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3,5-*O*-Isopropylidene-2-*C*-methyl-D-xylonolactone

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.074
Data-to-parameter ratio = 12.2

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

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The ring size of both the lactone and the ketal protecting group in the title compound, $C_9H_{14}O_5$, have been established by X-ray crystallographic analysis. The crystal structure consists of hydrogen-bonded spirals parallel to the *b* axis.

Comment

Almost all carbohydrate scaffolds contain linear carbon chains (Lichtenthaler & Peters, 2004). The two exceptions that do provide carbohydrates with branched carbon chains are (i) the Kiliani reaction on ketoses which provides efficient access to a set of 2-*C*-hydroxymethylaldonolactones (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005), and (ii) the treatment of sugars with base to give 2-*C*-methyl aldonic acids, also known as saccharinic acids (Bols, 1996). However, the reaction of base with sugars is complex: glucose gives a mixture of more than 50 compounds on treatment with calcium hydroxide, of which branched sugars comprise a very small percentage (Yang & Montgomery, 1996). Better yields are obtained from ketoses; however, even the optimized conditions (several weeks under careful control in a laborious procedure) for treatment of D-fructose with calcium hydroxide afford 2-*C*-methyl-D-ribonolactone in only 11% yield (Whistler & BeMiller, 1963). Very low yields of branched lactones have been isolated from similar treatment of L-sorbose (Ishizu *et al.*, 1972). A further ketohexose, D-tagatose (1), has recently become available in quantity as a new food additive (Skytte, 2002); (1) has the potential for making 2-*C*-methyl-D-xylonolactone as a branched-sugar building block under green environmentally friendly conditions. Treatment of D-tagatose with aqueous calcium hydroxide produces a very complex mixture of products. In order to identify the branched-chain sugar products, it was necessary to make authentic samples of easily crystallized derivatives.

(1) (2)

A crystalline acetonide was obtained from treatment of 2-*C*-methyl-D-xylonolactone with acetone in the presence of acid. The absolute stereochemistry of (2) is determined by using D-tagatose (1) as the starting material; however, there are ambiguities in the synthesis with regard to the relative stereochemistry at C-2 of the lactone, the ring size of the lactone and the ring size of the ketal. X-ray crystallographic analysis removed all the ambiguities and firmly established the structure of the acetonide as (2).

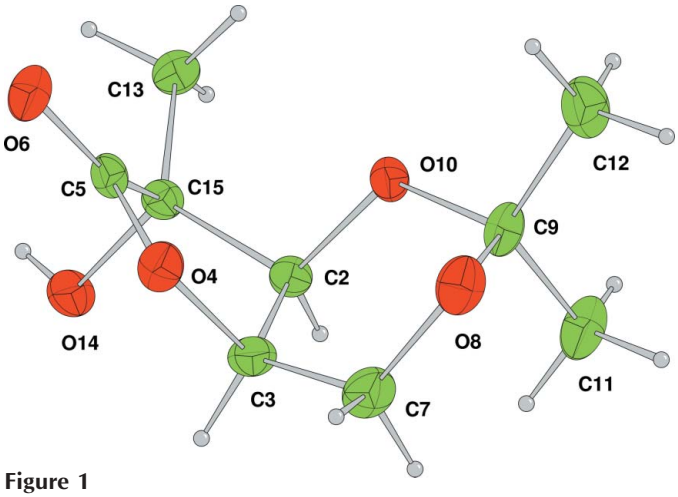

Figure 1
The title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

Experimental

The acetonide (2) was prepared as in the *Comment* section and crystallized from ethyl acetate:cyclohexane (m.p. 428–431 K) as long fibrous needles. $[\alpha]_D^{23}$ +82.2 (*c* 0.67 in $CHCl_3$).

