3,4-O-Isopropylidene-2-C-methyl-D-arabinono-1,5-lactone

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Key indicators

Single-crystal X-ray study
$T = 190$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.078
Data-to-parameter ratio = 12.0

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

The title δ-lactone, $C_9H_{14}O_5$, formed in high diastereoselectivity by the Kiliani reaction of a protected 1-deoxyketose, adopts a boat conformation in which an OH group occupies a flagpole position.

Comment

Although sugars provide the largest group of readily available chiral building blocks and bioactive scaffolds (Lichtenthaler & Peters, 2004), the potential of the Kiliani ascension of ketoses to provide readily available branched scaffolds has only just begun to be developed (Hotchkiss *et al.*, 2004; Shallard-Brown *et al.*, 2004 Cowley *et al.*, 2004; van Ameijde *et al.*, 2004). While the range of commercially available ketoses is restricted, 1-deoxyketoses may readily be generated by addition of organometallic reagents to sugar lactones. As an extension to the branching chemistry of ketoses, the protected 1-deoxyketose (1) was treated with sodium cyanide and gave a single diastereomeric product. The crystal structure reported in this paper firmly establishes that the lactone (2) was formed; none of the epimeric lactone (3) was isolated.
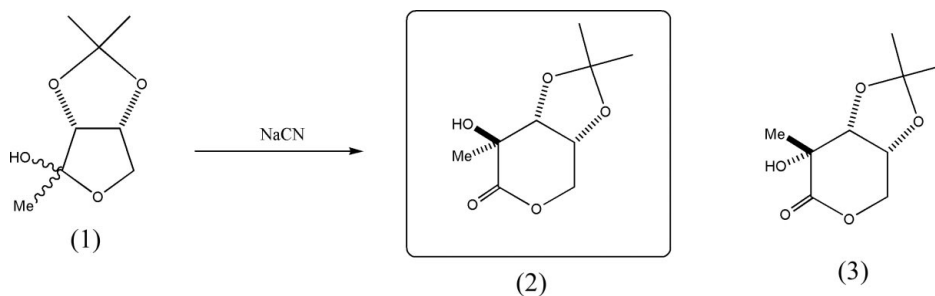

The δ-lactone (2) (Fig. 1) adopts a boat conformation. While there are several example of fused 3,4-ketals of δ-lactones that adopt boat conformations (Bruce *et al.*, 1990; Bichard *et al.*, 1991; Beacham *et al.*, 1991), very few of them have a flagpole substituent (Wheatley *et al.*, 1994); the hydroxy group at atom C1 is clearly in a very hindered position, being additionally attached to a tertiary C atom. Nonetheless, as usually expected for sugar derivatives, hydrogen bonding occurs between molecules (Fig. 2 and Table 2).

Experimental

The sugar was crystallized by dissolving it in diethyl ether, adding a few drops of cyclohexane and allowing the slow competitive evaporation of the two solvents until crystals formed.
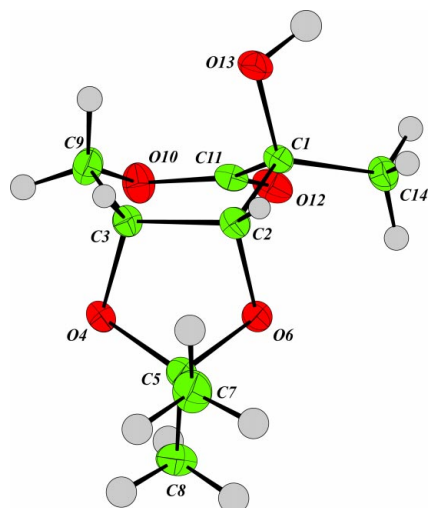
Figure 1
The molecular structure of (2), with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary.
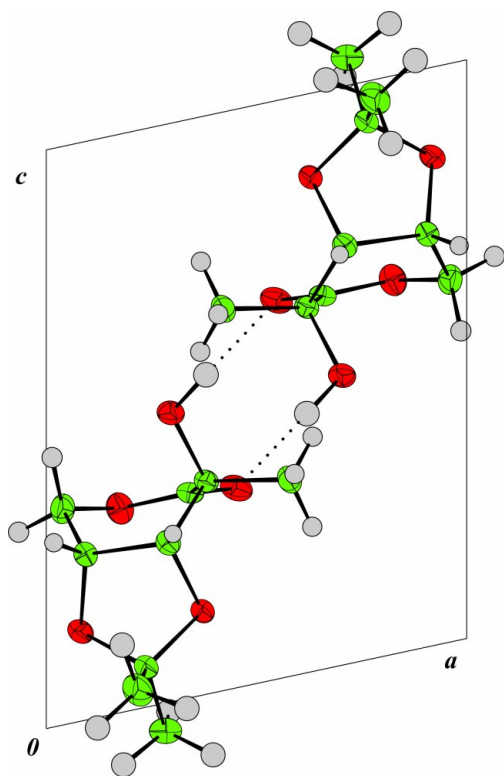
Figure 2
Partial packing diagram of (2), viewed down the b axis. Hydrogen bonds are shown as dotted lines.

