

3,4-*O*-Isopropylidene-2-*C*-methyl-*D*-arabinono-1,5-lactoneFrancesco Punzo,^{a*} David J. Watkin,^b Sarah F. Jenkinson^c and George W. J. Fleet^c^aDipartimento di Scienze Chimiche, Facoltà di Farmacia, Università di Catania, Viale A. Doria 6, 95125, Catania, Italy, ^bDepartment of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England, and ^cDepartment of Organic Chemistry, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England

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Key indicators

Single-crystal X-ray study
T = 190 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.031
wR factor = 0.078
Data-to-parameter ratio = 12.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title δ -lactone, $\text{C}_9\text{H}_{14}\text{O}_5$, 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.

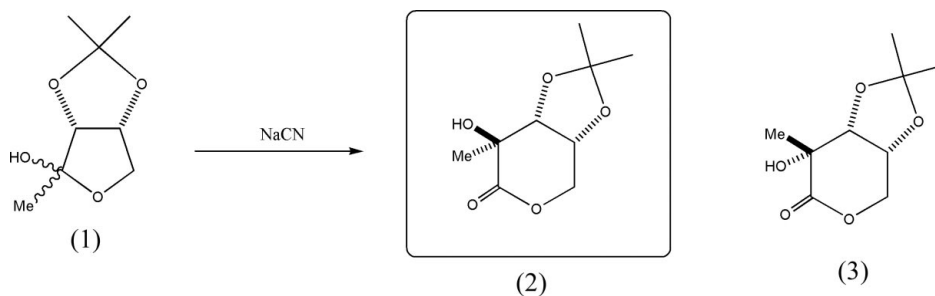
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Comment

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 examples 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.

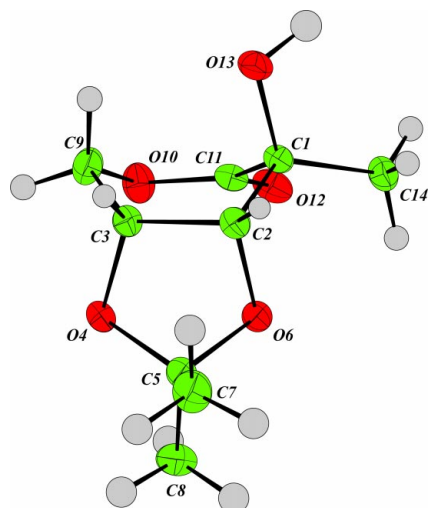


Figure 1
The molecular structure of (2), with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary.

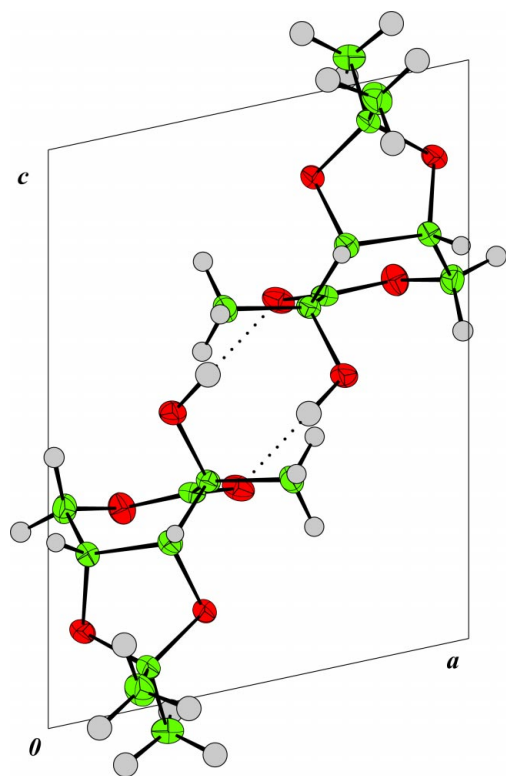


Figure 2
Partial packing diagram of (2), viewed down the *b* axis. Hydrogen bonds are shown as dotted lines.

Crystal data

$C_9H_{14}O_5$
 $M_r = 202.21$
 Monoclinic, $P2_1$
 $a = 7.7315$ (3) Å
 $b = 6.2859$ (3) Å
 $c = 10.4209$ (6) Å
 $\beta = 102.1024$ (17)°
 $V = 495.19$ (4) Å³
 $Z = 2$

$D_x = 1.356$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1264 reflections
 $\theta = 5-30^\circ$
 $\mu = 0.11$ mm⁻¹
 $T = 190$ K
 Needle, colourless
 $0.90 \times 0.20 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer
 ω scans
 2579 measured reflections
 1527 independent reflections
 1448 reflections with $I > 2\sigma(I)$

$R_{int} = 0.018$
 $\theta_{max} = 30.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -8 \rightarrow 8$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.078$
 $S = 0.99$
 1527 reflections
 127 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + 0.04 + 0.06P]$,
 where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.24$ e Å⁻³
 $\Delta\rho_{min} = -0.16$ e Å⁻³

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, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O13—H3...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 $U_{iso}(H) = 0.05$ Å² 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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