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2,3-*C*-Dimethyl-3,4-*O*-isopropylidene-D-allono-1,5-lactone

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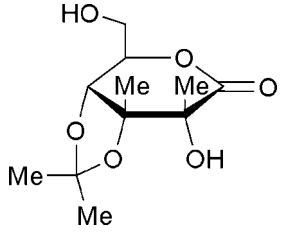
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.073; data-to-parameter ratio = 10.1.

The relative configuration of the title compound, $C_{11}H_{18}O_6$, was firmly established by X-ray crystallographic analysis. The absolute configuration was determined by the use of 2-*C*-methyl-D-ribono-1,4-lactone as the starting material. The structure exists as a hydrogen-bonded network, with each molecule acting as a donor and acceptor for two hydrogen bonds.

Related literature

For related literature see: Jones, Curran *et al.* (2007); Jones, Watkin *et al.* (2007); Mitchell *et al.* (2007); Hotchkiss *et al.* (2004, 2006); Soengas *et al.* (2005); Booth, Watkin *et al.* (2007); Booth *et al.* (2007*a*,*b*,*c*); Booth, Jenkinson, Watkin & Fleet (2007); Curran *et al.* (2007); Görbitz (1999).



Experimental

Crystal data

$C_{11}H_{18}O_6$
M_r = 246.26
Orthorhombic, $P2_12_12_1$
a = 6.9089 (2) Å
b = 12.2072 (5) Å
c = 14.2507 (5) Å
V = 1201.88 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 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} = 0.83, T_{max} = 0.99
5554 measured reflections
1561 independent reflections
1303 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.073
S = 0.92
1561 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O15—H5···O13^{i}	0.85	2.13	2.957 (2)	163
O13—H19···O14^{ii}	0.84	2.00	2.817 (2)	163

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

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: LH2448).

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.
Booth, K. V., Jenkinson, S. F., Fleet, G. J. W. & Watkin, D. J. (2007*b*). *Acta Cryst.* E**63**, o2427–o2429.
Booth, K. V., Jenkinson, S. F., Fleet, G. W. J. & Watkin, D. J. (2007*a*). *Acta Cryst.* E**63**, o2424–o2426.
Booth, K. V., Jenkinson, S. F., Fleet, G. W. J. & Watkin, D. J. (2007*c*). *Acta Cryst.* E**63**, o2204–o2206.
Booth, K. V., Jenkinson, S. F., Watkin, D. J. & Fleet, G. W. J. (2007). *Acta Cryst.* E**63**, o3386.
Booth, K. V., Watkin, D. J., Jenkinson, S. F. & Fleet, G. W. J. (2007). *Acta Cryst.* E**63**, o1128–o1130.
Curran, L. A., Jenkinson, S. F., Jones, N. A., Watkin, D. J. & Fleet, G. W. J. (2007). *Acta Cryst.* E**63**, o3388.
Görbitz, C. H. (1999). *Acta Cryst.* B**55**, 1090–1098.
Hotchkiss, D. J., Jenkinson, S. F., Storer, R., Heinz, T. & Fleet, G. W. J. (2006). *Tetrahedron Lett.* **47**, 315–318.
Hotchkiss, D. J., Soengas, R., Simone, M. I., van Ameijde, J., Hunter, S., Cowley, A. R. & Fleet, G. W. J. (2004). *Tetrahedron Lett.* **45**, 9461–9464.
Jones, N. A., Curran, L. A., Wormald, M. R., Dwek, R. A. & Fleet, G. W. J. (2007). In preparation.
Jones, N. A., Watkin, D. J., Curran, L. A., Jenkinson, S. F. & Fleet, G. W. J. (2007). *Acta Cryst.* E**63**, o992–o994.
Mitchell, D. A., Jones, N. A., Hunter, S. J., Cook, J. M. D., Jenkinson, S. F., Wormald, M. R., Dwek, R. A. & Fleet, G. W. J. (2007). *Tetrahedron: Asymmetry* **18**. In the press.
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.
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., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

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supplementary materials

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2,3-*C*-Dimethyl-3,4-*O*-isopropylidene-D-allono-1,5-lactone

