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5,6-*O*-Isopropylidene-3-*C*-methyl-D-mannono-1,4-lactone

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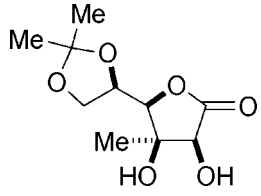
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.004 Å; R factor = 0.040; wR factor = 0.094; data-to-parameter ratio = 9.0.

The relative configuration of the title compound, $C_{10}H_{16}O_6$, was firmly established by X-ray crystallographic analysis. The absolute configuration was determined by the use of 2-*C*-methyl-D-arabinose as the starting material. The crystal structure exists as hydrogen-bonded sheets lying approximately perpendicular to *c*.

Related literature

For related literature see: Mitchell *et al.* (2007); Hotchkiss *et al.* (2006); Soengas *et al.* (2005); Bream *et al.* (2006); Simone *et al.* (2007); Fekete *et al.* (2006); Görbitz (1999); Jenkinson *et al.* (2007); Jones *et al.* (2007); Kocharova *et al.* (2000); Kwon *et al.* (2004); Lichtenthaler & Peters (2004); Parker *et al.* (2006); Schumacher *et al.* (1977).



Experimental

Crystal data

$C_{10}H_{16}O_6$
M_r = 232.23
Monoclinic, $P2_1$
a = 5.9838 (3) Å
b = 11.7424 (5) Å
c = 7.9189 (5) Å
β = 91.8112 (18)°
V = 556.14 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 150 K
0.20 × 0.20 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.87, T_{max} = 0.99
5136 measured reflections
1310 independent reflections
1078 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.094
S = 0.91
1310 reflections
145 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O13—H5···O4^{i}	0.85	1.95	2.787 (2)	170
O15—H14···O14^{ii}	0.83	2.05	2.848 (2)	163

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

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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2444).

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supplementary materials

Acta Cryst. (2007). E**63**, o3416 [**doi:10.1107/S160053680703125X**]

5,6-*O*-Isopropylidene-3-*C*-methyl-D-mannono-1,4-lactone

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Comment

Carbohydrates are one of the most varied cheap chiral building blocks (Lichtenthaler & Peters, 2004) available. Currently, free sugars and their lactones with a carbon branch at C-3 have been relatively unstudied with only limited examples in the literarture. Examples of sugars with a carbon branch at C-3 include: a 3-*C*-methylpentonolactone of unknown stereochemistry, isolated from cigarette smoke (Schumacher *et al.*, 1977); 3-*C*-methyl-D-mannose (Kwon *et al.*, 2004), one of the components of the trisaccharide repeating unit of the polysaccharide from Helicobacter pylori (Kocharova *et al.*, 2000); and a derivative of 3-*C*-methyl-*L*-mannose which is one of the sugars in a pentasaccharide hapten of the GPL of Mycobacterium avium serovar (Fekete *et al.*, 2006).

The Kiliani ascension of 2-*C*-carbon-substituted carbohydrates has proved to be a valuable route towards 3-*C*-hydroxymethyl branched sugars (Parker *et al.*, 2006; Simone *et al.*, 2007) and 3-*C*-methyl branched sugars (Bream *et al.*, 2006; Jones, Watkin *et al.* 2007). Recent biological studies on branched mannose derivatives have shown that this class of compound could have potential use as therapeutics (Mitchell *et al.* 2007).

The crystal structure exists as hydrogen bonded ribbons lying parallel to the *ab*-face (see Fig. 2).

Experimental

The reaction of cyanide in water with 2-*C*-methyl-D-arabinose (Jenkinson *et al.* 2007), derived from 2-*C*-methyl-D-arabinonolactone, (Hotchkiss *et al.*, 2006), gave a mixture of isomeric lactones that could be separated by treatment with acetone and copper sulfate, in the presence of sulfuric acid, to afford three protected lactones. The title compound was crystallized from cyclohexane and ethyl acetate: m.p. 390–391 K; $[\alpha]_D^{22}$ +25.9 (*c*, 0.34 in acetone).

