Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,3:5,6-Di-*O*-isopropylidene-2-*C*-hydroxymethyl-D-talono-1,4-lactone

Howard A. Shallard-Brown,[a]* Christopher C. Harding,[a] David J. Watkin,[a] Raquel Soengas,[b] Ulla P. Skytte[c] and George W. J. Fleet[b]

[a]Chemical Crystallography Laboratory, Chemical Research Laboratory, Oxford University, Mansfield Road, Oxford OX1 3TA, England, [b]Department of Organic Chemistry, Chemical Research Laboratory, Oxford University, Mansfield Road, Oxford OX1 3TA, England, and [c]Arla Foods Ingredients, Viby J, Denmark

Correspondence e-mail: howard.shallard-brown@lmh.ox.ac.uk

Key indicators

Single-crystal X-ray study
T = 190 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.073
Data-to-parameter ratio = 10.0

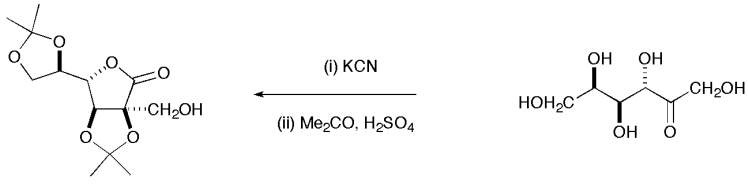
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 October 2004
Accepted 25 October 2004
Online 30 October 2004

The title diacetonide, $C_{13}H_{20}O_7$, readily available in quantity from D-tagatose, is likely to be a useful carbohydrate starting material. The current structure analysis resolves any ambiguities arising from the synthetic route over the configuration at the new chiral centre and the size of the lactone ring, but otherwise shows no unusual features.

Comment

Sugars provide the largest group of readily available chiral building blocks and bio-active scaffolds (Lichtenthaler & Peters, 2004; Bols, 1996). Although little studied since initial investigations by Kiliani (Kiliani, 1885, 1928; Gorin & Perlin, 1958), the reaction of ketoses with aqueous potassium cyanide easily produces a mixture of branched sugar lactones under aqueous conditions. The reaction of the lactones produced from D-fructose and L-sorbose with acetone in the presence of acid gives rise to readily crystallized diacetonides likely to furnish a new family of carbohydrate-derived chiral building blocks with branched carbon chains (Hotchkiss *et al.*, 2004). The full exploitation of this technology requires access to a wide range of ketoses; in the past, only D-fructose and L-sorbose have been readily available. However, the impetus for the development of low calorie sweeteners has led to an extensive biotechnology which provides almost any hexose by combinations of microbial oxidations and enzyme-catalysed epimerizations (Granstrom *et al.*, 2004). Thus D-tagatose (2) (see scheme), previously considered a rare sugar, is prepared on an industrial scale for use in soft drinks and ready-to-eat cereals (Skytte, 2002).



(1) (2)

The Kiliani reaction of cyanide with D-tagatose (2) gave an excellent yield of different amounts of two lactones. Extraction of this mixture with acetone in the presence of sulfuric acid gave a mixture of diacetonides; the major product (1) was easily isolated as a crystalline material. The current structure analysis of (1) resolves any ambiguities arising from the synthetic route over the configuration at the new chiral centre and the size of the lactone ring. The diacetonide (1) is likely to be a useful starting material for the preparation of a number of branched sugar mimics.