Crystal data

$C_9H_{14}O_5$
M_r = 202.21
Monoclinic, $P2_1$
a = 8.3764 (3) Å
b = 5.9861 (2) Å
c = 10.4690 (4) Å
β = 110.0336 (12)°
V = 493.17 (3) Å^3
Z = 2
D_x = 1.362 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1419 reflections
θ = 5–30°
μ = 0.11 mm^{-1}
T = 150 K
Lath, colourless
1.00 × 0.28 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.81, T_{max} = 0.99
7941 measured reflections
1549 independent reflections
1549 reflections with $I > -3.0\sigma(I)$
R_{int} = 0.034
θ_{max} = 30.0°
h = −11 → 11
k = −8 → 8
l = −14 → 14

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.074
S = 0.94
1549 reflections
127 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.03P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O14—H1···O6^{i}	0.84	2.00	2.837 (2)	176

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

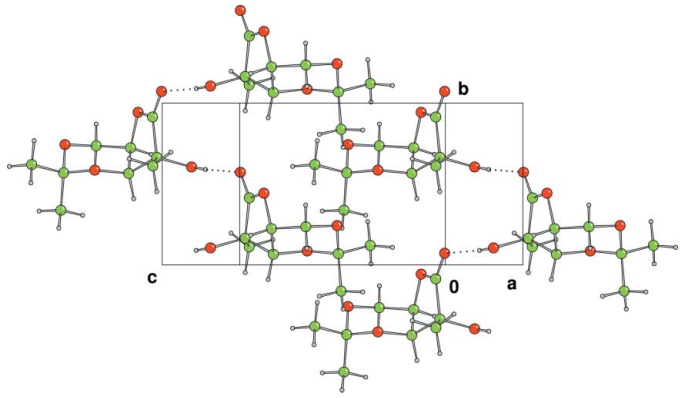

Figure 2
Projection of the structure perpendicular to the *b* axis, showing the molecules linked into hydrogen-bonded spirals parallel to *b*.

In the absence of significant anomalous scattering, Friedel pairs were merged, and the absolute configuration assigned from the known staring materials.

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 to regularize their geometry (C—H in the range 0.93–0.98 and O—H = 0.82 Å) and displacement parameters [U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent 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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supporting information

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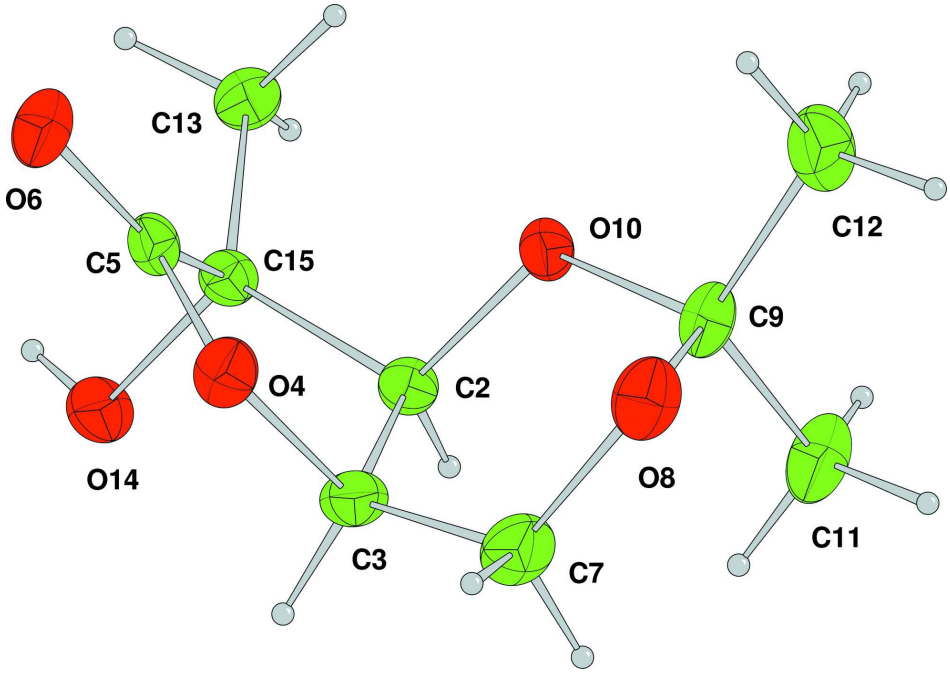