L. A. Curran, S. F. Jenkinson, N. A. Jones, D. J. Watkin and G. W. J. Fleet

Comment

Branched sugars are a relatively unstudied class of compounds but recent biological results have indicated they could have a potential use as therapeutics (Mitchell *et al.* 2007). The Kiliani ascension on ketoses and deoxy ketoses has proved a valuable route towards branched sugars (Hotchkiss *et al.*, 2004,2006; Soengas *et al.*, 2005; Jones, Watkin *et al.* 2007). Currently, there are very limited examples of di-branched carbohydrates reported. Examples of sugars that contain two carbon branches in the literature include 2,4-*C*-dimethyl-3,4-*O*-isopropylidene-*L*-arabinono-1,5-lactone (Booth, Watkin *et al.* 2007) and various protected forms of 3,5-*C*-dimethyl-mannono and glucono lactone (Booth, Jenkinson, Fleet & Watkin, 2007*a*, 2007*b*, 2007*c*). 2-*C*-Hydroxymethyl-2,3-*O*-isopropylidene-3-*C*-methyl-β-L– erythrose (Booth, Jenkinson, Watkin & Fleet, 2007*d*) is a rare example of a sugar with adjacent branched centres.

The crystal structure of the title compound (Fig. 1) exists as a three dimensionally hydrogen bonded network (Fig. 2) with each molecule acting as an acceptor and a donor for two hydrogen bonds.

Experimental

Treatment of 1-deoxy-3-*C*-methyl-D-psicose **2** (Jones *et al.* in preparation) derived from 2-*C*-methyl-D-ribono-1,4-lactone **1** (Hotchkiss *et al.*, 2006), with sodium cyanide, gave a mixture of the 2,6-anhydro derivative **3** (Curran *et al.* 2007) and the lactone **4** (Fig. 3). X-Ray crystallographic analysis of the title lactone **3** removed any ambiguity as to the stereochemistry at the new C-2 chiral centre. The title compound was recrystallized from a mixture of cyclohexane and ethyl acetate; m.p. 420 K; $[\alpha]_D^{22}$ +106.1 (c, 0.64 in chlororform).

Refinement

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 multiscan process (1:1.19) 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

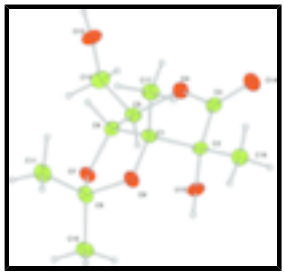


Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

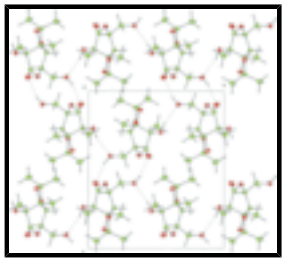


Fig. 2. The packing of the title compound projected along the *a*-axis. Hydrogen bonds are shown as dotted lines.

Fig. 3. The reaction scheme.

2,3-*C*-Dimethyl-3,4-*O*-isopropylidene-D-allono-1,5-lactone

Crystal data

$C_{11}H_{18}O_6$	F_{000} = 528
M_r = 246.26	D_x = 1.361 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 1357 reflections
a = 6.9089 (2) Å	θ = 5–27°
b = 12.2072 (5) Å	μ = 0.11 mm^{-1}
c = 14.2507 (5) Å	T = 150 K
V = 1201.88 (7) Å^3	Plate, colourless
Z = 4	0.20 × 0.20 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer	1303 reflections with $I > 2.0\sigma(I)$
Monochromator: graphite	R_{int} = 0.031
T = 150 K	θ_{max} = 27.5°
ω scans	θ_{min} = 5.2°
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	h = −8→8
T_{min} = 0.83, T_{max} = 0.99	k = −15→15
5554 measured reflections	l = −18→18
1561 independent reflections	

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.073$

$S = 0.92$

1561 reflections

154 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.22P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{max} = 0.0002$

