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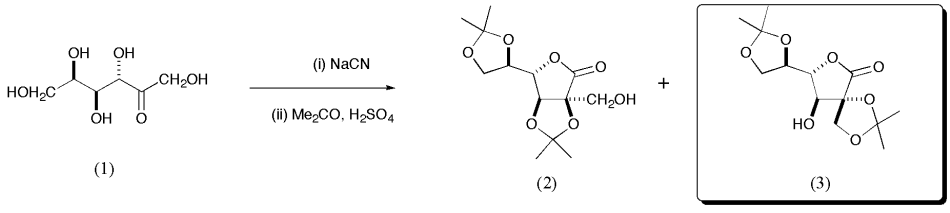
A second crystalline diacetonide, the title compound, $C_{13}H_{20}O_7$, has been isolated from the sequential treatment of D-tagatose with aqueous sodium cyanide, followed by acetone in the presence of acid. Structural ambiguities with regard to the size of both the lactone and ketal rings are resolved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

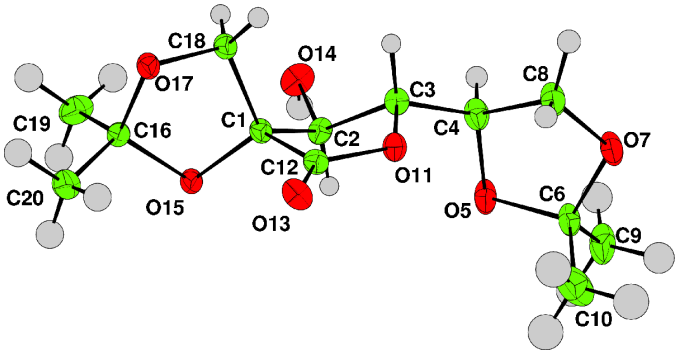


Figure 1
The title molecule at 120 K, with displacement ellipsoids drawn at the 50% probability level. Note the fairly large displacement parameters on fragment C6/C9/C10, suggesting some minor disorder of atoms in this part of the molecule.

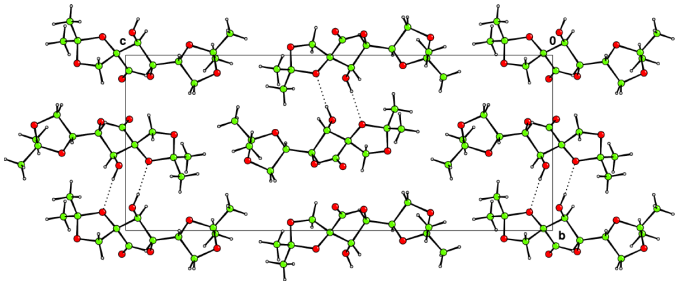


Figure 2
Packing diagram of the title molecule, viewed along the *a* axis. The molecules form independent hydrogen-bonded ribbons (dashed lines) parallel to *a*.

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}

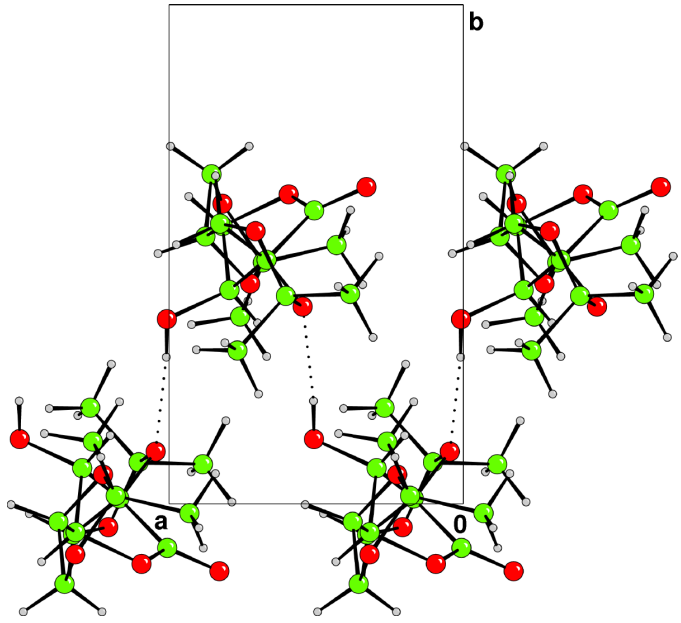


Figure 3
View of a section of one hydrogen-bonded ribbon (dashed lines), viewed along *c*.

