Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-*C*-Hydroxymethyl-2,3-*O*-isopropylidene-3-*C*-methyl-β-L-erythrose

Kathrine V. Booth,[a] Sarah F. Jenkinson,[a]* David J. Watkin[b] 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: sarah.jenkinson@chem.ox.ac.uk

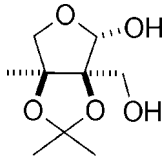
Received 25 June 2007; accepted 27 June 2007

Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; R factor = 0.031; wR factor = 0.074; data-to-parameter ratio = 10.5.

The relative configuration of the title compound, $C_9H_{16}O_5$, has been firmly established by X-ray crystallographic analysis. The absolute configuration of this sugar 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 being a donor and an acceptor for two hydrogen bonds.

Related literature

For related literature, see: Booth *et al.* (2007*a*,*b*,*c*); Booth, Best *et al.* (2007); Booth, Watkin *et al.* (2007); Chapleur & Chrétien (1997); Ho (1978); Hotchkiss *et al.* (2006, 2007); Jones *et al.* (2007); Koos & Mosher (1986); Mitchell *et al.* (2007); Soengas *et al.* (2005).



Experimental

Crystal data

$C_9H_{16}O_5$
M_r = 204.22
Orthorhombic, $P2_12_12_1$
a = 6.2840 (2) Å
b = 11.2043 (3) Å
c = 14.1345 (5) Å
V = 995.18 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 150 K
0.40 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.89, T_{max} = 0.98
6798 measured reflections
1329 independent reflections
1174 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.074
S = 0.94
1329 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H15···O14^{i}	0.85	1.88	2.724 (2)	172
O14—H16···O3^{ii}	0.86	2.07	2.867 (2)	154

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+2$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

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: LH2446).

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., Best, D., Jenkinson, S. F. & Fleet, G. W. J. (2007). In preparation.
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., Watkin, D. J., Jenkinson, S. F. & Fleet, G. W. J. (2007). *Acta Cryst.* E**63**, o1128–o1130.
Chapleur, Y. & Chrétien, F. (1997). *Preparative Carbohydrate Chemistry*, edited by S. Hanessian, p. 207. Boca Raton: CRC Press.
Ho, P.-T. (1978). *Tetrahedron Lett.* **19**, 1623–1626.
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., Booth, K. V., Weymouth-Wilson, A. C., Eastwick-Field, V. & Fleet, G. W. J. (2007). *Tetrahedron Lett.* **48**, 517–520.
Jones, N. J., Jenkinson, S. F., Curran, L. A., Watkin, D. J. & Fleet, G. W. J. (2007). *Acta Cryst.* E**63**. In the press.
Koos, M. & Mosher, H. S. (1986). *Carbohydr. Res.* **146**, 335–341.
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.

  doi:10.1107/S1600536807031522

supplementary materials

Acta Cryst. (2007). E**63**, o3386 [**doi:10.1107/S1600536807031522**]

2-*C*-Hydroxymethyl-2,3-*O*-isopropylidene-3-*C*-methyl-β-L-erythrose

K. V. Booth, S. F. Jenkinson, D. J. Watkin and G. W. J. Fleet

Comment

Singly branched sugars have been found in nature and their occurrence has prompted interest in their synthesis and biological evaluation (Chapleur & Chrétien, 1997). For example, 2-*C*-substituted mannose derivatives have been shown to have therapeutic potential (Mitchell *et al.*, 2007). The Kiliani reaction of ketoses with cyanide (Hotchkiss *et al.*, 2006, Soengas *et al.*, 2005) and calcium oxide treatment of Amadori compounds have proved to be valuable routes towards branched sugars (Hotchkiss *et al.*, 2006, 2007). In addition the Aldol reaction using formaldehyde and potassium carbonate can be used to introduce hydroxymethyl branches to sugars, for example in the synthesis of hamamalose (Ho, 1978) and apiose (Koos & Mosher, 1986).

Sugars containing more than one branch are very rare. Examples of sugars that contain two carbon branches include 2,4-dimethyl-3,4-*O*-isopropylidene-*L*-arabinono-1,5-lactone (Booth, Watkin *et al.*, 2007) and various protected forms of 3,5-di-*C*-methyl-mannono and glucono lactone (Booth *et al.*, 2007*a*, 2007*b*, 2007*c*). 2,3-*C*-Dimethyl-D-allono-1,4-lactone (Jones *et al.*, 2007) is an example of a sugar with adjacent branching centres.

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

Experimental

Protected 3-*C*-methyl-*L*-erythrose (Booth, Best *et al.*, 2007) **2**, derived from 2-*C*-methyl-D-ribono-1,4-lactone **1**, was treated with potassium carbonate and an excess of formaldehyde (Fig. 3). This gave a single product **3**, a mixture of anomers in solution, which was found to crystallize as the pure β form (Fig. 1). The title compound was recrystallized from methanol; m.p. 337–343 K; $[\alpha]_D^{21}$ +66.2 (*c*, 1.34 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 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

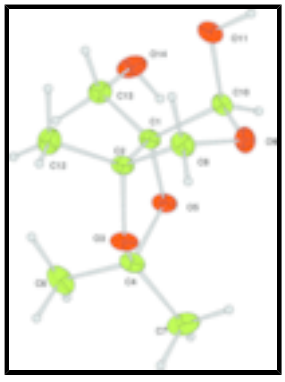


Fig. 1. The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

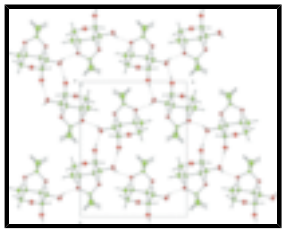


Fig. 2. Packing of the title compound projected along the *a*-axis. Hydrogen bonds are shown as dotted lines.

