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#### Key indicators

Single-crystal X-ray study  
 T = 150 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$   
 R factor = 0.034  
 wR factor = 0.073  
 Data-to-parameter ratio = 10.0

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

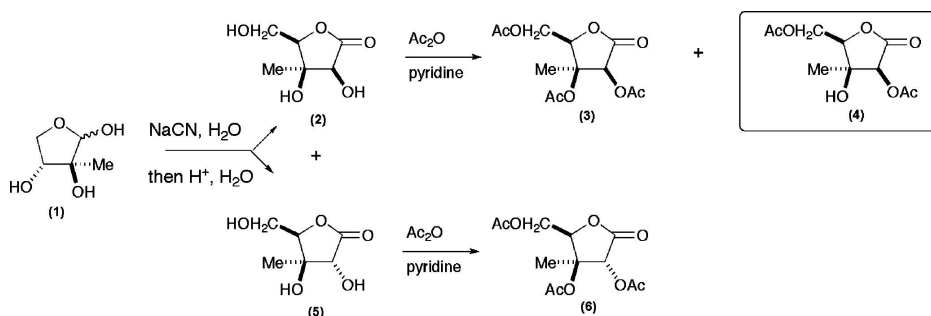
## 2,5-Di-O-acetyl-3-C-methyl-D-lyxono-1,4-lactone

The structures of both lactones derived from the Kiliani ascension of 2-C-methyl-D-threose were defined by the crystal structure of the title compound,  $\text{C}_{10}\text{H}_{14}\text{O}_7$ . The structure consists of hydrogen-bonded ribbons of molecules.

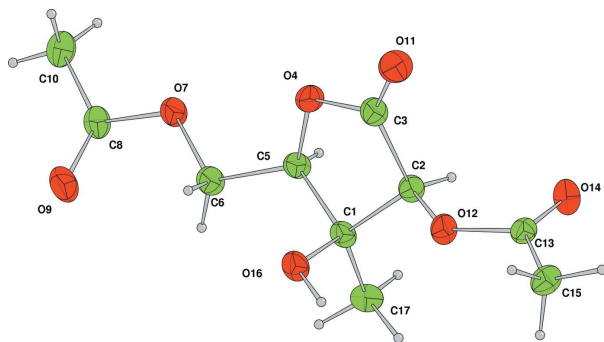
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### Comment

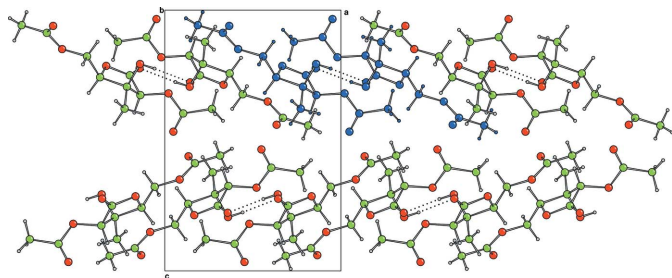
The Kiliani reaction of ketoses with cyanide, followed by acetonation, has provided a simple and environmentally friendly procedure for the generation of a set of carbohydrate scaffolds with a branched hydroxymethyl group at C-2 (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005). Branched sugar lactones bearing a C-2 methyl group may be accessed either by a Kiliani reaction on 1-deoxyketoses or by treatment of an Amadori ketose with aqueous calcium hydroxide (Hotchkiss *et al.*, 2006). X-ray crystallographic analysis has been crucial in establishing the structures of the products in these reactions (Punzo *et al.*, 2006; Watkin *et al.*, 2005; Harding *et al.*, 2005). Although these syntheses provide convenient access to C-2 carbon-branched carbohydrates, there are very few reports of sugars with a carbon branch at C-3; a 3-C-methyl-pentonolactone of unknown stereochemistry has been isolated from cigarette smoke (Schumacher *et al.*, 1977) and 3-C-methyl-D-mannose is one of the components of the trisaccharide repeating unit of the polysaccharide from *Helicobacter Pylori* (Kwon *et al.*, 2004).



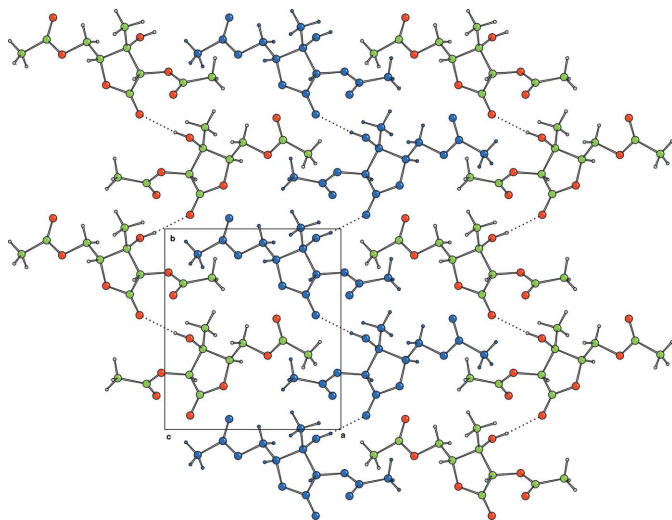
3-C-Methyl aldonolactones should be accessible through a Kiliani reaction on a branched 2-C-methyl aldose. Reaction of 2-C-methyl-D-threose (1) with aqueous sodium cyanide afforded an inseparable mixture of the C-3-methyl branched lactones (2) and (5); the mixture was treated with an excess of acetic anhydride in pyridine to give a separable mixture of two triacetates (3) and (6) together with a crystalline diacetate (4) (Soengas & Fleet, 2006). Determination of the relative stereochemistry of the diacetate (4) as a lyxono-1,4-lactone by X-ray crystallographic analysis (Fig. 1) allowed unambiguous structural assignments of both the triacetates (3) and (6), and