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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supporting information

Acta Cryst. (2005). E**61**, o250–o252 [https://doi.org/10.1107/S1600536804033549]

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Cell parameters from 2281 reflections
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$\mu = 0.11$ mm^{-1}
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Plate, colourless
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Graphite monochromator
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$\theta_{max} = 30.0°$, $\theta_{min} = 5.3°$
$h = -8\rightarrow8$
$k = -13\rightarrow13$
$l = -33\rightarrow34$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.078$
$S = 0.96$
2337 reflections
261 parameters
83 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters not defined
$w = 1/[\sigma^2(F^2) + 0.04 + 0.32P]$ 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}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1689 (3)	0.01089 (13)	0.52121 (6)	0.0168
C2	0.2950 (3)	0.07139 (14)	0.47152 (6)	0.0180
C3	0.3181 (3)	−0.05664 (14)	0.43610 (6)	0.0181

C4	0.3765 (3)	−0.03576 (15)	0.37596 (6)	0.0231
O5	0.2247 (3)	0.05865 (10)	0.35061 (4)	0.0281
C6	0.1814 (3)	0.01631 (16)	0.29466 (6)	0.0238
O7	0.3191 (2)	−0.10136 (12)	0.28587 (4)	0.0278
C8	0.3557 (4)	−0.16024 (16)	0.33913 (6)	0.0266
C9	0.2589 (4)	0.12464 (19)	0.25547 (7)	0.0367
C10	−0.0687 (4)	−0.0186 (3)	0.28992 (11)	0.0487
O11	0.09362 (19)	−0.12025 (11)	0.44206 (4)	0.0191
C12	0.0067 (3)	−0.08815 (14)	0.49236 (6)	0.0182
O13	−0.1707 (2)	−0.13485 (11)	0.50882 (5)	0.0249
O14	0.5078 (2)	0.12981 (11)	0.48428 (5)	0.0261
O15	0.0460 (2)	0.10481 (10)	0.55412 (4)	0.0198
C16	0.1035 (3)	0.08323 (15)	0.61233 (6)	0.0197
O17	0.2065 (2)	−0.04655 (10)	0.61372 (4)	0.0200
C18	0.3270 (3)	−0.06166 (15)	0.56271 (6)	0.0200
C19	0.2683 (4)	0.19259 (17)	0.63039 (8)	0.0311
C20	−0.1146 (3)	0.0792 (2)	0.64570 (7)	0.0307
H21	0.200 (3)	0.1372 (15)	0.4519 (6)	0.0244 (18)*
H31	0.433 (3)	−0.1159 (16)	0.4525 (6)	0.0252 (18)*
H41	0.537 (3)	−0.0016 (16)	0.3746 (6)	0.0322 (19)*
H81	0.228 (3)	−0.2165 (17)	0.3499 (7)	0.0352 (19)*
H82	0.495 (3)	−0.2165 (17)	0.3399 (7)	0.0371 (19)*
H91	0.232 (4)	0.094 (2)	0.2183 (7)	0.0642 (19)*
H92	0.169 (4)	0.2046 (18)	0.2630 (8)	0.0645 (19)*
H93	0.424 (3)	0.141 (2)	0.2611 (8)	0.0645 (19)*
H101	−0.101 (4)	−0.048 (2)	0.2525 (7)	0.0857 (19)*
H102	−0.157 (4)	0.0607 (19)	0.2965 (10)	0.0849 (19)*
H103	−0.116 (4)	−0.089 (2)	0.3153 (9)	0.0860 (19)*
H181	0.342 (3)	−0.1574 (14)	0.5542 (6)	0.0283 (18)*
H182	0.475 (3)	−0.0195 (16)	0.5634 (6)	0.0265 (18)*
H191	0.311 (3)	0.1772 (19)	0.6686 (7)	0.0546 (19)*
H192	0.196 (3)	0.2799 (16)	0.6274 (8)	0.0538 (19)*
H193	0.407 (3)	0.191 (2)	0.6072 (8)	0.0550 (19)*
H201	−0.075 (3)	0.0641 (19)	0.6844 (7)	0.0531 (19)*
H202	−0.213 (3)	0.0038 (18)	0.6322 (8)	0.0532 (19)*
H203	−0.193 (3)	0.1664 (17)	0.6419 (8)	0.0533 (19)*
H18	0.509 (4)	0.2061 (17)	0.4707 (9)	0.0471 (19)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0214 (7)	0.0135 (6)	0.0156 (6)	0.0019 (6)	0.0006 (6)	−0.0003 (5)
C2	0.0237 (7)	0.0144 (6)	0.0160 (6)	−0.0014 (6)	−0.0017 (6)	0.0012 (5)
C3	0.0209 (7)	0.0157 (6)	0.0176 (6)	−0.0019 (6)	0.0014 (6)	0.0005 (5)
C4	0.0331 (9)	0.0179 (7)	0.0184 (7)	0.0003 (7)	0.0049 (7)	0.0009 (6)
O5	0.0520 (8)	0.0181 (5)	0.0141 (5)	0.0081 (6)	0.0012 (5)	−0.0004 (4)
C6	0.0321 (9)	0.0217 (7)	0.0175 (7)	0.0007 (7)	0.0027 (7)	−0.0057 (6)
O7	0.0420 (7)	0.0240 (5)	0.0175 (5)	0.0070 (6)	0.0060 (5)	−0.0030 (4)

