Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-*C*-Methyl-D-allono-1,5-lactone

Nigel A. Jones,[a]* David J. Watkin,[b] Louise A. Curran,[a] Sarah F. Jenkinson[a] and George W. J. Fleet[a]

[a]Department of Organic Chemistry, Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford OX1 3TA, England, and [b]Department of Chemical Crystallography, Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford OX1 3TA, England

Correspondence e-mail: nigel.jones@chem.ox.ac.uk

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.075
Data-to-parameter ratio = 8.5

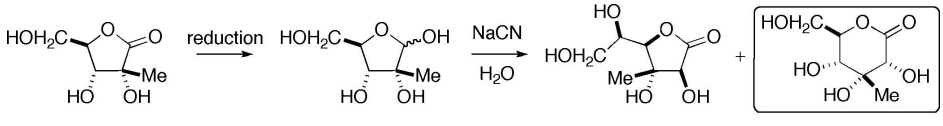
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 11 January 2007
Accepted 18 January 2007

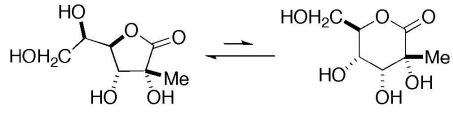
The relative configuration and ring size of the title compound, $C_7H_{12}O_6$, were established by X-ray crystallographic analysis. The absolute configuration was determined by the use of 2-*C*-methyl-D-ribonolactone as a starting material. Almost all unprotected carbohydrate lactones are five-membered ring 1,4-lactones; the title compound provides a very rare example of a stable six-membered ring lactone.

Comment

Although carbohydrates are the most varied of cheap chiral building blocks (Lichtenthaler & Peters, 2004), only recently have the first examples of branched 2-*C*-methylpentoses become readily available by treatment of an Amadori ketose with aqueous calcium hydroxide (Hotchkiss *et al.*, 2007). The recognition of the value of a family of 2-*C*-methylnucleosides in the treatment of hepatitis C has led to current interest in the synthesis of 2-*C*-carbon-substituted sugars (Sorbera *et al.*, 2006). The Kiliani reaction of ketoses and deoxyketoses with cyanide has provided an environmentally friendly procedure for the generation of a set of carbohydrate scaffolds with a branched carbon substituent at C-2 (Hotchkiss *et al.*, 2004; Soengas *et al.*, 2005). X-ray crystallographic analysis was vital in determining the structures of the products in these reactions (Punzo *et al.*, 2006; Watkin *et al.*, 2005). At present, free sugars and their lactones with a carbon branch at C-3 are essentially unknown. A 3-*C*-methylpentonolactone of unknown stereochemistry has been isolated from cigarette smoke (Schumacher *et al.*, 1977), 3-*C*-methyl-D-mannose (Kwon *et al.*, 2004) is one of the components of the trisaccharide repeating unit of the polysaccharide from *Helicobacter pylori* (Kocharova *et al.*, 2000) and 3-*C*-methyl-L-mannose is one of the sugars in a pentasaccharide hapten of the GPL of *Mycobacterium avium* serovar (Fekete *et al.*, 2006).



(1) (2) (3) (4)



(5) (6)

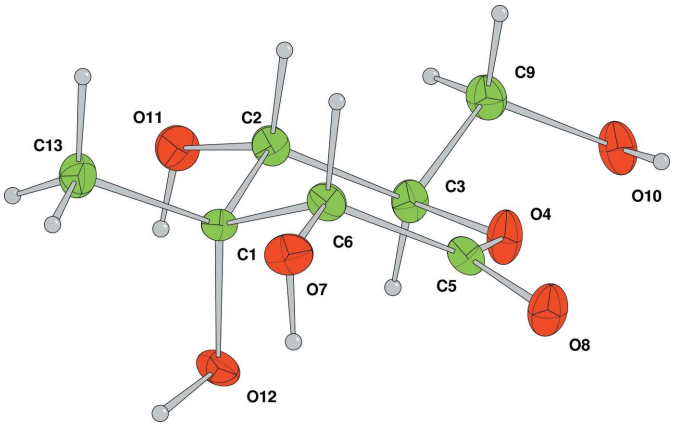


Figure 1
The molecular structure of (4), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radii.