Refinement

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

The relatively large ratio of minimum to maximum corrections applied in the multiscan process (1:1.15) reflect changes in the illuminated volume of the crystal. Changes in illuminated volume were kept to a minimum, and were taken into account (Görbitz, 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 carbon 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, O—H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

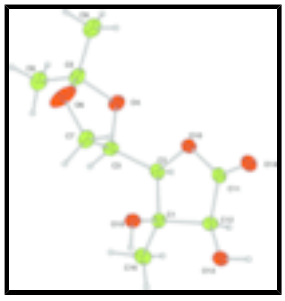

Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

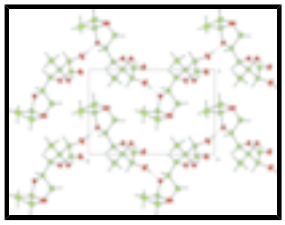

Fig. 2. The packing of the title compound projected along the *a*-axis. Hydrogen bonds are shown as dotted lines.

Fig. 3. The reaction scheme.

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Crystal data

$C_{10}H_{16}O_6$	F_{000} = 248
M_r = 232.23	D_x = 1.387 Mg m^{-3}
Monoclinic, $P2_1$	Melting point: ?? K
Hall symbol: P 2yb	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 5.9838 (3) Å	Cell parameters from 1263 reflections
b = 11.7424 (5) Å	θ = 5–27º
c = 7.9189 (5) Å	μ = 0.12 mm^{-1}
β = 91.8112 (18)º	*T* = 150 K
V = 556.14 (5) Å^3	Plate, colourless
Z = 2	0.20 × 0.20 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer	1078 reflections with $I > 2.0\sigma(I)$
Monochromator: graphite	R_{int} = 0.059
T = 150 K	θ_{max} = 27.4º
ω scans	θ_{min} = 5.2º
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	*h* = −7→7
T_{min} = 0.87, T_{max} = 0.99	*k* = −15→15
5136 measured reflections	*l* = −10→10

1310 independent reflections

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.094$

$S = 0.91$

1310 reflections

145 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.06P)^2 + 0.02P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{max} = 0.0001$

$\Delta\rho_{max} = 0.27$ e Å^{-3}

$\Delta\rho_{min} = -0.29$ e Å^{-3}

Extinction correction: None

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3390 (4)	0.2320 (2)	0.9976 (3)	0.0194
C2	0.1635 (4)	0.3068 (2)	0.9080 (3)	0.0202
C3	0.2339 (4)	0.3664 (2)	0.7497 (3)	0.0209
O4	0.0474 (3)	0.43187 (18)	0.6849 (2)	0.0241
C5	0.0862 (4)	0.4539 (3)	0.5098 (3)	0.0262
O6	0.2150 (4)	0.3591 (2)	0.4546 (3)	0.0505
C7	0.2924 (4)	0.2945 (3)	0.5966 (4)	0.0269
C8	0.2197 (5)	0.5628 (3)	0.4909 (4)	0.0385
C9	−0.1355 (5)	0.4558 (3)	0.4145 (4)	0.0353
O10	−0.0229 (3)	0.22944 (17)	0.8686 (2)	0.0216
C11	−0.0132 (4)	0.1416 (2)	0.9765 (3)	0.0207
C12	0.1838 (4)	0.1572 (2)	1.1009 (3)	0.0215
O13	0.2833 (3)	0.05512 (19)	1.1556 (2)	0.0284
O14	−0.1473 (3)	0.06496 (18)	0.9717 (2)	0.0263
O15	0.4355 (3)	0.16416 (18)	0.8701 (2)	0.0222
C16	0.5120 (4)	0.2978 (3)	1.1032 (3)	0.0266
H21	0.1127	0.3647	0.9932	0.0251*
H31	0.3612	0.4177	0.7788	0.0250*
H71	0.4529	0.2827	0.5951	0.0338*
H72	0.2128	0.2210	0.6050	0.0333*
H81	0.2604	0.5685	0.3759	0.0592*
H82	0.3528	0.5599	0.5632	0.0594*
H83	0.1252	0.6273	0.5184	0.0589*
H91	−0.1026	0.4632	0.2952	0.0543*
H92	−0.2096	0.3842	0.4309	0.0545*
H93	−0.2261	0.5192	0.4510	0.0548*
H121	0.1288	0.2008	1.2001	0.0268*