C8	0.0401 (10)	0.0211 (7)	0.0185 (7)	0.0042 (8)	0.0044 (7)	−0.0009 (6)
C9	0.0634 (14)	0.0295 (8)	0.0172 (7)	0.0065 (10)	0.0052 (9)	0.0019 (6)
C10	0.0353 (10)	0.0465 (12)	0.0642 (14)	0.0012 (10)	0.0024 (11)	−0.0275 (11)
O11	0.0224 (5)	0.0172 (5)	0.0178 (5)	−0.0032 (5)	0.0013 (5)	−0.0018 (4)
C12	0.0222 (7)	0.0133 (6)	0.0192 (7)	0.0016 (6)	0.0002 (6)	0.0008 (5)
O13	0.0238 (5)	0.0203 (5)	0.0306 (6)	−0.0022 (5)	0.0056 (5)	−0.0022 (4)
O14	0.0286 (6)	0.0197 (5)	0.0300 (6)	−0.0090 (5)	−0.0042 (5)	0.0038 (5)
O15	0.0276 (5)	0.0165 (5)	0.0154 (5)	0.0068 (5)	−0.0019 (5)	−0.0016 (4)
C16	0.0233 (7)	0.0202 (7)	0.0156 (6)	0.0051 (7)	−0.0022 (6)	−0.0015 (5)
O17	0.0272 (6)	0.0181 (5)	0.0146 (5)	0.0054 (5)	0.0018 (5)	0.0014 (4)
C18	0.0257 (7)	0.0188 (6)	0.0156 (6)	0.0059 (7)	0.0009 (6)	0.0005 (5)
C19	0.0359 (10)	0.0214 (7)	0.0358 (9)	0.0021 (8)	−0.0144 (8)	−0.0034 (7)
C20	0.0294 (9)	0.0410 (9)	0.0218 (8)	0.0095 (9)	0.0041 (7)	0.0010 (7)

Geometric parameters (Å, º)