Crystal data

$C_9H_{14}O_5$	$D_x = 1.356$ Mg m^{-3}
$M_r = 202.21$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1264
$a = 7.7315$ (3) Å	reflections
$b = 6.2859$ (3) Å	$\theta = 5$–30°
$c = 10.4209$ (6) Å	$\mu = 0.11$ mm^{-1}
$\beta = 102.1024$ (17)°	$T = 190$ K
$V = 495.19$ (4) Å^3	Needle, colourless
$Z = 2$	$0.90 \times 0.20 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.018$
ω scans	$\theta_{max} = 30.0°$
2579 measured reflections	$h = -10 \rightarrow 10$
1527 independent reflections	$k = -8 \rightarrow 8$
1448 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F^2) + 0.04$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.06P]$,
$wR(F^2) = 0.078$	where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$S = 0.99$	$(\Delta/\sigma)_{max} < 0.001$
1527 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.5284 (18)	O4—C5	1.4312 (16)
C1—C11	1.5318 (19)	C5—O6	1.4314 (16)
C1—O13	1.4334 (15)	C5—C7	1.522 (2)
C1—C14	1.5237 (17)	C5—C8	1.508 (2)
C2—C3	1.5468 (18)	C9—O10	1.4581 (18)
C2—O6	1.4261 (16)	O10—C11	1.3367 (16)
C3—O4	1.4268 (16)	C11—O12	1.2124 (17)
C3—C9	1.509 (2)		
C2—C1—C11	108.66 (10)	O4—C5—O6	103.66 (10)
C2—C1—O13	106.76 (10)	O4—C5—C7	111.02 (13)
C11—C1—O13	106.76 (11)	O6—C5—C7	110.14 (13)
C2—C1—C14	111.22 (11)	O4—C5—C8	109.15 (13)
C11—C1—C14	111.17 (12)	O6—C5—C8	108.63 (12)
O13—C1—C14	112.04 (10)	C7—C5—C8	113.74 (14)
C1—C2—C3	113.22 (11)	C5—O6—C2	106.26 (9)
C1—C2—O6	107.54 (10)	C3—C9—O10	111.94 (11)
C3—C2—O6	103.56 (10)	C9—O10—C11	119.10 (11)
C2—C3—O4	104.50 (10)	C1—C11—O10	117.08 (12)
C2—C3—C9	113.06 (11)	C1—C11—O12	124.42 (12)
O4—C3—C9	109.33 (13)	O10—C11—O12	118.49 (13)
C3—O4—C5	108.01 (10)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O13—H3$\cdots$O12^i	0.94	1.87	2.8103 (14)	175

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

The multi-scan technique (Otwinowski & Minor, 1997) was used to correct for changes in the illuminated volume of the long needle crystal. In the absence of significant anomalous scattering effects, Friedel pairs were merged. The absolute configuration was assigned from the known configuration of the starting material in the synthesis. 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 = 0.97–1.01 Å and O—H = 0.94 Å), after which they were refined as riding, with U_{iso}(H) = $1.2U_{eq}$(C) for those bonded to C atoms, and U_{iso}(H) = 0.05 Å^2 for the hydroxy group.

