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2,2′:5,6-Di-*O*-isopropylidene-2-*C*-hydroxymethyl-D-talono-1,4-lactone

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.034
wR factor = 0.078
Data-to-parameter ratio = 9.0

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

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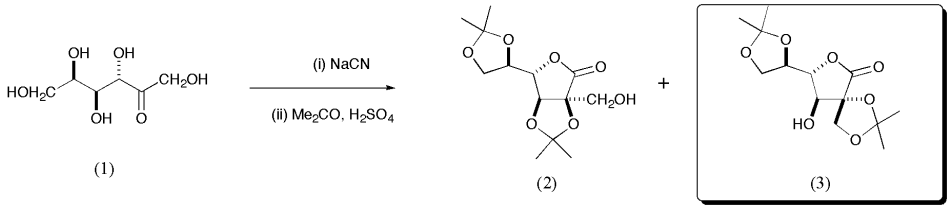
A second crystalline diacetonide, the title compound, $C_{13}H_{20}O_7$, has been isolated from the sequential treatment of D-tagatose with aqueous sodium cyanide, followed by acetone in the presence of acid. Structural ambiguities with regard to the size of both the lactone and ketal rings are resolved by the X-ray crystallographic analysis.

Comment

Although the branched carbon-chain lactones formed by the Kiliani extension of ketoses are not readily separated, treatment of the crude product mixture forms a series of diacetonides, from which the major products can be separated (Hotchkiss *et al.*, 2004) and their structures determined by X-ray crystallographic analysis (Cowley *et al.*, 2004; van Ameijde *et al.*, 2004). Such materials have considerable potential as a new class of readily available chiral building blocks and bioactive scaffolds (Lichtenthaler & Peters, 2004; Bols, 1996). Developments in biotechnology are leading to the ready availability of almost any ketohexose or ketopentose by a combination of microbial oxidation and enzyme-catalysed epimerizations (Granstrom *et al.*, 2004). In particular, D-tagatose, (1), hitherto considered a rare sugar, is a healthy sweetener prepared cheaply from whey, and used in soft drinks and ready-to-eat cereals (Skytte, 2002).



(1) (2) (3)

The sequential treatment of D-tagatose, (1), with sodium cyanide, followed by extraction of the crude lactones with acetone in the presence of sulfuric acid, gave a mixture of diacetonides; the *cis*-fused diacetonide (2) was easily crystallized as one of two major products (Shallard-Brown *et al.*, 2004). Further purification allowed the crystallization of a second diacetonide; NMR and other spectroscopic studies on this material left considerable ambiguity with regard to the ring sizes of both the acetonides and the lactone. X-ray crystallographic analysis firmly established the structure as the acetonide, (3), in which there is a spiro-acetonide. It is anticipated that both the diacetonides, (2) and (3), will rapidly be established as ideal starting materials for a range of complex bioactive products.

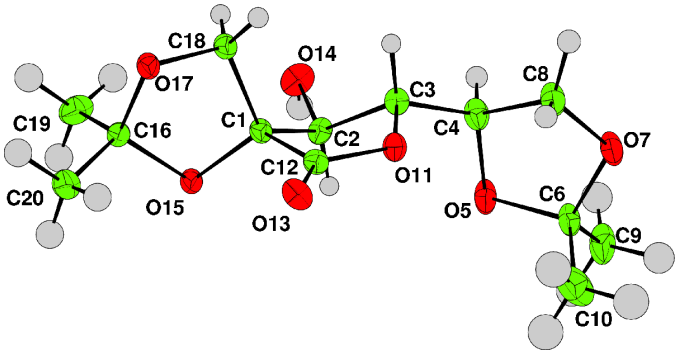


Figure 1
The title molecule at 120 K, with displacement ellipsoids drawn at the 50% probability level. Note the fairly large displacement parameters on fragment C6/C9/C10, suggesting some minor disorder of atoms in this part of the molecule.