$\Delta\rho_{max} = 0.26$ e Å^{-3}

$\Delta\rho_{min} = -0.24$ 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	0.6355 (3)	0.35060 (15)	0.21409 (12)	0.0168
C2	0.7020 (3)	0.45680 (13)	0.26378 (12)	0.0185
C3	0.7261 (3)	0.42656 (14)	0.36718 (13)	0.0225
O4	0.5794 (2)	0.37424 (10)	0.40921 (8)	0.0233
C5	0.4030 (3)	0.34688 (15)	0.35788 (12)	0.0191
C6	0.4458 (3)	0.30862 (13)	0.25760 (12)	0.0173
O7	0.29790 (19)	0.34924 (10)	0.19778 (8)	0.0190
C8	0.3790 (3)	0.35046 (16)	0.10563 (12)	0.0194
O9	0.57947 (19)	0.38010 (10)	0.12033 (8)	0.0198
C10	0.2817 (3)	0.43932 (15)	0.04956 (13)	0.0249
C11	0.3659 (3)	0.23797 (15)	0.06080 (13)	0.0262
C12	0.3044 (3)	0.25957 (14)	0.41507 (13)	0.0234
O13	0.4187 (2)	0.16239 (10)	0.41357 (8)	0.0249
O14	0.8717 (2)	0.44346 (11)	0.41227 (9)	0.0336
O15	0.54750 (19)	0.53432 (9)	0.26178 (9)	0.0216
C16	0.8859 (3)	0.50609 (16)	0.22511 (14)	0.0263
C17	0.7921 (3)	0.26278 (15)	0.21373 (13)	0.0238
H51	0.3215	0.4124	0.3552	0.0251*
H61	0.4470	0.2263	0.2567	0.0225*
H101	0.3438	0.4423	−0.0118	0.0346*
H102	0.2985	0.5093	0.0839	0.0349*
H103	0.1455	0.4193	0.0424	0.0349*
H111	0.4183	0.2437	−0.0033	0.0397*
H112	0.4415	0.1852	0.0988	0.0394*
H113	0.2318	0.2141	0.0579	0.0391*
H121	0.2880	0.2871	0.4802	0.0300*
H122	0.1741	0.2432	0.3886	0.0301*
H161	0.9086	0.5757	0.2581	0.0405*
H162	0.9937	0.4554	0.2353	0.0400*

H163	0.8697	0.5198	0.1581	0.0397*
H171	0.7428	0.1979	0.1804	0.0363*
H172	0.9047	0.2937	0.1824	0.0372*
H173	0.8235	0.2434	0.2792	0.0366*
H5	0.5431	0.5604	0.2065	0.0319*
H19	0.3990	0.1194	0.4586	0.0389*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0184 (9)	0.0180 (9)	0.0140 (8)	0.0009 (8)	−0.0006 (8)	0.0008 (7)
C2	0.0215 (10)	0.0159 (7)	0.0181 (8)	0.0009 (8)	−0.0027 (8)	0.0033 (8)
C3	0.0301 (12)	0.0158 (8)	0.0216 (9)	−0.0012 (9)	−0.0041 (9)	−0.0001 (8)
O4	0.0286 (8)	0.0239 (7)	0.0173 (6)	−0.0042 (7)	−0.0033 (6)	0.0011 (6)
C5	0.0204 (10)	0.0199 (9)	0.0169 (8)	0.0024 (9)	0.0000 (8)	0.0005 (8)
C6	0.0181 (9)	0.0165 (8)	0.0172 (8)	0.0006 (8)	0.0003 (9)	0.0003 (8)
O7	0.0157 (7)	0.0246 (7)	0.0166 (6)	0.0007 (6)	−0.0010 (6)	0.0013 (6)
C8	0.0157 (10)	0.0267 (10)	0.0158 (8)	−0.0028 (9)	0.0016 (8)	0.0012 (8)
O9	0.0172 (7)	0.0270 (7)	0.0153 (6)	−0.0030 (6)	−0.0005 (6)	0.0012 (5)
C10	0.0229 (11)	0.0283 (10)	0.0234 (9)	−0.0010 (10)	−0.0045 (9)	0.0060 (9)
C11	0.0289 (11)	0.0287 (10)	0.0210 (9)	−0.0025 (10)	−0.0037 (9)	−0.0021 (9)
C12	0.0267 (11)	0.0234 (9)	0.0202 (9)	0.0010 (10)	0.0057 (9)	0.0011 (8)
O13	0.0355 (8)	0.0184 (6)	0.0208 (6)	0.0030 (7)	0.0048 (6)	0.0049 (5)
O14	0.0384 (9)	0.0354 (8)	0.0272 (7)	−0.0107 (8)	−0.0143 (7)	0.0073 (7)
O15	0.0279 (8)	0.0153 (5)	0.0217 (6)	0.0026 (6)	−0.0007 (7)	0.0029 (6)
C16	0.0242 (11)	0.0258 (10)	0.0288 (10)	−0.0055 (9)	−0.0040 (10)	0.0066 (9)
C17	0.0223 (10)	0.0223 (9)	0.0268 (10)	0.0049 (9)	−0.0008 (9)	−0.0014 (8)