C1—C2	1.530 (2)	C9—H92	0.968 (16)
C1—C12	1.530 (2)	C9—H93	0.985 (16)
C1—O15	1.4179 (17)	C10—H101	0.969 (17)
C1—C18	1.539 (2)	C10—H102	0.953 (17)
C2—C3	1.535 (2)	C10—H103	0.967 (17)
C2—O14	1.4030 (19)	O11—C12	1.3545 (18)
C2—H21	0.978 (14)	C12—O13	1.2003 (19)
C3—C4	1.507 (2)	O14—H18	0.823 (15)
C3—O11	1.4593 (18)	O15—C16	1.4614 (17)
C3—H31	0.975 (14)	C16—O17	1.4183 (18)
C4—O5	1.425 (2)	C16—C19	1.512 (2)
C4—C8	1.525 (2)	C16—C20	1.506 (2)
C4—H41	0.998 (15)	O17—C18	1.4265 (18)
O5—C6	1.4376 (18)	C18—H181	0.974 (14)
C6—O7	1.431 (2)	C18—H182	0.960 (14)
C6—C9	1.500 (2)	C19—H191	0.967 (16)
C6—C10	1.503 (3)	C19—H192	0.963 (15)
O7—C8	1.4288 (19)	C19—H193	0.984 (16)
C8—H81	0.965 (15)	C20—H201	0.975 (15)
C8—H82	0.987 (15)	C20—H202	0.997 (16)
C9—H91	0.963 (16)	C20—H203	0.981 (16)
C2—C1—C12	100.99 (11)	C6—C9—H93	108.9 (12)
C2—C1—O15	115.24 (11)	H91—C9—H93	109.8 (14)
C12—C1—O15	111.28 (13)	H92—C9—H93	111.9 (14)
C2—C1—C18	113.96 (13)	C6—C10—H101	109.2 (13)
C12—C1—C18	111.58 (11)	C6—C10—H102	108.9 (13)
O15—C1—C18	104.07 (11)	H101—C10—H102	107.5 (15)
C1—C2—C3	98.99 (11)	C6—C10—H103	113.3 (13)
C1—C2—O14	114.45 (12)	H101—C10—H103	108.7 (15)
C3—C2—O14	112.67 (13)	H102—C10—H103	109.2 (15)
C1—C2—H21	111.5 (9)	C3—O11—C12	108.84 (11)

C3—C2—H21	109.3 (9)	C1—C12—O11	109.11 (12)
O14—C2—H21	109.5 (9)	C1—C12—O13	128.93 (14)
C2—C3—C4	116.37 (12)	O11—C12—O13	121.96 (14)
C2—C3—O11	102.87 (12)	C2—O14—H18	107.5 (18)
C4—C3—O11	110.93 (12)	C1—O15—C16	109.14 (10)
C2—C3—H31	109.3 (9)	O15—C16—O17	104.61 (11)
C4—C3—H31	108.6 (9)	O15—C16—C19	108.60 (13)
O11—C3—H31	108.5 (9)	O17—C16—C19	111.89 (13)
C3—C4—O5	111.35 (13)	O15—C16—C20	108.98 (13)
C3—C4—C8	115.71 (13)	O17—C16—C20	108.71 (13)
O5—C4—C8	103.27 (13)	C19—C16—C20	113.64 (14)
C3—C4—H41	107.0 (9)	C16—O17—C18	106.44 (11)
O5—C4—H41	110.3 (10)	C1—C18—O17	102.65 (12)
C8—C4—H41	109.2 (9)	C1—C18—H181	111.9 (10)
C4—O5—C6	108.79 (11)	O17—C18—H181	109.2 (9)
O5—C6—O7	106.16 (13)	C1—C18—H182	110.4 (9)
O5—C6—C9	109.39 (13)	O17—C18—H182	112.5 (9)
O7—C6—C9	108.60 (14)	H181—C18—H182	110.1 (12)
O5—C6—C10	108.02 (16)	C16—C19—H191	108.9 (11)
O7—C6—C10	110.25 (15)	C16—C19—H192	110.1 (11)
C9—C6—C10	114.11 (19)	H191—C19—H192	108.9 (13)
C6—O7—C8	106.38 (11)	C16—C19—H193	110.4 (11)
C4—C8—O7	102.00 (12)	H191—C19—H193	109.3 (13)
C4—C8—H81	111.7 (10)	H192—C19—H193	109.2 (13)
O7—C8—H81	111.3 (10)	C16—C20—H201	108.5 (12)
C4—C8—H82	112.2 (10)	C16—C20—H202	109.3 (11)
O7—C8—H82	111.7 (10)	H201—C20—H202	109.6 (13)
H81—C8—H82	107.8 (12)	C16—C20—H203	108.7 (11)
C6—C9—H91	108.2 (12)	H201—C20—H203	109.6 (13)
C6—C9—H92	107.6 (12)	H202—C20—H203	111.1 (13)
H91—C9—H92	110.4 (14)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O14—H18···O15^{i}	0.82 (2)	1.98 (2)	2.7947 (15)	172 (2)

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