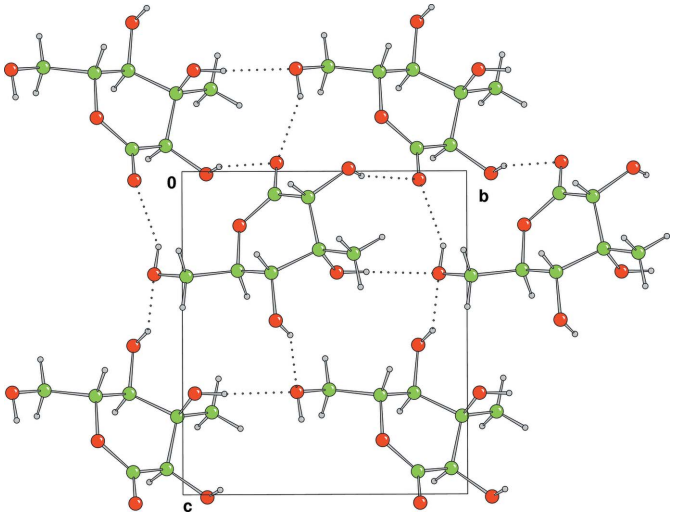


Figure 2
A projection along the *a* axis of part of a hydrogen-bonded sheet of (I). There are no strong interactions between the sheets. Hydrogen bonds are shown as dotted lines.

The value of the Kiliani reaction on 2-C-carbon-substituted carbohydrates in the synthesis of 3-*C*-hydroxymethyl branched sugars (Parker *et al.*, 2006; Simone *et al.*, 2007) and 3-*C*-methyl branched sugars (Bream *et al.*, 2006) has been established. Under completely environmentally friendly aqueous conditions, the reaction of cyanide in water with 2-*C*-methyl-D-ribose, (2), derived from 2-*C*-methyl-D-ribonolactone, (1) (Hotchkiss *et al.*, 2006), gave a major product which crystallized from the reaction mixture. X-ray crystallographic analysis shows (Fig. 1) that the structure is the title compound, (4), removing ambiguities as to the stereochemistry at the new C-2 chiral centre and the ring size of the lactone. The minor product is most likely the five-membered ring altrono-lactone, (3). The strain in five-membered ring lactones is generally considerably less than in six-membered ring lactones (Luisa *et al.*, 1990; Brown *et al.*, 1989). Compound (4) is thus a very rare example of the preferential formation of a six-membered ring lactone. Its C-2 isomer crystallizes as the 2-*C*-methyl-D-allono-1,4-lactone, (5), rather than the six-membered ring isomer, (6) (Harding *et al.*, 2005). The absolute configuration of compound (4) was determined by the use of the D-sugar (1) as the starting material.

The isolated molecule of (4) (Fig. 1) shows no unusual bond lengths or angles, in spite of the strain mentioned above. The largest differences from the *MOGUL* norms (Bruno *et al.*, 2004) are C6—O7 (00.01 Å; *MOGUL* s.u. 0.02 Å) and C3—C5—O4 (5.0°; *MOGUL* s.u. 2.2°).

The crystal structure of (4) is composed of hydrogen-bonded sheets of molecules lying parallel to the *bc* plane. Both the ketonic atom O8 and the hydroxyl atom O10 act as acceptors for two hydrogen bonds (Table 1 and Fig. 2).

Experimental

3-*C*-Methyl-D-allono-1,5-lactone, (4), was crystallized from a 3:1:1 mixture of ethyl acetate, methanol and cyclohexane. Analysis: m.p. 421–423 K; $[\alpha]_D^{23}$ 63.5 (*c*, 0.795 in MeOH).

Crystal data

$C_7H_{12}O_6$
M_r = 192.17
Monoclinic, $P2_1$
a = 5.6603 (2) Å
b = 8.0045 (2) Å
c = 9.3242 (3) Å
β = 103.1470 (13)°
V = 411.39 (2) Å^3
Z = 2
D_x = 1.551 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 150 K
Needle, colourless
0.20 × 0.05 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*DENZO* and *SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.75, T_{max} = 1.0
5511 measured reflections
1000 independent reflections
930 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.076
S = 1.16
1000 reflections
118 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.02P)^2 + 0.12P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O10—H7···O8^{i}	0.84	2.08	2.856 (2)	153
O7—H8···O8^{ii}	0.85	2.06	2.832 (2)	152
O11—H12···O10^{iii}	0.82	2.09	2.836 (2)	152
O12—H3···O10^{iv}	0.83	2.07	2.901 (2)	173

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z$; (ii) $-x+2, y+\frac{1}{2}, -z$; (iii) $-x+2, y+\frac{1}{2}, -z+1$; (iv) $x, y+1, z$.

In the absence of significant anomalous scattering, Friedel pairs were merged and the absolute configuration assigned from the starting material.

The relatively large ratio of minimum to maximum corrections applied in the multiscan process (1:1.33) reflects changes in the illuminated volume of the very thin needle-like crystal. These changes were kept to a minimum and were taken into account (Görbitz, 1999) by multiscan interframe scaling (*DENZO* and *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, with C—H in the range 0.93–0.98 Å and O—H = 0.82 Å, and with U_{iso}(H) = 1.2–1.5U_{eq}(parent atom), after which the positions were refined with riding constraints.

Data collection: *COLLECT* (Nonius, 1997–2001); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *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*.

The generous gift of 2-*C*-methyl-*D*-ribonolactone from Novartis Pharma AG, Basel, is gratefully acknowledged.

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