Geometric parameters (Å, °)

C1—C2	1.547 (2)	C8—C11	1.517 (3)
C1—C6	1.538 (2)	C10—H101	0.975
C1—O9	1.437 (2)	C10—H102	0.991
C1—C17	1.524 (2)	C10—H103	0.977
C2—C3	1.528 (2)	C11—H111	0.985
C2—O15	1.427 (2)	C11—H112	0.990
C2—C16	1.510 (3)	C11—H113	0.972
C3—O4	1.339 (2)	C12—O13	1.425 (2)
C3—O14	1.212 (2)	C12—H121	0.994
O4—C5	1.460 (2)	C12—H122	0.996
C5—C6	1.532 (2)	O13—H19	0.840
C5—C12	1.505 (3)	O15—H5	0.850
C5—H51	0.979	C16—H161	0.983
C6—O7	1.420 (2)	C16—H162	0.979
C6—H61	1.005	C16—H163	0.976
O7—C8	1.428 (2)	C17—H171	0.984
C8—O9	1.447 (2)	C17—H172	0.972
C8—C10	1.506 (3)	C17—H173	0.987

C2—C1—C6	110.36 (15)	C10—C8—C11	113.71 (15)
C2—C1—O9	107.19 (13)	C8—O9—C1	109.25 (14)
C6—C1—O9	103.24 (13)	C8—C10—H101	107.8
C2—C1—C17	112.35 (15)	C8—C10—H102	107.8
C6—C1—C17	111.86 (14)	H101—C10—H102	111.0
O9—C1—C17	111.37 (14)	C8—C10—H103	107.8
C1—C2—C3	105.74 (13)	H101—C10—H103	109.8
C1—C2—O15	108.93 (14)	H102—C10—H103	112.3
C3—C2—O15	105.12 (15)	C8—C11—H111	107.8
C1—C2—C16	114.64 (16)	C8—C11—H112	109.1
C3—C2—C16	110.89 (16)	H111—C11—H112	111.1
O15—C2—C16	110.97 (13)	C8—C11—H113	110.2
C2—C3—O4	117.66 (17)	H111—C11—H113	109.3
C2—C3—O14	124.09 (18)	H112—C11—H113	109.3
O4—C3—O14	118.19 (16)	C5—C12—O13	109.30 (15)
C3—O4—C5	121.10 (13)	C5—C12—H121	108.6
O4—C5—C6	112.08 (15)	O13—C12—H121	111.0
O4—C5—C12	105.58 (14)	C5—C12—H122	110.2
C6—C5—C12	112.12 (15)	O13—C12—H122	109.2
O4—C5—H51	108.2	H121—C12—H122	108.6
C6—C5—H51	108.9	C12—O13—H19	114.7
C12—C5—H51	109.9	C2—O15—H5	107.0
C1—C6—C5	116.03 (15)	C2—C16—H161	107.7
C1—C6—O7	104.76 (12)	C2—C16—H162	109.5
C5—C6—O7	108.34 (14)	H161—C16—H162	110.7
C1—C6—H61	108.7	C2—C16—H163	109.2
C5—C6—H61	108.5	H161—C16—H163	109.8
O7—C6—H61	110.4	H162—C16—H163	109.9
C6—O7—C8	105.87 (13)	C1—C17—H171	108.8
O7—C8—O9	104.19 (13)	C1—C17—H172	107.3
O7—C8—C10	108.69 (15)	H171—C17—H172	111.6
O9—C8—C10	108.91 (15)	C1—C17—H173	108.7
O7—C8—C11	110.77 (15)	H171—C17—H173	109.9
O9—C8—C11	110.13 (16)	H172—C17—H173	110.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O15—H5···O13^{i}	0.85	2.13	2.957 (2)	163
O13—H19···O14^{ii}	0.84	2.00	2.817 (2)	163

