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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 = 0.102
 Data-to-parameter ratio = 10.4

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

2,4-Dimethyl-3,4-O-isopropylidene-L-arabinono-1,5-lactone

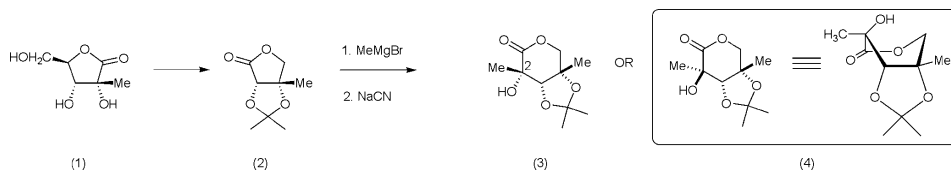
The relative configuration at C-2 of 2,4-dimethyl-3,4-O-isopropylidene-L-arabinono lactone, C₁₀H₁₆O₅, which exists in the boat form, was unequivocally established by X-ray crystallographic analysis. The absolute configuration was determined by the use of 2-C-methyl-D-ribonolactone as a starting material.

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Comment

Rare and new monosaccharides have potential both as healthy dietary alternatives (Sun *et al.*, 2007; Skytte, 2002) and for specific chemotherapeutic uses (Nakajima *et al.*, 2004; Menavuvu *et al.*, 2006; Hossain *et al.*, 2006). Branched 2-C-methyl pentoses have become readily available by treatment of an Amadori ketose with aqueous calcium hydroxide (Hotchkiss *et al.*, 2007) and are key intermediates in the synthesis of 2-C-methyl nucleosides, a new class of drugs for the treatment of hepatitis C (Sorbera *et al.*, 2006). Carbohydrates with a branch at C-2 may also be accessed by the reaction of ketoses and deoxyketoses with cyanide (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005). In contrast, there have been no biological studies on unprotected monosaccharides with more than one carbon branch.



The protected lactone (4) is a key intermediate in the synthesis of monosaccharides with two C-methyl branches (Booth *et al.*, 2007). 2-C-Methyl-D-ribonolactone, (1), prepared by the green environmentally friendly aqueous isomerization of D-glucose (Hotchkiss *et al.*, 2006), may be converted to the 3-C-methyl-L-erythronolactone (2) as previously described (Barrett & Dhanak, 1987; Barrett *et al.*, 1989). Sequential treatment of (2) with methyl magnesium bromide followed by aqueous cyanide leads to the isolation of a major crystalline product which has a new stereogenic centre, which could be either the epimeric *ribo*- (3) or *arabino*-lactone (4). X-ray crystallographic analysis resolved the ambiguity at C-2 and unequivocally established the relative stereochemistry as the arabinono-1,5-lactone (4), which exists in a boat form; the absolute configuration of (4) is determined by the use of 2-C-methyl-D-ribonolactone (1) as the starting material.

The molecular structure of (4) is shown in Fig. 1. The molecular geometry contains no unusual features. The largest