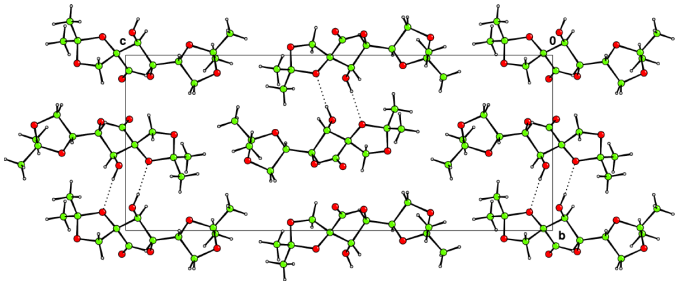


Figure 2
Packing diagram of the title molecule, viewed along the *a* axis. The molecules form independent hydrogen-bonded ribbons (dashed lines) parallel to *a*.

Experimental

The title material was crystallized from diethyl ether by inward diffusion of *n*-hexane, to yield very fragile plate-like colourless crystals. The full experimental method is currently being prepared for publication.

Crystal data

$C_{13}H_{20}O_7$
M_r = 288.30
Orthorhombic, $P2_12_12_1$
a = 5.8303 (1) Å
b = 9.8983 (2) Å
c = 24.1599 (4) Å
V = 1394.27 (4) Å^3
Z = 4
D_x = 1.373 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2281 reflections
θ = 5–30°
μ = 0.11 mm^{-1}
T = 120 K
Plate, colourless
0.30 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan *DENZO/SCALEPACK* (Otwinowski & Minor, 1997)
T_{min} = 0.99, T_{max} = 0.99
3990 measured reflections
2337 independent reflections
2033 reflections with $I > 2.00\,u(I)$
R_{int} = 0.012
θ_{max} = 30.0°
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -33 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.078
S = 0.96
2337 reflections
261 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F^2) + 0.04 + 0.32P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

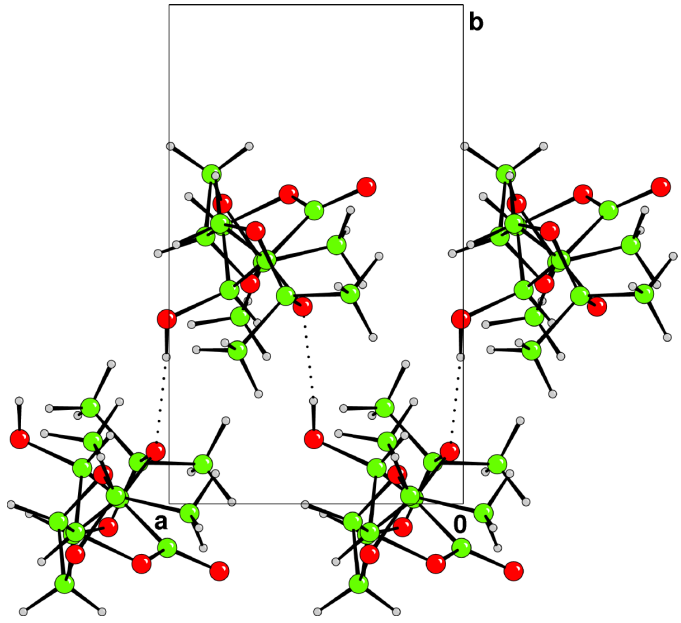


Figure 3
View of a section of one hydrogen-bonded ribbon (dashed lines), viewed along *c*.

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

D—H···A	D—H	H···A	D···A	D—H···A
O14—H18···O15^{i}	0.823 (15)	1.977 (16)	2.7947 (15)	172 (2)

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

All H atoms were observed in a difference electron-density map. The hydroxyl H atom was placed as found and the others were positioned geometrically (C—H = 1.00 Å). All were refined with slack restraints [distance s.u. values of 0.02 Å and angle s.u. values of 2.0°; U_{iso}(H) = 1.2U_{eq}(parent), s.u. = 0.02 Å^2]. In the absence of significant anomalous scattering effects, Friedel pairs were merged. The absolute configuration is known from the synthesis.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR*92 (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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