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

3,4-*O*-Isopropylidene-2-*C*-methyl-D-arabinono-1,5-lactone

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3,4-*O*-Isoprpylidene-D-arabinono-1,5-lactone

Crystal data

$C_9H_{14}O_5$	$F(000) = 216$
$M_r = 202.21$	$D_x = 1.356$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.7315$ (3) Å	Cell parameters from 1264 reflections
$b = 6.2859$ (3) Å	$\theta = 5–30°$
$c = 10.4209$ (6) Å	$\mu = 0.11$ mm^{-1}
$\beta = 102.1024$ (17)°	$T = 190$ K
$V = 495.19$ (4) Å^3	Needle, colourless
$Z = 2$	$0.90 \times 0.20 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer	1448 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.018$
ω scans	$\theta_{max} = 30.0°$, $\theta_{min} = 5.3°$
2579 measured reflections	$h = -10 \rightarrow 10$
1527 independent reflections	$k = -8 \rightarrow 8$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.078$	
$S = 0.99$	H-atom parameters constrained
1527 reflections	$w = 1/[\sigma^2(F^2) + 0.04 + 0.06P]$,
127 parameters	where $P = (\max(F_o^2,0) + 2F_c^2)/3$
1 restraint	$(\Delta/\sigma)_{max} = 0.000343$
	$\Delta\rho_{max} = 0.24$ e Å^{-3}
	$\Delta\rho_{min} = -0.16$ e Å^{-3}

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.38045 (16)	0.7432 (2)	0.63155 (12)	0.0190
C2	0.28987 (16)	0.8696 (2)	0.72414 (13)	0.0206
C3	0.09390 (16)	0.8070 (2)	0.71356 (13)	0.0221
O4	0.08151 (12)	0.7559 (2)	0.84474 (9)	0.0292
C5	0.23824 (17)	0.8319 (3)	0.93106 (13)	0.0254
O6	0.37167 (12)	0.81163 (18)	0.85511 (9)	0.0231

C7	0.2183 (2)	1.0639 (3)	0.96718 (18)	0.0372
C8	0.2838 (2)	0.6857 (3)	1.04806 (15)	0.0382
C9	0.03922 (18)	0.6164 (3)	0.62648 (15)	0.0269
O10	0.17525 (13)	0.45193 (18)	0.64662 (11)	0.0274
C11	0.34223 (18)	0.5063 (2)	0.64601 (13)	0.0207
O12	0.45221 (14)	0.36653 (18)	0.65495 (10)	0.0273
O13	0.29608 (12)	0.80258 (19)	0.50056 (9)	0.0261
C14	0.57875 (16)	0.7863 (3)	0.65965 (13)	0.0244
H21	0.3019	1.0247	0.7105	0.0248*
H31	0.0179	0.9270	0.6816	0.0280*
H71	0.3345	1.1210	1.0175	0.0488*
H72	0.1220	1.0707	1.0178	0.0488*
H73	0.1804	1.1428	0.8838	0.0488*
H81	0.3965	0.7308	1.1071	0.0479*
H82	0.1833	0.7025	1.0914	0.0479*
H83	0.2915	0.5387	1.0159	0.0479*
H91	−0.0661	0.5480	0.6502	0.0333*
H92	0.0135	0.6646	0.5337	0.0333*
H141	0.6340	0.7072	0.5946	0.0310*
H142	0.5908	0.9419	0.6521	0.0310*
H143	0.6324	0.7393	0.7493	0.0310*
H3	0.3800	0.8152	0.4478	0.0500*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0200 (5)	0.0201 (6)	0.0178 (6)	0.0008 (5)	0.0061 (4)	0.0015 (4)
C2	0.0211 (5)	0.0193 (6)	0.0222 (6)	0.0010 (5)	0.0062 (4)	0.0002 (5)
C3	0.0193 (5)	0.0257 (6)	0.0218 (6)	0.0004 (5)	0.0057 (4)	−0.0008 (5)
O4	0.0230 (4)	0.0451 (7)	0.0214 (5)	−0.0088 (5)	0.0086 (4)	−0.0016 (5)
C5	0.0200 (5)	0.0368 (9)	0.0204 (6)	−0.0006 (6)	0.0068 (4)	−0.0051 (6)
O6	0.0194 (4)	0.0302 (5)	0.0205 (4)	0.0011 (4)	0.0063 (3)	−0.0042 (4)
C7	0.0321 (7)	0.0436 (10)	0.0381 (9)	0.0032 (7)	0.0127 (7)	−0.0163 (8)
C8	0.0360 (7)	0.0563 (11)	0.0230 (7)	0.0015 (8)	0.0075 (6)	0.0031 (7)
C9	0.0201 (5)	0.0299 (7)	0.0297 (7)	−0.0024 (6)	0.0029 (5)	−0.0053 (6)
O10	0.0261 (5)	0.0216 (5)	0.0355 (5)	−0.0041 (4)	0.0089 (4)	−0.0027 (4)
C11	0.0252 (6)	0.0219 (6)	0.0162 (5)	0.0010 (5)	0.0071 (4)	−0.0002 (5)
O12	0.0356 (5)	0.0228 (5)	0.0265 (5)	0.0061 (4)	0.0134 (4)	0.0020 (4)
O13	0.0256 (4)	0.0331 (5)	0.0205 (4)	0.0043 (5)	0.0069 (3)	0.0080 (4)
C14	0.0204 (5)	0.0275 (7)	0.0269 (6)	0.0003 (6)	0.0084 (5)	0.0015 (6)