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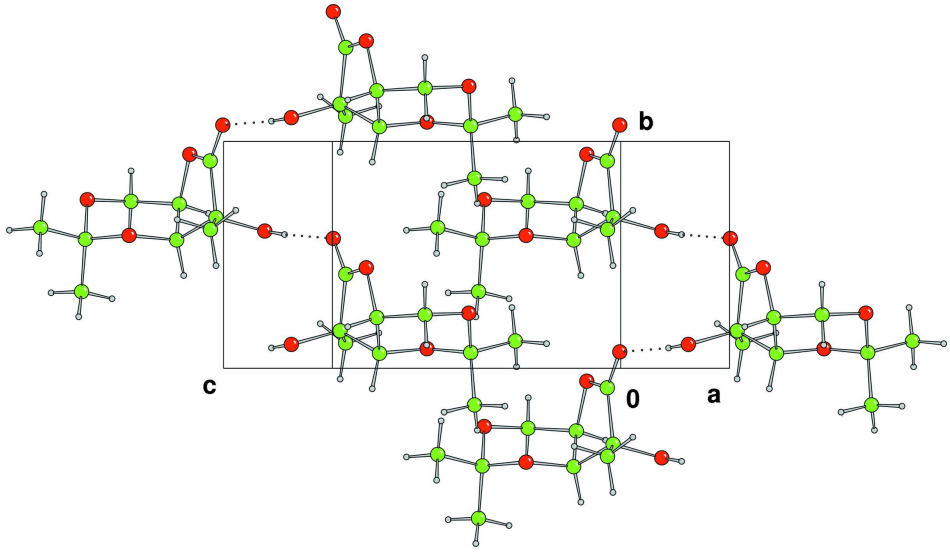

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Refinement on F^2
Least-squares matrix: full
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$wR(F^2) = 0.074$
$S = 0.94$
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1 restraint
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.03P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.000276$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C15	0.3718 (2)	0.6651 (3)	0.12110 (16)	0.0178
C2	0.25213 (19)	0.5660 (3)	0.18739 (15)	0.0184
C3	0.1006 (2)	0.7239 (3)	0.13919 (17)	0.0224
O4	0.17777 (14)	0.94293 (19)	0.13389 (12)	0.0229
C5	0.3328 (2)	0.9145 (3)	0.12495 (15)	0.0186
O6	0.41821 (15)	1.0723 (2)	0.11673 (12)	0.0263
C7	−0.0008 (2)	0.7359 (3)	0.23305 (18)	0.0293
O8	0.10426 (16)	0.7433 (2)	0.37196 (12)	0.0287
C9	0.2271 (2)	0.5693 (3)	0.41041 (17)	0.0241
O10	0.33568 (13)	0.5859 (2)	0.33001 (10)	0.0202
C11	0.1474 (3)	0.3382 (3)	0.3982 (2)	0.0342
C12	0.3401 (3)	0.6203 (4)	0.55389 (17)	0.0359
C13	0.55828 (19)	0.6121 (3)	0.18621 (16)	0.0223
O14	0.30492 (14)	0.6050 (2)	−0.02003 (10)	0.0248

H21	0.2210	0.4095	0.1608	0.0219*
H31	0.0257	0.6832	0.0454	0.0259*
H71	−0.0734	0.6026	0.2171	0.0361*
H72	−0.0703	0.8703	0.2135	0.0359*
H111	0.2352	0.2273	0.4293	0.0549*
H112	0.0802	0.3068	0.3029	0.0551*
H113	0.0743	0.3331	0.4548	0.0544*
H121	0.4335	0.5066	0.5825	0.0553*
H122	0.2716	0.6088	0.6138	0.0542*
H123	0.3885	0.7681	0.5587	0.0549*
H131	0.6208	0.6964	0.1394	0.0328*
H132	0.5756	0.4529	0.1770	0.0330*
H133	0.5967	0.6557	0.2803	0.0330*
H1	0.3875	0.5895	−0.0472	0.0382*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C15	0.0187 (8)	0.0185 (7)	0.0161 (8)	−0.0012 (6)	0.0057 (6)	−0.0027 (6)
C2	0.0198 (7)	0.0176 (7)	0.0175 (7)	−0.0014 (6)	0.0061 (6)	−0.0023 (6)
C3	0.0171 (8)	0.0232 (8)	0.0247 (8)	−0.0016 (7)	0.0042 (6)	0.0007 (6)
O4	0.0227 (6)	0.0202 (6)	0.0271 (6)	0.0043 (5)	0.0101 (5)	0.0042 (5)
C5	0.0214 (8)	0.0218 (8)	0.0136 (7)	0.0006 (6)	0.0072 (6)	0.0004 (6)
O6	0.0342 (7)	0.0210 (6)	0.0286 (6)	−0.0032 (6)	0.0172 (5)	0.0009 (5)
C7	0.0202 (8)	0.0336 (10)	0.0359 (10)	0.0032 (8)	0.0117 (7)	0.0050 (8)
O8	0.0310 (7)	0.0287 (7)	0.0327 (7)	0.0044 (5)	0.0190 (6)	0.0012 (6)
C9	0.0281 (8)	0.0247 (8)	0.0255 (8)	−0.0008 (7)	0.0168 (7)	0.0023 (7)
O10	0.0204 (5)	0.0240 (6)	0.0170 (5)	0.0005 (5)	0.0073 (4)	0.0024 (5)
C11	0.0439 (12)	0.0287 (10)	0.0374 (11)	−0.0060 (9)	0.0234 (9)	0.0037 (8)
C12	0.0444 (11)	0.0417 (11)	0.0241 (9)	−0.0041 (9)	0.0149 (8)	0.0001 (8)
C13	0.0198 (7)	0.0230 (8)	0.0248 (8)	−0.0003 (7)	0.0087 (6)	−0.0008 (7)
O14	0.0260 (6)	0.0315 (7)	0.0179 (5)	−0.0026 (5)	0.0088 (4)	−0.0058 (5)