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

Fig. 1

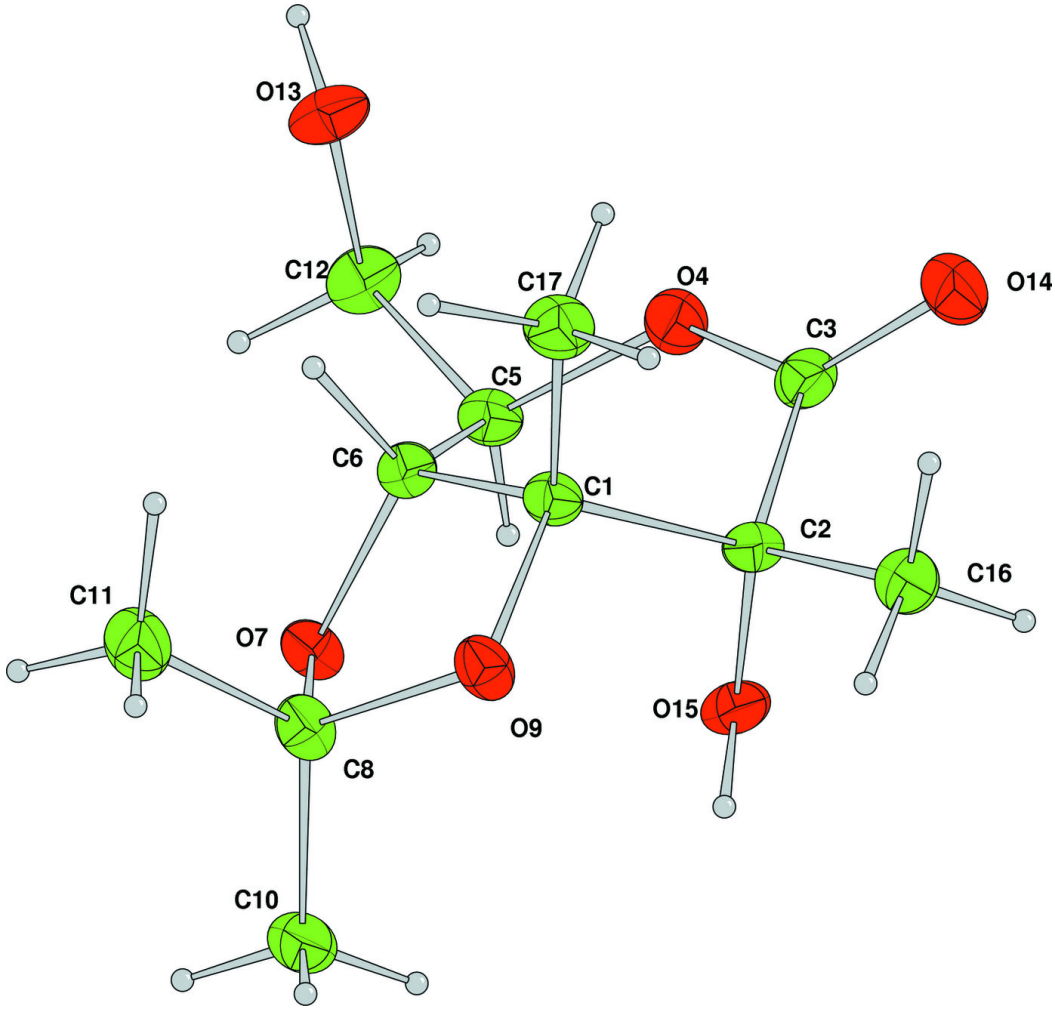


Fig. 2

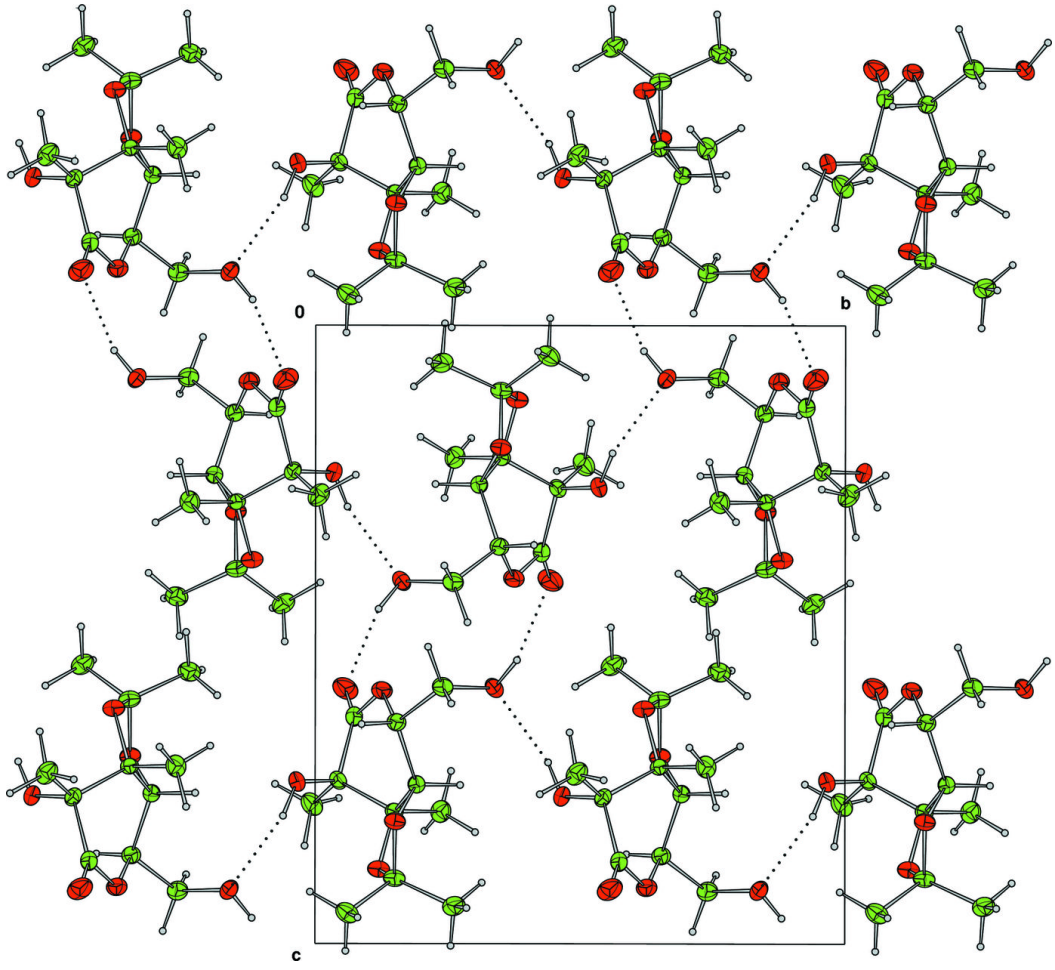
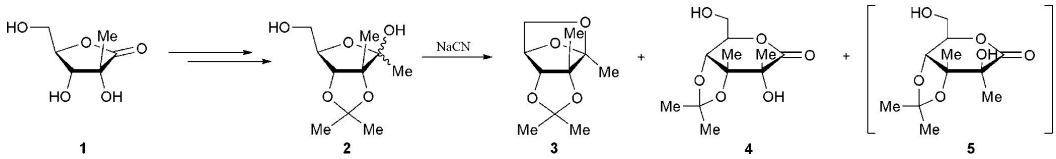


Fig. 3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+
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OH
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