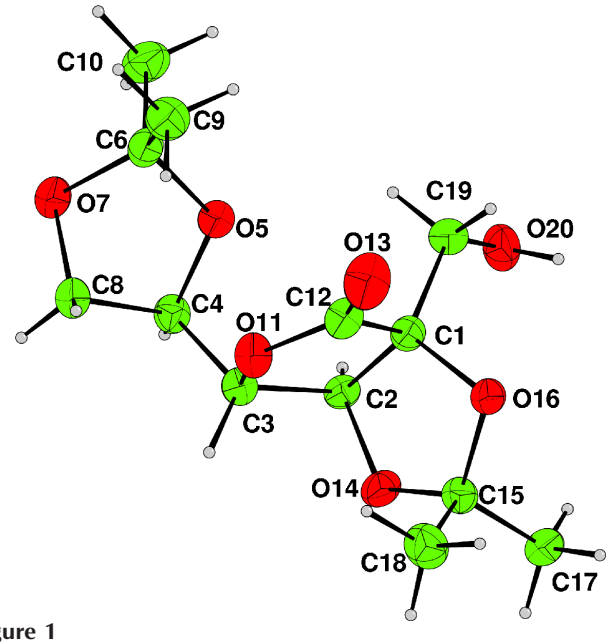


Figure 1
The title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are of arbitrary radii.

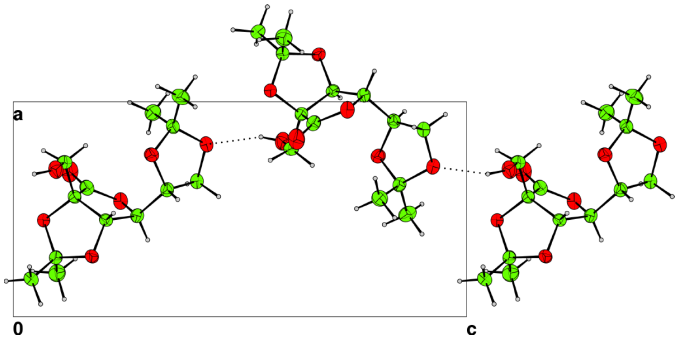


Figure 2
Packing diagram viewed along the *b* axis. Molecules are linked into ribbons by hydrogen bonds (dashed lines).

The crystal and molecular structures of (1) show no unusual features. As expected for sugar derivatives, hydrogen bonding occurs between molecules, in this case, linking molecules into ribbons parallel to the *c* axis.

Experimental

The title compound was crystallized from diethyl ether by inward diffusion of *n*-hexane to yield plate-like colourless crystals. These did not cleave well, leading to the use of a large crystal. The multi-scan technique was used to correct for changes in illuminated volume.

Crystal data

$C_{13}H_{20}O_7$
M_r = 288.30
Orthorhombic, $P2_12_12_1$
a = 7.8609 (3) Å
b = 10.7470 (4) Å
c = 16.5516 (6) Å
V = 1398.30 (9) Å^3
Z = 4
D_x = 1.369 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1577 reflections
θ = 5–27°
μ = 0.11 mm^{-1}
T = 190 K
Block, colourless
0.65 × 0.25 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.97, T_{max} = 0.98
2981 measured reflections
1804 independent reflections
1544 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 27.5°
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.074
S = 0.92
1803 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.028 + 0.385P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

All H atoms were observed in a difference electron-density map. The hydroxyl H atom was placed as found and the others were placed geometrically with isotropic displacement parameters related to the U_{eq} values of the adjacent atoms. The H-atom positions and U_{iso} values were regularized by refinement with slack restraints and the refinement completed with H-atom riding constraints [C—H = 0.98±0.02 Å; U_{iso}(H) = U_{eq}(C) ± 0.002 Å^2; O—H no restraints]. In the absence of significant anomalous scattering effects, Friedel pairs were merged.

Data collection: *COLLECT* (Nonius, 1997); 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*.

Financial support (to RS) provided through the European Community's Human Potential Programme under contract HPRN–CT-2002–00173 is gratefully acknowledged. A generous gift of D-tagatose from Arla Foods allowed this work to be performed.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Bols, M. (1996). *Carbohydrate Building Blocks*. New York: Wiley.
Gorin, P. A. J. & Perlin, A. S. (1958). *Can. J. Chem.* **36**, 480–485.
Granstrom, T. B., Takata, G., Tokuda, M. & Izumori, K. (2004). *J. Biosci. Bioeng.* **97**, 89–94.
Hotchkiss, D., Soengas, R., Simone, M. I., Van Ameijde, J., Hunter, S., Cowley, A. R. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**. In the press.
Kiliani, H. (1885). *Ber. Dtsch Chem. Ges.* **18**, 3066–3074.
Kiliani, H. (1928). *Ber. Dtsch Chem. Ges.* **61**, 1155–1169.
Lichtenthaler, F. W. & Peters, S.(2004). *Compt. Rend. Chim.* **7**, 65–90.
Nonius (1997). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
Skytte, U. P. (2002). *Cereal Foods World*, **47**, 224–227.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