H161	0.6123	0.2442	1.1622	0.0432*
H162	0.6000	0.3479	1.0344	0.0429*
H163	0.4378	0.3414	1.1921	0.0431*
H5	0.1952	0.0124	1.2084	0.0458*
H14	0.5420	0.1310	0.9170	0.0361*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0201 (11)	0.0210 (14)	0.0170 (13)	−0.0016 (11)	0.0011 (10)	−0.0006 (11)
C2	0.0193 (11)	0.0194 (13)	0.0219 (14)	−0.0025 (11)	0.0016 (9)	−0.0030 (12)
C3	0.0213 (12)	0.0166 (13)	0.0245 (14)	−0.0003 (11)	−0.0030 (10)	0.0021 (12)
O4	0.0276 (8)	0.0221 (10)	0.0227 (10)	0.0063 (8)	0.0027 (7)	0.0030 (8)
C5	0.0315 (13)	0.0271 (15)	0.0203 (14)	0.0050 (13)	0.0058 (11)	0.0033 (13)
O6	0.0806 (17)	0.0499 (15)	0.0216 (11)	0.0378 (14)	0.0091 (11)	0.0060 (11)
C7	0.0299 (13)	0.0251 (15)	0.0260 (15)	0.0049 (13)	0.0060 (11)	0.0031 (13)
C8	0.0337 (14)	0.048 (2)	0.0341 (17)	−0.0084 (16)	−0.0006 (13)	0.0133 (17)
C9	0.0393 (14)	0.0369 (18)	0.0295 (16)	−0.0079 (15)	−0.0010 (13)	0.0073 (16)
O10	0.0182 (8)	0.0204 (10)	0.0261 (10)	−0.0005 (8)	−0.0011 (7)	0.0039 (8)
C11	0.0177 (10)	0.0200 (14)	0.0246 (15)	0.0029 (11)	0.0038 (10)	0.0013 (12)
C12	0.0198 (11)	0.0214 (14)	0.0232 (14)	0.0026 (11)	−0.0005 (10)	0.0039 (12)
O13	0.0205 (8)	0.0270 (10)	0.0376 (11)	0.0013 (8)	−0.0011 (8)	0.0139 (10)
O14	0.0204 (8)	0.0224 (10)	0.0361 (11)	−0.0016 (9)	0.0004 (8)	0.0061 (9)
O15	0.0210 (8)	0.0241 (10)	0.0215 (10)	0.0052 (8)	0.0008 (7)	0.0002 (9)
C16	0.0241 (12)	0.0303 (16)	0.0251 (15)	−0.0078 (13)	−0.0032 (11)	−0.0030 (13)

Geometric parameters (Å, °)

C1—C2	1.526 (3)	C8—H81	0.952
C1—C12	1.534 (4)	C8—H82	0.967
C1—O15	1.423 (3)	C8—H83	0.974
C1—C16	1.521 (3)	C9—H91	0.975
C2—C3	1.507 (4)	C9—H92	0.961
C2—O10	1.465 (3)	C9—H93	0.970
C2—H21	1.011	O10—C11	1.339 (3)
C3—O4	1.436 (3)	C11—C12	1.523 (3)
C3—C7	1.527 (4)	C11—O14	1.206 (3)
C3—H31	0.993	C12—O13	1.401 (3)
O4—C5	1.436 (3)	C12—H121	1.002
C5—O6	1.431 (4)	O13—H5	0.848
C5—C8	1.518 (4)	O15—H14	0.825
C5—C9	1.506 (4)	C16—H161	0.978
O6—C7	1.422 (3)	C16—H162	0.969
C7—H71	0.971	C16—H163	0.987
C7—H72	0.989		
C2—C1—C12	99.13 (18)	H71—C7—H72	110.9
C2—C1—O15	106.35 (19)	C5—C8—H81	107.7
C12—C1—O15	108.9 (2)	C5—C8—H82	109.7