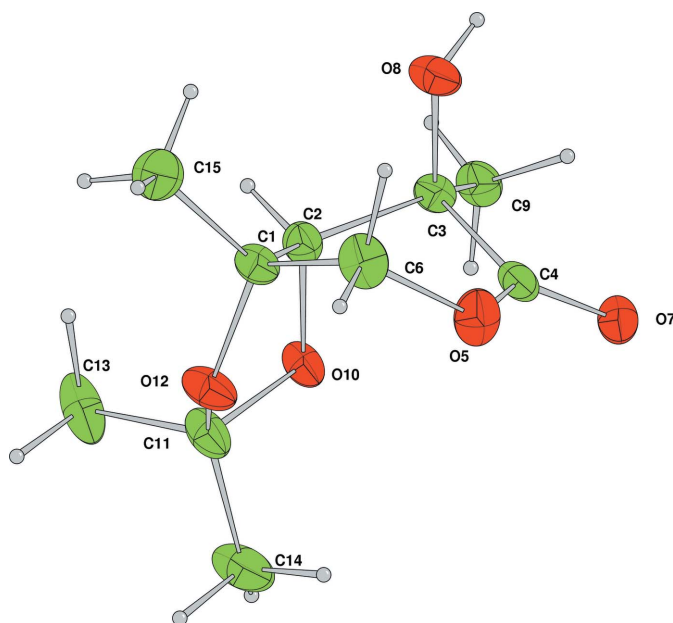


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

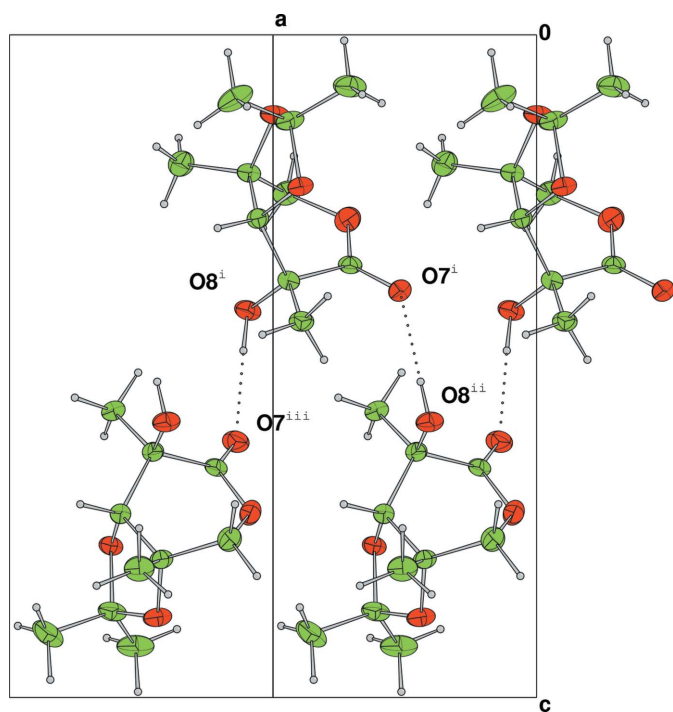


Figure 2
Part of the hydrogen-bonded (dotted lines) ribbon lying parallel to *a*. The image has been rotated about *c* (out of the plane of the ribbon) to clarify the hydrogen-bonding chain. The molecule corresponding to the published coordinates does not form any hydrogen bonds within the natural unit cell. [Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$]

differences from the *Mogul* norms (Bruno *et al.*, 2004) are C2–O3 (0.02 Å, *Mogul* s.u. 0.01 Å) and C3–C9–O8 (3.4 Å, *Mogul* s.u. 1.9°). The crystal structure consists of broad

ribbons of hydrogen-bonded molecules lying with the plane of the ribbon perpendicular to *b*, and the length of the ribbon lying along *a* (Fig. 2). The hydrogen bonds form the backbone of the ribbon, with the individual molecules lying alternately on either side. The backbone of each ribbon lies above and parallel to the interface between two ribbons in the adjacent layers.

Experimental

2,4-Dimethyl-3,4-*O*-isopropylidene-L-arabinono lactone (4) was crystallized from a mix of ethyl acetate and cyclohexane by vapour diffusion: m.p. 385–391 K; $[\alpha]_D^{25} +131$ (*c*, 1.5 in chloroform)

Crystal data

$C_{10}H_{16}O_5$
 $M_r = 216.23$
Orthorhombic, $P2_12_12_1$
 $a = 6.3457$ (2) Å
 $b = 12.0530$ (4) Å
 $c = 14.1034$ (5) Å
 $V = 1078.69$ (6) Å³

$Z = 4$
 $D_x = 1.331$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 150$ K
Plate, colourless
0.40 × 0.40 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
 ω scans
Absorption correction: multi-scan
(*DENZO/SCALEPACK*;
Otwinowski & Minor, 1997)
 $T_{\min} = 0.82, T_{\max} = 0.98$

6458 measured reflections
1421 independent reflections
1301 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.051$
 $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.102$
 $S = 0.86$
1421 reflections
136 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.07P)^2 + 0.5P]$,
where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.26$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O8–H1 \cdots O7 ^{iv}	0.88	1.99	2.870 (2)	178

Symmetry code: (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, -z$.

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration was assigned from the starting material. The relatively large ratio of minimum to maximum corrections applied in the multi-scan process (1:1.2) reflects effects in addition to absorption, possibly connected with the flake-like aspect of the sample. Changes in illuminated volume were kept to a minimum, and were taken into account (Görlitz, 1999) by the multi-scan inter-frame scaling (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997).

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 Å, O–H = 0.82 Å) and $U_{\text{iso}}(\text{H})$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions 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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