supporting information

Acta Cryst. (2004). E**60**, o2163–o2164 [https://doi.org/10.1107/S160053680402700X]

2,3:5,6-Di-*O*-isopropylidene-2-*C*-hydroxymethyl-D-talono-1,4-lactone

Howard A. Shallard-Brown, Christopher C. Harding, David J. Watkin, Raquel Soengas, Ulla P. Skytte and George W. J. Fleet

(1)

Crystal data

$C_{13}H_{20}O_7$
$M_r = 288.30$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 7.8609$ (3) Å
$b = 10.7470$ (4) Å
$c = 16.5516$ (6) Å
$V = 1398.30$ (9) Å^3
$Z = 4$
$F(000) = 616$
$D_x = 1.369$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1577 reflections
$\theta = 5$–27°
$\mu = 0.11$ mm^{-1}
$T = 190$ K
Plate, colourless
0.65 × 0.25 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1996)
$T_{min} = 0.97$, $T_{max} = 0.98$
2981 measured reflections
1804 independent reflections
1544 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.5°$, $\theta_{min} = 5.2°$
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.074$
$S = 0.92$
1803 reflections
181 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F) + 0.028 + 0.385P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.000174$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5577 (2)	0.41009 (18)	0.13539 (11)	0.0255
C2	0.4493 (2)	0.46106 (17)	0.20459 (10)	0.0242
C3	0.4697 (3)	0.36718 (17)	0.27347 (11)	0.0257

C4	0.5906 (2)	0.41013 (19)	0.33943 (11)	0.0277
O5	0.75307 (17)	0.43700 (13)	0.30500 (8)	0.0319
C6	0.8851 (3)	0.37695 (19)	0.35196 (11)	0.0297
O7	0.80175 (19)	0.34335 (14)	0.42604 (8)	0.0336
C8	0.6298 (3)	0.3145 (2)	0.40505 (12)	0.0314
C9	0.9493 (3)	0.2631 (2)	0.30810 (13)	0.0378
C10	1.0224 (3)	0.4706 (2)	0.36946 (15)	0.0418
O11	0.53763 (19)	0.25469 (12)	0.23691 (8)	0.0303
C12	0.5999 (3)	0.27713 (18)	0.16246 (12)	0.0300
O13	0.6742 (2)	0.19899 (14)	0.12498 (9)	0.0466
O14	0.28029 (17)	0.46392 (13)	0.17367 (7)	0.0326
C15	0.2752 (2)	0.41027 (19)	0.09403 (11)	0.0281
O16	0.44814 (17)	0.40904 (13)	0.06706 (7)	0.0283
C17	0.1748 (3)	0.4956 (2)	0.03974 (12)	0.0334
C18	0.2023 (3)	0.2800 (2)	0.09667 (14)	0.0412
C19	0.7181 (3)	0.4807 (2)	0.11313 (13)	0.0328
O20	0.6840 (2)	0.60645 (13)	0.09396 (8)	0.0384
H21	0.4815	0.5438	0.2213	0.0277*
H31	0.3573	0.3459	0.2967	0.0300*
H41	0.5457	0.4871	0.3628	0.0331*
H81	0.5588	0.3269	0.4530	0.0368*
H82	0.6180	0.2274	0.3840	0.0363*
H91	1.0395	0.2233	0.3412	0.0452*
H92	0.8567	0.2039	0.2983	0.0454*
H93	0.9972	0.2931	0.2570	0.0453*
H101	1.1156	0.4318	0.4015	0.0496*
H102	0.9762	0.5389	0.4013	0.0491*
H103	1.0713	0.5046	0.3186	0.0498*
H171	0.1653	0.4613	−0.0154	0.0402*
H172	0.0586	0.5091	0.0606	0.0408*
H173	0.2317	0.5765	0.0361	0.0403*
H181	0.2114	0.2441	0.0426	0.0484*
H182	0.2692	0.2298	0.1368	0.0481*
H183	0.0817	0.2850	0.1126	0.0487*
H191	0.7955	0.4778	0.1597	0.0391*
H192	0.7723	0.4376	0.0670	0.0387*
H1	0.6637	0.6131	0.0465	0.0686*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0251 (9)	0.0275 (9)	0.0238 (9)	0.0017 (9)	−0.0013 (8)	−0.0007 (8)
C2	0.0233 (8)	0.0238 (9)	0.0255 (9)	0.0010 (9)	−0.0021 (8)	−0.0022 (7)
C3	0.0285 (10)	0.0236 (9)	0.0251 (9)	0.0004 (9)	0.0010 (9)	−0.0017 (8)
C4	0.0299 (10)	0.0282 (10)	0.0251 (9)	0.0027 (9)	0.0011 (8)	−0.0016 (8)
O5	0.0283 (7)	0.0376 (7)	0.0299 (7)	−0.0010 (7)	−0.0018 (6)	0.0059 (6)
C6	0.0309 (10)	0.0329 (10)	0.0253 (9)	0.0018 (9)	−0.0029 (9)	0.0016 (8)
O7	0.0343 (7)	0.0415 (8)	0.0251 (7)	0.0004 (7)	−0.0028 (6)	0.0004 (6)