C2—C1—C16	114.2 (2)	H81—C8—H82	109.8
C12—C1—C16	114.2 (2)	C5—C8—H83	108.8
O15—C1—C16	112.96 (19)	H81—C8—H83	109.1
C1—C2—C3	116.6 (2)	H82—C8—H83	111.7
C1—C2—O10	104.5 (2)	C5—C9—H91	106.6
C3—C2—O10	109.98 (19)	C5—C9—H92	108.8
C1—C2—H21	107.1	H91—C9—H92	108.4
C3—C2—H21	109.9	C5—C9—H93	110.7
O10—C2—H21	108.4	H91—C9—H93	110.6
C2—C3—O4	108.1 (2)	H92—C9—H93	111.5
C2—C3—C7	118.7 (2)	C2—O10—C11	108.93 (17)
O4—C3—C7	101.98 (19)	O10—C11—C12	109.7 (2)
C2—C3—H31	108.7	O10—C11—O14	122.6 (2)
O4—C3—H31	109.9	C12—C11—O14	127.6 (2)
C7—C3—H31	109.1	C1—C12—C11	101.1 (2)
C3—O4—C5	107.09 (19)	C1—C12—O13	113.38 (19)
O4—C5—O6	105.1 (2)	C11—C12—O13	114.2 (2)
O4—C5—C8	110.4 (2)	C1—C12—H121	110.1
O6—C5—C8	109.6 (2)	C11—C12—H121	107.5
O4—C5—C9	108.6 (2)	O13—C12—H121	110.0
O6—C5—C9	109.5 (3)	C12—O13—H5	113.2
C8—C5—C9	113.3 (2)	C1—O15—H14	105.7
C5—O6—C7	109.8 (2)	C1—C16—H161	109.4
C3—C7—O6	104.8 (2)	C1—C16—H162	111.8
C3—C7—H71	109.9	H161—C16—H162	108.8
O6—C7—H71	111.3	C1—C16—H163	110.0
C3—C7—H72	107.9	H161—C16—H163	106.0
O6—C7—H72	111.9	H162—C16—H163	110.6

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O13—H5···O4^{i}	0.85	1.95	2.787 (2)	170
O15—H14···O14^{ii}	0.83	2.05	2.848 (2)	163

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+2; (ii) *x*+1, *y*, *z*.

