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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.038
wR factor = 0.079
Data-to-parameter ratio = 9.4

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

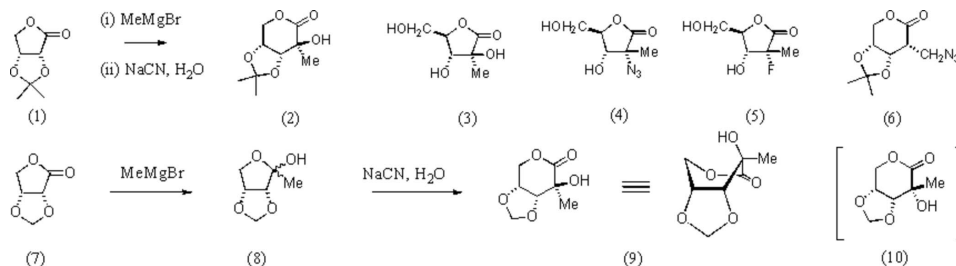
2-C-Methyl-3,4-O-methylidene-D-arabinono-1,5-lactone

The relative stereochemistry at C-2 of the title compound, $\text{C}_7\text{H}_{10}\text{O}_5$, was determined by X-ray crystallographic analysis of the arabinonolactone, which adopts a boat conformation with a flagpole hydroxyl group. Its absolute configuration was determined by the use of D-erythronolactone as the starting material.

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Comment

Until recently, only linear carbohydrate chirons have been available as scaffolds for the synthesis of complex synthetic targets (Lichtenthaler & Peters, 2004). However, the Kiliani cyanide reaction on ketohexoses (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005) affords versatile intermediates with carbon branches at C-2 of the sugar for the synthesis of imino sugars and complex sugar amino acids with non-linear carbon chains (Simone *et al.*, 2005). The Kiliani reaction on hama-melose provides access to carbohydrates with a branch at C-3 (Parker, Watkin, Simone & Fleet, 2006).



Carbohydrate building blocks with a C-2 methyl group can be formed by the reaction of cyanide on 1-deoxyketoses, themselves prepared by the addition of organometallic reagents to sugar lactones (Hotchkiss *et al.*, 2006). Thus, reaction of the isopropylidene-protected D-erythronolactone, (1), with methyl magnesium bromide followed by sodium cyanide gave the *arabino*-protected derivative, (2), as the only 1,5-lactone isolated (Punzo *et al.*, 2005a). The potential of (2) as a route to sugar derivatives with a C-2 methyl group bearing a functional group at the tertiary centre is shown by its easy conversion to the branched arabinose, (3) (Punzo *et al.*, 2005b), the quaternary *ribo*-azide, (4) (Punzo, Watkin, Jenkinson, Cruz & Fleet, 2005), and the quaternary *ribo*-fluoride, (5) (Parker, Watkin, Mayes *et al.*, 2006). The branched azidomethyl lactone, (6), has also been prepared from (2) and is a precursor to complex piperidine amino acids and iminosugars (Punzo *et al.*, 2006).

In order to optimize the protecting group strategy for the synthesis of complex targets (and to investigate the diastereoselectivity of the Kiliani cyanide extension), the

