# organic papers

# 3,5-O-Isopropylidene-2-C-methyl-D-xylonolactone

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**Key indicators**

Single-crystal X-ray study
$T$ = 150 K
Mean $\sigma$(C–C) = 0.002 Å
$R$ factor = 0.044
$wR$ factor = 0.074
Data-to-parameter ratio = 12.2

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

The ring size of both the lactone and the ketal protecting group in the title compound, $C_9H_{14}O_5$, have been established by X-ray crystallographic analysis. The crystal structure consists of hydrogen-bonded spirals parallel to the $b$ axis.

## Comment

Almost all carbohydrate scaffolds contain linear carbon chains (Lichtenthaler & Peters, 2004). The two exceptions that do provide carbohydrates with branched carbon chains are (i) the Kiliani reaction on ketoses which provides efficient access to a set of 2-C-hydroxymethylaldonolactones (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005), and (ii) the treatment of sugars with base to give 2-C-methyl aldonic acids, also known as saccharinic acids (Bols, 1996). However, the reaction of base with sugars is complex: glucose gives a mixture of more than 50 compounds on treatment with calcium hydroxide, of which branched sugars comprise a very small percentage (Yang & Montgomery, 1996). Better yields are obtained from ketoses; however, even the optimized conditions (several weeks under careful control in a laborious procedure) for treatment of D-fructose with calcium hydroxide afford 2-C-methyl-D-ribono-lactone in only 11% yield (Whistler & BeMiller, 1963). Very low yields of branched lactones have been isolated from similar treatment of L-sorbose (Ishizu *et al.*, 1972). A further ketohexose, D-tagatose (1), has recently become available in quantity as a new food additive (Skytte, 2002); (1) has the potential for making 2-C-methyl-D-xylonolactone as a branched-sugar building block under green environmentally friendly conditions. Treatment of D-tagatose with aqueous calcium hydroxide produces a very complex mixture of products. In order to identify the branched-chain sugar products, it was necessary to make authentic samples of easily crystallized derivatives.



A crystalline acetonide was obtained from treatment of 2-C-methyl-D-xylonolactone with acetone in the presence of acid. The absolute stereochemistry of (2) is determined by using D-tagatose (1) as the starting material; however, there are ambiguities in the synthesis with regard to the relative stereochemistry at C-2 of the lactone, the ring size of the lactone and the ring size of the ketal. X-ray crystallographic analysis removed all the ambiguities and firmly established the structure of the acetonide as (2).
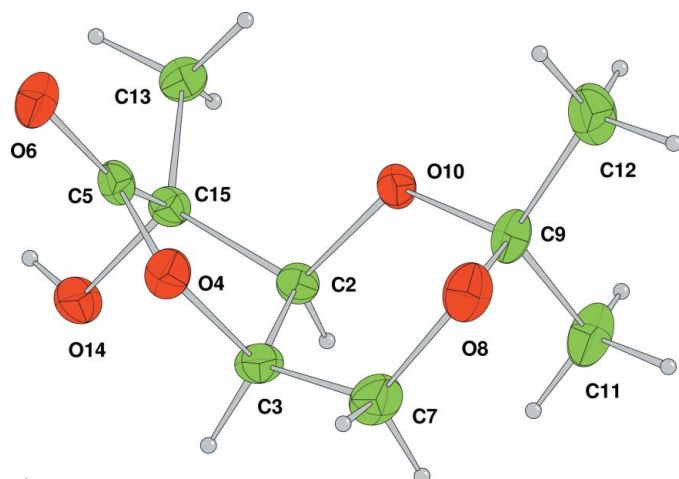
**Figure 1**
The title compound, with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

## Experimental

The acetonide (2) was prepared as in the *Comment* section and crystallized from ethyl acetate:cyclohexane (m.p. 428–431 K) as long fibrous needles. $[\alpha]_D^{23}$ +82.2 (*c* 0.67 in CHCl$_3$).

*Crystal data*

| | |
|---|---|
| C$_9$H$_{14}$O$_5$ | $D_x = 1.362$ Mg m$^{-3}$ |
| $M_r = 202.21$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1$ | Cell parameters from 1419 |
| $a = 8.3764$ (3) Å | reflections |
| $b = 5.9861$ (2) Å | $\theta = 5$–30° |
| $c = 10.4690$ (4) Å | $\mu = 0.11$ mm$^{-1}$ |
| $\beta = 110.0336$ (12)° | $T = 150$ K |
| $V = 493.17$ (3) Å$^3$ | Lath, colourless |
| $Z = 2$ | $1.00 \times 0.28 \times 0.12$ mm |

*Data collection*

| | |
|---|---|
| Nonius KappaCCD diffractometer | 1549 independent reflections |
| $\omega$ scans | 1549 reflections with $I > -3.0\sigma(I)$ |
| Absorption correction: multi-scan | $R_{int} = 0.034$ |
| (*DENZO/SCALEPACK*; | $\theta_{max} = 30.0°$ |
| Otwinowski & Minor, 1997) | $h = -11 \rightarrow 11$ |
| $T_{min} = 0.81$, $T_{max} = 0.99$ | $k = -8 \rightarrow 8$ |
| 7941 measured reflections | $l = -14 \rightarrow 14$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F^2) + (0.04P)^2$ |
| $R[F^2 > 2\sigma(F^2)] = 0.044$ | $+ 0.03P]$, |
| $wR(F^2) = 0.074$ | where $P = (\max(F_o^2,0) + 2F_c^2)/3$ |
| $S = 0.94$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 1549 reflections | $\Delta\rho_{max} = 0.28$ e Å$^{-3}$ |
| 127 parameters | $\Delta\rho_{min} = -0.24$ e Å$^{-3}$ |
| H-atom parameters constrained | |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O14—H1$\cdots$O6$^i$ | 0.84 | 2.00 | 2.837 (2) | 176 |

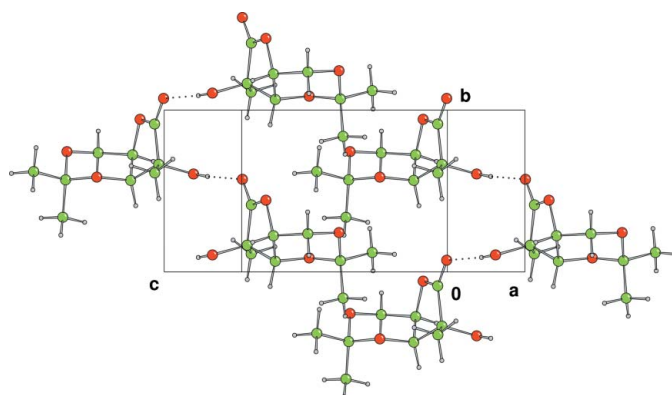Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z$.



**Figure 2**
Projection of the structure perpendicular to the *b* axis, showing the molecules linked into hydrogen-bonded spirals parallel to *b*.

In the absence of significant anomalous scattering, Friedel pairs were merged, and the absolute configuration assigned from the known staring materials.

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 and O—H = 0.82 Å) and displacement parameters [$U_{iso}$(H) in the range 1.2–1.5 times $U_{eq}$ of the parent atom], after which they were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 1997-2001); 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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