Fig. 1

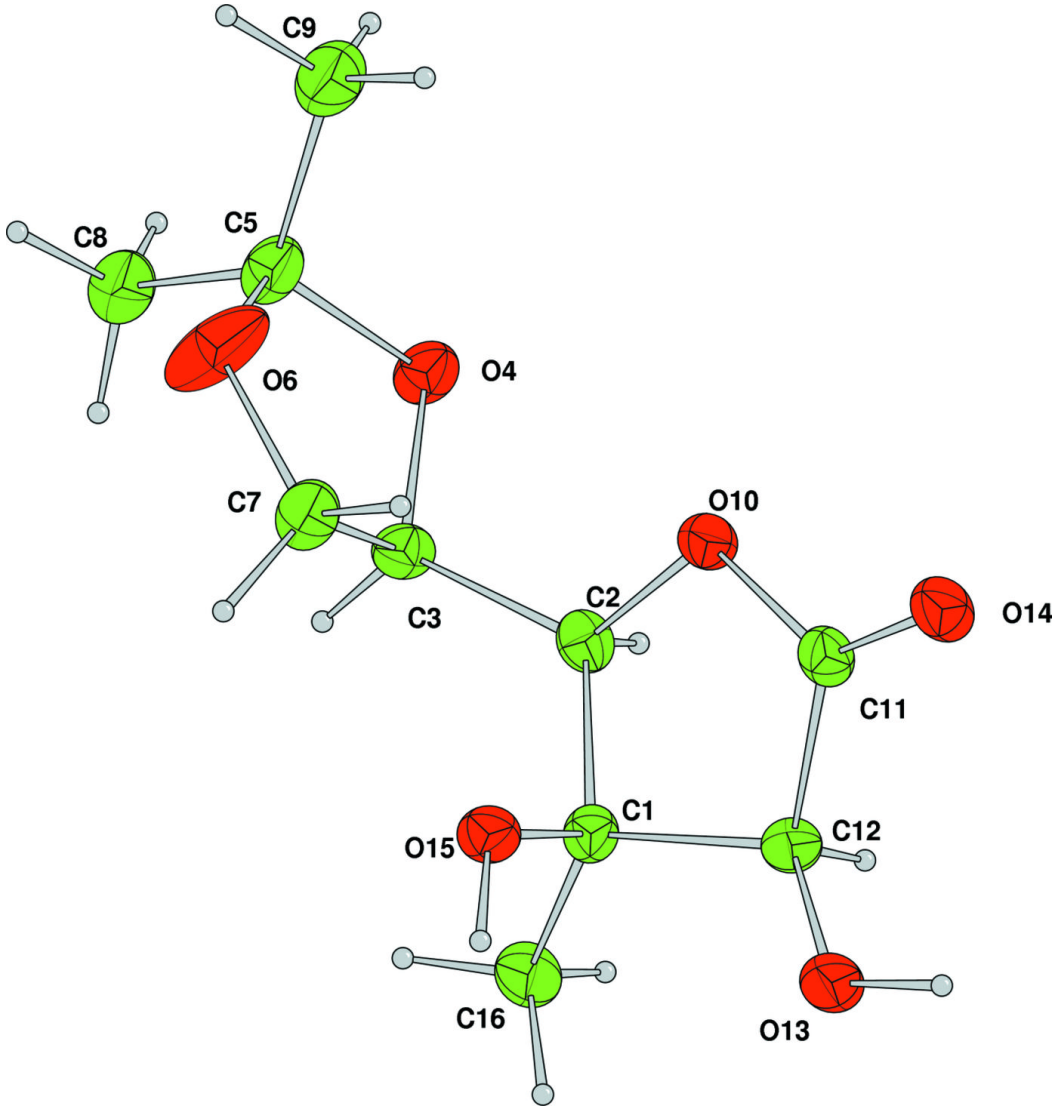


Fig. 2

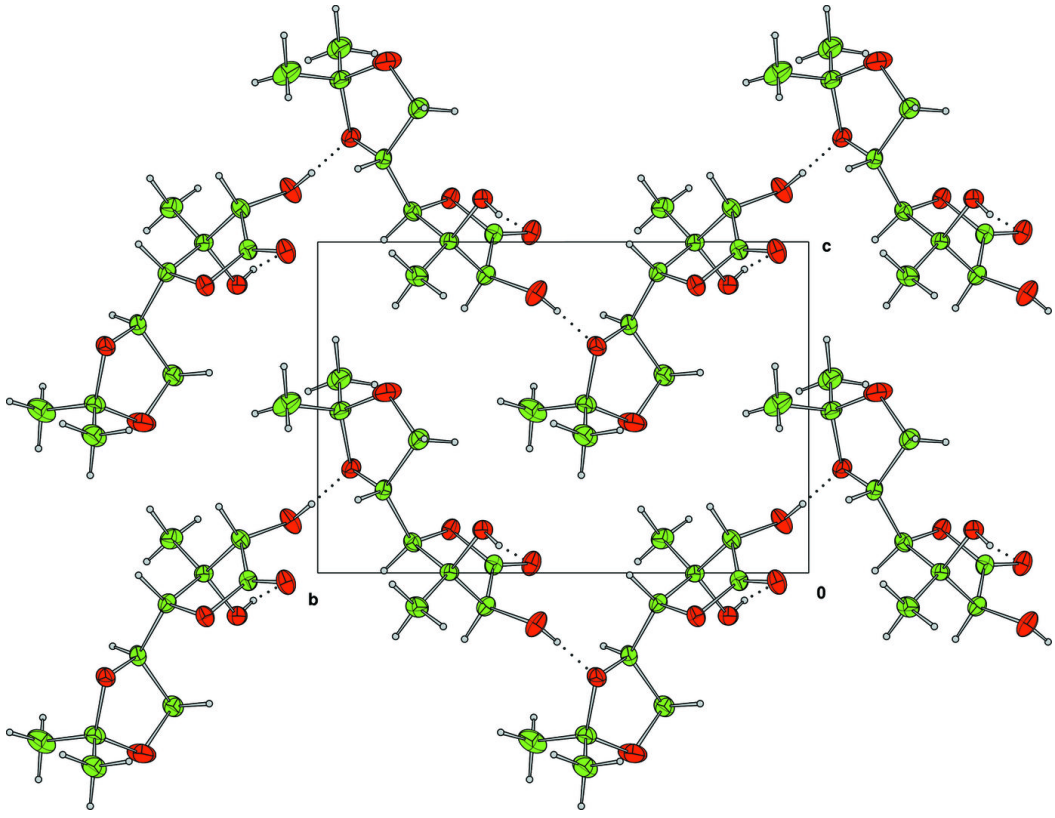
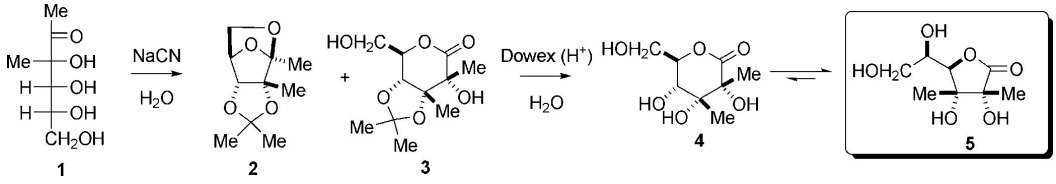


Fig. 3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