C8	0.0330 (10)	0.0368 (11)	0.0245 (9)	0.0003 (10)	−0.0001 (9)	0.0021 (8)
C9	0.0371 (11)	0.0395 (11)	0.0369 (11)	0.0040 (11)	0.0016 (10)	−0.0038 (10)
C10	0.0356 (11)	0.0445 (13)	0.0454 (12)	−0.0052 (11)	−0.0084 (11)	−0.0009 (11)
O11	0.0413 (8)	0.0213 (6)	0.0283 (7)	0.0003 (7)	−0.0001 (7)	−0.0008 (5)
C12	0.0335 (10)	0.0277 (10)	0.0287 (10)	0.0040 (9)	−0.0033 (9)	−0.0027 (8)
O13	0.0621 (11)	0.0401 (8)	0.0377 (8)	0.0207 (9)	0.0012 (8)	−0.0096 (7)
O14	0.0256 (7)	0.0462 (8)	0.0261 (7)	0.0081 (7)	−0.0024 (6)	−0.0065 (6)
C15	0.0269 (9)	0.0332 (10)	0.0242 (9)	−0.0022 (10)	0.0008 (8)	−0.0018 (8)
O16	0.0257 (6)	0.0370 (7)	0.0223 (6)	0.0012 (7)	0.0000 (5)	−0.0014 (6)
C17	0.0279 (10)	0.0426 (12)	0.0297 (10)	−0.0003 (10)	−0.0045 (9)	0.0004 (9)
C18	0.0431 (13)	0.0412 (12)	0.0394 (11)	−0.0087 (12)	0.0015 (11)	0.0017 (10)
C19	0.0264 (10)	0.0397 (11)	0.0322 (10)	−0.0026 (10)	−0.0007 (9)	0.0031 (9)
O20	0.0462 (9)	0.0385 (8)	0.0306 (7)	−0.0123 (8)	−0.0028 (7)	0.0065 (6)

Geometric parameters (Å, º)