Geometric parameters (Å, º)

C15—C2	1.522 (2)	O8—C9	1.422 (2)
C15—C5	1.532 (2)	C9—O10	1.4391 (19)
C15—C13	1.508 (2)	C9—C11	1.522 (3)
C15—O14	1.4350 (18)	C9—C12	1.507 (2)
C2—C3	1.523 (2)	C11—H111	0.961
C2—O10	1.4204 (18)	C11—H112	0.981
C2—H21	0.987	C11—H113	0.988
C3—O4	1.471 (2)	C12—H121	1.002
C3—C7	1.504 (2)	C12—H122	0.987
C3—H31	0.997	C12—H123	0.967
O4—C5	1.3447 (19)	C13—H131	0.972
C5—O6	1.206 (2)	C13—H132	0.974
C7—O8	1.419 (2)	C13—H133	0.961

C7—H71	0.982	O14—H1	0.838
C7—H72	0.973		
C2—C15—C5	100.84 (13)	C7—O8—C9	113.68 (13)
C2—C15—C13	117.01 (13)	O8—C9—O10	108.96 (13)
C5—C15—C13	112.97 (14)	O8—C9—C11	112.85 (14)
C2—C15—O14	106.60 (12)	O10—C9—C11	111.11 (15)
C5—C15—O14	105.06 (13)	O8—C9—C12	106.30 (15)
C13—C15—O14	113.04 (13)	O10—C9—C12	105.17 (14)
C15—C2—C3	102.22 (13)	C11—C9—C12	112.06 (16)
C15—C2—O10	106.39 (12)	C9—O10—C2	115.24 (12)
C3—C2—O10	110.53 (13)	C9—C11—H111	109.7
C15—C2—H21	113.2	C9—C11—H112	110.0
C3—C2—H21	112.7	H111—C11—H112	108.6
O10—C2—H21	111.3	C9—C11—H113	108.8
C2—C3—O4	103.79 (12)	H111—C11—H113	109.5
C2—C3—C7	113.95 (15)	H112—C11—H113	110.2
O4—C3—C7	109.62 (15)	C9—C12—H121	108.7
C2—C3—H31	110.3	C9—C12—H122	108.4
O4—C3—H31	108.5	H121—C12—H122	109.1
C7—C3—H31	110.4	C9—C12—H123	110.2
C3—O4—C5	109.70 (12)	H121—C12—H123	109.6
C15—C5—O4	110.20 (14)	H122—C12—H123	110.8
C15—C5—O6	128.67 (15)	C15—C13—H131	108.5
O4—C5—O6	121.08 (15)	C15—C13—H132	109.1
C3—C7—O8	112.36 (14)	H131—C13—H132	109.5
C3—C7—H71	107.8	C15—C13—H133	109.7
O8—C7—H71	109.3	H131—C13—H133	109.0
C3—C7—H72	109.5	H132—C13—H133	110.9
O8—C7—H72	107.8	C15—O14—H1	107.5
H71—C7—H72	110.1		

Hydrogen-bond geometry (Å, º)

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