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



**Figure 2**  
A *b*-axis projection showing layers of molecules. Dashed lines indicate hydrogen bonds.



**Figure 3**  
A *c*-axis projection of one layer of molecules, showing the hydrogen-bonded (dashed lines) ribbons lying parallel to *b*.

thus of the C-3 branched lyxono- (2) and xylono- (5) lactones. The use of 2-*C*-methyl-D-threose (1) as the starting material in the synthesis defines the absolute configuration of (4). Both C-2 and C-3 branched sugars are likely to increase significantly the range of carbohydrate chirons (Lichtenthaler & Peters, 2004) available for the efficient synthesis of complex homochiral targets (Simone *et al.*, 2005) and also to provide material for the first time for the study of interactions of such unnatural monosaccharides with biological receptors.

The crystal structure consists of layers of molecules lying perpendicular to the *c* axis (Fig. 2). Within each layer are

interlocking zigzag ribbons of hydrogen-bonded molecules (Fig. 3).

## Experimental

The material was prepared (Soengas & Fleet, 2006) using a Kiliani reaction. The diacetate (4) was crystallized from chloroform; m.p. 521–523 K,  $[\alpha]_D^{23} +60.0$  (*c*, 1.7 in acetone).

### Crystal data

$C_{10}H_{14}O_7$   
 $M_r = 246.22$   
 Orthorhombic,  $P2_12_12_1$   
 $a = 8.8524$  (1) Å  
 $b = 10.0821$  (2) Å  
 $c = 13.1198$  (2) Å  
 $V = 1170.95$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.397$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 1560 reflections  
 $\theta = 5\text{--}27^\circ$   
 $\mu = 0.12$  mm<sup>-1</sup>  
 $T = 150$  K  
 Plate, colourless  
 0.20 × 0.20 × 0.08 mm

### Data collection

Nonius KappaCCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (DENZO/SCALEPACK;  
 Otwinowski & Minor, 1997)  
 $T_{\min} = 0.869$ ,  $T_{\max} = 0.990$   
 2688 measured reflections

1545 independent reflections  
 1545 reflections with  $I > -3.0\sigma(I)$   
 $R_{\text{int}} = 0.009$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -13 \rightarrow 13$   
 $l = -16 \rightarrow 16$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.073$   
 $S = 0.91$   
 1545 reflections  
 154 parameters  
 H-atom parameters constrained

Modified Chebyshev polynomial  
 (Watkin, 1994; Prince, 1982) with  
 the coefficients 11.3, 16.9, 8.59,  
 2.51  
 $(\Delta\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.27$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.24$  e Å<sup>-3</sup>

**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>
O16–H8···O11 <sup>i</sup>	0.83	2.11	2.926 (2)	167

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

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 = 0.93–0.98 and O–H = 0.82 Å) and displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}$  of the parent atom], after which they were refined with riding constraints. In the absence of significant anomalous dispersion effects, Friedel pairs were averaged.

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*.

## References

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Harding, C. C., Watkin, D. J., Sawyer, N. K., Jenkinson, S. F. & Fleet, G. W. J. (2005). *Acta Cryst.* **E61**, o1472–o1474.
- Hotchkiss, D. J., Jenkinson, S. F., Storer, R., Heinz, T. & Fleet, G. W. J. (2006). *Tetrahedron Lett.* **47**, 315–318.
- Hotchkiss, D., Soengas, R., Simone, M. I., van Ameijde, J., Hunter, S., Cowley, A. R. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**, 9461–9464.
- Kwon, Y. T., Lee, Y. J., Lee, K. & Kim, K. S. (2004). *Org. Lett.* **6**, 3901–3904.
- Lichtenthaler, F. W. & Peters, S. (2004). *C. R. Chim.* **7**, 65–90.
- Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Prince, E. (1982). *Mathematical Techniques in Crystallography and Materials Science*. New York: Springer-Verlag.
- Punzo, F., Watkin, D. J., Hotchkiss, D. & Fleet, G. W. J. (2006). *Acta Cryst.* **E62**, o98–o100.
- Schumacher, J. N., Green, C. R., Best, F. W. & Newell, M. P. (1977). *J. Agric. Food. Chem.* **25**, 310–320.
- Simone, M. I., Soengas, R., Newton, C. R., Watkin, D. J. & Fleet, G. W. J. (2005). *Tetrahedron Lett.* **46**, 5761–5765.
- Soengas, R. & Fleet, G. W. J. (2006). *Tetrahedron Lett.* In preparation.
- Soengas, R., Izumori, K., Simone, M. I., Watkin, D. J., Skytte, U. P., Soetaert, W. & Fleet, G. W. J. (2005). *Tetrahedron Lett.* **46**, 5755–5759.
- Watkin, D. J. (1994). *Acta Cryst.* **A50**, 411–437.
- Watkin, D. J., Parry, L. L., Hotchkiss, D. J., Eastwick-Field, V. & Fleet, G. W. J. (2005). *Acta Cryst.* **E61**, o3302–o3303.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.