C1—C2	1.529 (3)	C9—H92	0.981
C1—C12	1.534 (3)	C9—H93	0.980
C1—O16	1.421 (2)	C10—H101	0.996
C1—C19	1.517 (3)	C10—H102	0.974
C2—C3	1.531 (3)	C10—H103	0.996
C2—O14	1.424 (2)	O11—C12	1.348 (2)
C2—H21	0.965	C12—O13	1.196 (2)
C3—C4	1.519 (3)	O14—C15	1.439 (2)
C3—O11	1.454 (2)	C15—O16	1.431 (2)
C3—H31	0.990	C15—C17	1.507 (3)
C4—O5	1.428 (2)	C15—C18	1.513 (3)
C4—C8	1.527 (3)	C17—H171	0.987
C4—H41	0.979	C17—H172	0.987
O5—C6	1.449 (2)	C17—H173	0.979
C6—O7	1.437 (2)	C18—H181	0.976
C6—C9	1.509 (3)	C18—H182	1.005
C6—C10	1.504 (3)	C18—H183	0.986
O7—C8	1.430 (3)	C19—O20	1.414 (3)
C8—H81	0.979	C19—H191	0.983
C8—H82	1.003	C19—H192	0.989
C9—H91	0.994	O20—H1	0.805
C2—C1—C12	103.61 (15)	C6—C9—H93	106.107
C2—C1—O16	105.14 (14)	H91—C9—H93	110.057
C12—C1—O16	110.86 (15)	H92—C9—H93	110.800
C2—C1—C19	117.78 (16)	C6—C10—H101	110.508
C12—C1—C19	110.91 (16)	C6—C10—H102	109.925
O16—C1—C19	108.32 (15)	H101—C10—H102	107.531
C1—C2—C3	105.26 (15)	C6—C10—H103	111.096
C1—C2—O14	104.97 (14)	H101—C10—H103	108.681
C3—C2—O14	112.33 (16)	H102—C10—H103	109.013
C1—C2—H21	113.439	C3—O11—C12	111.42 (14)

C3—C2—H21	111.502	C1—C12—O11	110.81 (16)
O14—C2—H21	109.170	C1—C12—O13	127.44 (18)
C2—C3—C4	113.61 (16)	O11—C12—O13	121.73 (18)
C2—C3—O11	106.07 (13)	C2—O14—C15	110.28 (13)
C4—C3—O11	108.78 (15)	O14—C15—O16	105.25 (14)
C2—C3—H31	110.304	O14—C15—C17	108.47 (16)
C4—C3—H31	110.477	O16—C15—C17	108.49 (15)
O11—C3—H31	107.301	O14—C15—C18	110.78 (16)
C3—C4—O5	109.52 (15)	O16—C15—C18	111.11 (17)
C3—C4—C8	115.63 (16)	C17—C15—C18	112.46 (17)
O5—C4—C8	103.88 (15)	C15—O16—C1	109.10 (14)
C3—C4—H41	108.333	C15—C17—H171	111.309
O5—C4—H41	107.994	C15—C17—H172	111.435
C8—C4—H41	111.181	H171—C17—H172	107.957
C4—O5—C6	109.68 (13)	C15—C17—H173	109.723
O5—C6—O7	104.06 (15)	H171—C17—H173	107.997
O5—C6—C9	110.03 (16)	H172—C17—H173	108.303
O7—C6—C9	111.06 (17)	C15—C18—H181	108.134
O5—C6—C10	108.64 (17)	C15—C18—H182	108.548
O7—C6—C10	109.34 (16)	H181—C18—H182	110.829
C9—C6—C10	113.29 (18)	C15—C18—H183	108.724
C6—O7—C8	106.18 (14)	H181—C18—H183	109.643
C4—C8—O7	102.53 (16)	H182—C18—H183	110.889
C4—C8—H81	111.741	C1—C19—O20	112.00 (17)
O7—C8—H81	108.162	C1—C19—H191	107.952
C4—C8—H82	111.239	O20—C19—H191	108.905
O7—C8—H82	111.980	C1—C19—H192	108.151
H81—C8—H82	110.888	O20—C19—H192	110.815
C6—C9—H91	108.835	H191—C19—H192	108.928
C6—C9—H92	110.979	C19—O20—H1	109.949
H91—C9—H92	109.980		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O20—H1···O7^{i}	0.80	2.07	2.833 (3)	159 (1)

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