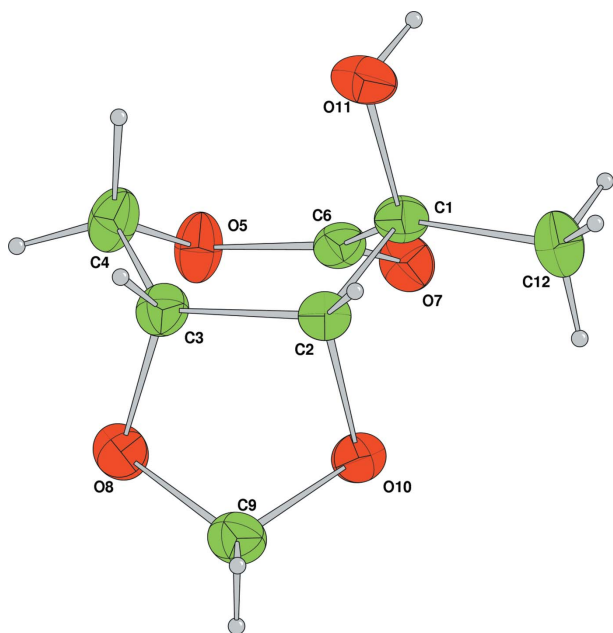


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

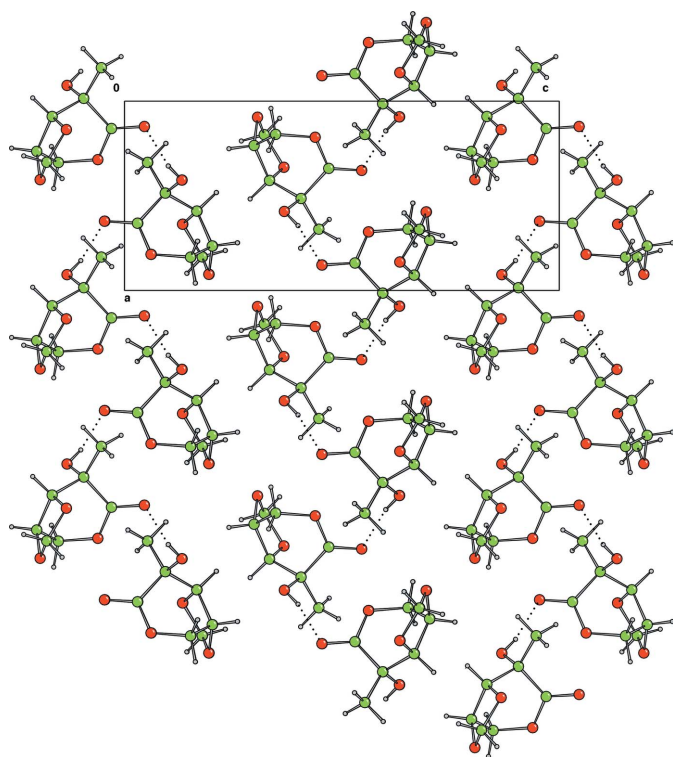


Figure 2
The crystal packing, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

formaldehyde acetal of D-erythronolactone, (7), was treated with methyl magnesium bromide to give the 1-deoxy-D-ribose, (8). The Kiliani reaction of (8) with sodium cyanide gave a single diastereomeric product, (9), as the only 1,5-lactone isolated (Jenkinson *et al.*, 2006). This paper shows, by X-ray

crystallography, that the arabinolactone, (9), was formed in this reaction with none of the epimeric ribono diastereomer, (10), isolated.

The X-ray crystal structure determination shows that (9) is in a boat conformation (Fig. 1). The formation of (9) with the smaller hydroxyl group in the flagpole position may be due to the alternative product, (10), having the larger methyl group in the more hindered flagpole environment. The potential of (9) as a chiron is under investigation.

In the crystal structure, intermolecular O—H...O hydrogen bonds (Table 1) link the molecules into zigzag chains extending along the *a* axis (Fig. 2).

Experimental

The title arabinono-1,5-lactone, (9), was obtained (Jenkinson *et al.*, 2006) by vapour diffusion of cyclohexane into a solution in ethyl acetate until crystals of a suitable size were formed (m.p. 373–375 K). $[\alpha]_D -126.0$ (*c* 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃, δ , p.p.m.): 1.67 (3H, *s*, Me), 3.04 (1H, *s*, OH), 4.25 (1H, *d*, $J_{3,4} = 7.9$ Hz, H3), 4.46–4.50 (2H, *m*, H4, H5a), 4.82 (1H, *s*, OCH₂O), 4.97 (1H, *dd*, $J_{4,5b} = 1.9$ Hz, $J_{5a,5b} = 12.0$ Hz, H5b), 5.17 (1H, *s*, OCH₂O); ¹³C NMR (100 MHz, CDCl₃, δ , p.p.m.): 22.1 (Me), 68.7 (C5), 71.5 (C4), 72.2 (C3), 78.8 (C2), 94.9 (OCH₂O), 171.4 (CO).

Crystal data

C ₇ H ₁₀ O ₅	<i>Z</i> = 4
<i>M_r</i> = 174.15	<i>D_x</i> = 1.515 Mg m ⁻³
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Mo <i>K</i> α radiation
<i>a</i> = 6.8693 (3) Å	μ = 0.13 mm ⁻¹
<i>b</i> = 7.0382 (3) Å	<i>T</i> = 150 K
<i>c</i> = 15.7909 (7) Å	Needle, colourless
<i>V</i> = 763.45 (6) Å ³	0.50 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer	1726 measured reflections
ω scans	1032 independent reflections
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	784 reflections with <i>I</i> > 2 σ (<i>I</i>)
<i>T</i> _{min} = 0.882, <i>T</i> _{max} = 0.974	<i>R</i> _{int} = 0.032
	θ _{max} = 27.5°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.03P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (\max(F_o^2, 0) + 2F_c^2)/3$
$wR(F^2) = 0.080$	$(\Delta/\sigma)_{\max} < 0.001$
<i>S</i> = 1.00	$\Delta\rho_{\max} = 0.36 \text{ e } \text{Å}^{-3}$
1027 reflections	$\Delta\rho_{\min} = -0.34 \text{ e } \text{Å}^{-3}$
109 parameters	
H-atom parameters constrained	

Table 1

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>
O11—H1...O7 ⁱ	0.83	2.10	2.911 (2)	167

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

A $[\sin(\theta)/\lambda]^2$ threshold of 0.01 was used to guard against the risk of including low angle reflections partially occluded by the beam stop. In the absence of significant anomalous scattering, 873 Friedel pairs

were merged and the absolute configuration was assigned from the known starting material. All H atoms were 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 Å, and O—H = 0.825 Å) and isotropic displacement parameters [$U_{\text{iso}}(\text{H})$ in the range 1.2–1.5 U_{eq} of the parent atom], after which they were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 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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