of atoms in the adjacent ring, and in particular of O15. A single-temperature experiment cannot resolve static from dynamic disorder.

Experimental

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

Crystal data

$C_{12}H_{20}O_6$
$M_r = 260.29$
Orthorhombic, $P2_12_12_1$
$a = 5.8241$ (1) Å
$b = 8.4972$ (2) Å
$c = 27.1899$ (7) Å
$V = 1345.59$ (5) Å^3
$Z = 4$
$D_x = 1.285$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 1961 reflections
$\theta = 5$–$30°$
$\mu = 0.10$ mm^{-1}
$T = 190$ K
Prism, 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)
$T_{\min} = 0.84$, $T_{\max} = 0.98$
7561 measured reflections

2239 independent reflections
1980 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 30.0°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -37 \rightarrow 37$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.087$
$S = 0.97$
2239 reflections
163 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.29P]$
where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H15···O15$^{\rm i}$	0.81	2.06	2.862 (2)	167

Symmetry code: (i) $x, y+1, z$.

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from known chiral centres. The relatively large ratio of minimum to maximum corrections applied in the multi-scan process (1:1.16) is due to the prismatic shape of the crystal. 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 their bond lengths and angles to regularize their geometry (C—H distances in the range 0.93–0.98 Å and O—H distances of 0.82 Å) and displacement parameters [$U_{\rm iso}$(H) in the range 1.2–1.5 times $U_{\rm eq}$ of the parent atom], after which they were refined with riding constraints.

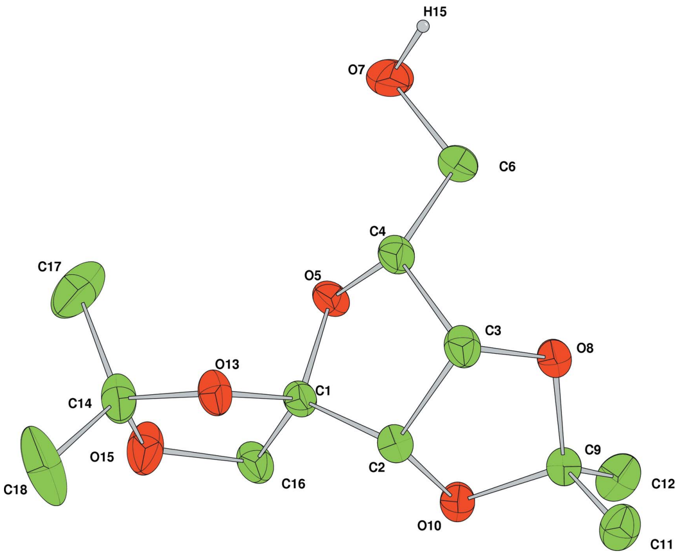


Figure 1
A view of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms (except for the hydroxyl atom H15) have been omitted for clarity; atom H15 is shown as a sphere of arbitary radius.

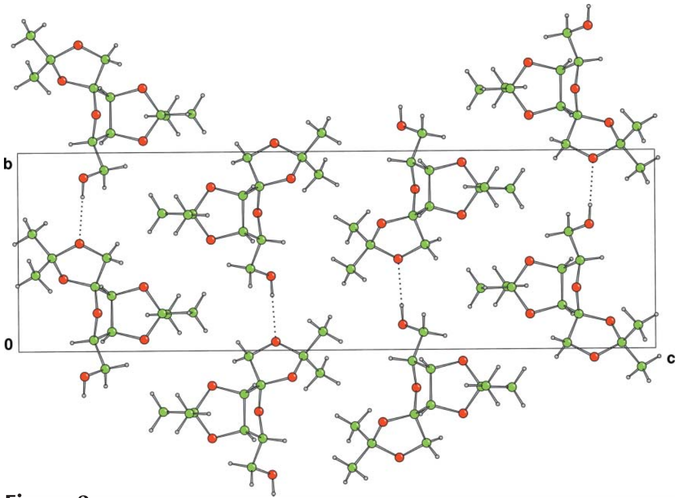


Figure 2
A diagram showing a projection along the *a* axis of the title compound, with hydrogen bonds indicated as dotted lines.

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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o2892 Watkin *et al.* • $C_{12}H_{20}O_6$ *Acta Cryst.* (2005). E**61**, o2891–o2893

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