Geometric parameters (Å, º)

C1—C2	1.5284 (18)	C7—H72	0.999
C1—C11	1.5318 (19)	C7—H73	0.990
C1—O13	1.4334 (15)	C8—H81	0.997
C1—C14	1.5237 (17)	C8—H82	0.983
C2—C3	1.5468 (18)	C8—H83	0.989

C2—O6	1.4261 (16)	C9—O10	1.4581 (18)
C2—H21	0.992	C9—H91	0.996
C3—O4	1.4268 (16)	C9—H92	0.993
C3—C9	1.509 (2)	O10—C11	1.3367 (16)
C3—H31	0.971	C11—O12	1.2124 (17)
O4—C5	1.4312 (16)	O13—H3	0.938
C5—O6	1.4314 (16)	C14—H141	1.006
C5—C7	1.522 (2)	C14—H142	0.987
C5—C8	1.508 (2)	C14—H143	0.985
C7—H71	1.007		
C2—C1—C11	108.66 (10)	H71—C7—H72	113.1
C2—C1—O13	106.76 (10)	C5—C7—H73	106.8
C11—C1—O13	106.76 (11)	H71—C7—H73	110.2
C2—C1—C14	111.22 (11)	H72—C7—H73	109.0
C11—C1—C14	111.17 (12)	C5—C8—H81	110.5
O13—C1—C14	112.04 (10)	C5—C8—H82	103.5
C1—C2—C3	113.22 (11)	H81—C8—H82	111.0
C1—C2—O6	107.54 (10)	C5—C8—H83	108.4
C3—C2—O6	103.56 (10)	H81—C8—H83	111.6
C1—C2—H21	110.6	H82—C8—H83	111.5
C3—C2—H21	111.1	C3—C9—O10	111.94 (11)
O6—C2—H21	110.6	C3—C9—H91	109.5
C2—C3—O4	104.50 (10)	O10—C9—H91	105.1
C2—C3—C9	113.06 (11)	C3—C9—H92	108.5
O4—C3—C9	109.33 (13)	O10—C9—H92	110.3
C2—C3—H31	109.9	H91—C9—H92	111.5
O4—C3—H31	110.2	C9—O10—C11	119.10 (11)
C9—C3—H31	109.7	C1—C11—O10	117.08 (12)
C3—O4—C5	108.01 (10)	C1—C11—O12	124.42 (12)
O4—C5—O6	103.66 (10)	O10—C11—O12	118.49 (13)
O4—C5—C7	111.02 (13)	C1—O13—H3	110.4
O6—C5—C7	110.14 (13)	C1—C14—H141	109.6
O4—C5—C8	109.15 (13)	C1—C14—H142	105.6
O6—C5—C8	108.63 (12)	H141—C14—H142	112.1
C7—C5—C8	113.74 (14)	C1—C14—H143	109.6
C5—O6—C2	106.26 (9)	H141—C14—H143	109.7
C5—C7—H71	110.2	H142—C14—H143	110.2
C5—C7—H72	107.3		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O13—H3···O12[i]	0.94	1.87	2.8103 (14)	175

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