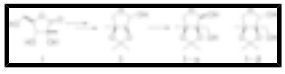


Fig. 3. The reaction scheme.

2-*C*-Hydroxymethyl-2,3-*O*-isopropylidene-3-*C*-methyl- β-*L*-erythrose

Crystal data

$C_9H_{16}O_5$	F_{000} = 440
M_r = 204.22	D_x = 1.363 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 1304 reflections
a = 6.2840 (2) Å	θ = 5–27°
b = 11.2043 (3) Å	μ = 0.11 mm^{-1}
c = 14.1345 (5) Å	T = 150 K
V = 995.18 (5) Å^3	Plate, colourless
Z = 4	0.40 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer	1174 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.030
T = 150 K	θ_{max} = 27.5°
ω scans	θ_{min} = 5.4°
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	h = −8→8

T_{min} = 0.89, T_{max} = 0.98
6798 measured reflections
1329 independent reflections

k = −14→14
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.074
S = 0.94
1329 reflections
127 parameters
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.26P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max}$ = 0.0003
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 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	0.4004 (3)	0.62732 (15)	0.82157 (12)	0.0170
C2	0.4011 (3)	0.48976 (15)	0.80312 (11)	0.0175
O3	0.4963 (2)	0.47844 (10)	0.71058 (7)	0.0207
C4	0.5033 (3)	0.59116 (14)	0.66416 (11)	0.0192
O5	0.4968 (2)	0.67791 (10)	0.73859 (8)	0.0190
C6	0.3161 (4)	0.60448 (18)	0.59812 (14)	0.0310
C7	0.7142 (3)	0.60183 (18)	0.61403 (15)	0.0297
C8	0.5634 (3)	0.44334 (16)	0.87399 (12)	0.0220
O9	0.70020 (19)	0.54266 (11)	0.89385 (8)	0.0226
C10	0.5609 (3)	0.64203 (16)	0.90340 (11)	0.0194
O11	0.4474 (2)	0.63675 (12)	0.98858 (8)	0.0255
C12	0.1885 (3)	0.42543 (16)	0.80539 (13)	0.0238
C13	0.1860 (3)	0.68450 (15)	0.83936 (13)	0.0203
O14	0.2049 (2)	0.80853 (11)	0.86261 (9)	0.0251
H61	0.3262	0.6813	0.5628	0.0499*
H62	0.3133	0.5390	0.5506	0.0503*
H63	0.1852	0.6027	0.6356	0.0507*
H71	0.7202	0.6830	0.5847	0.0470*
H72	0.7185	0.5393	0.5626	0.0469*
H73	0.8304	0.5901	0.6610	0.0479*
H81	0.6440	0.3754	0.8455	0.0286*
H82	0.4869	0.4191	0.9330	0.0282*
H101	0.6441	0.7203	0.8990	0.0242*
H121	0.2147	0.3398	0.7899	0.0380*
H122	0.0922	0.4610	0.7571	0.0387*
H123	0.1219	0.4341	0.8684	0.0382*
H131	0.0965	0.6764	0.7798	0.0269*

H132	0.1112	0.6441	0.8918	0.0265*
H15	0.5366	0.6493	1.0330	0.0412*
H16	0.3095	0.8395	0.8319	0.0416*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0193 (8)	0.0180 (8)	0.0137 (8)	−0.0014 (7)	0.0007 (6)	0.0000 (6)
C2	0.0204 (8)	0.0182 (8)	0.0137 (7)	−0.0005 (7)	0.0018 (7)	−0.0017 (7)
O3	0.0293 (7)	0.0176 (6)	0.0152 (5)	0.0020 (6)	0.0051 (6)	−0.0006 (4)
C4	0.0256 (8)	0.0166 (8)	0.0154 (7)	0.0007 (8)	0.0009 (8)	−0.0020 (6)
O5	0.0253 (6)	0.0170 (5)	0.0148 (5)	−0.0015 (6)	0.0035 (5)	−0.0010 (4)
C6	0.0360 (11)	0.0342 (11)	0.0226 (9)	−0.0004 (10)	−0.0090 (10)	−0.0014 (9)
C7	0.0348 (11)	0.0248 (10)	0.0294 (10)	−0.0024 (9)	0.0138 (9)	−0.0023 (8)
C8	0.0253 (9)	0.0191 (8)	0.0216 (9)	−0.0010 (8)	−0.0020 (8)	−0.0004 (7)
O9	0.0180 (6)	0.0251 (6)	0.0247 (6)	0.0002 (6)	−0.0043 (6)	−0.0013 (5)
C10	0.0195 (8)	0.0219 (8)	0.0168 (8)	−0.0026 (8)	−0.0017 (7)	−0.0028 (7)
O11	0.0274 (7)	0.0331 (7)	0.0161 (6)	−0.0020 (6)	−0.0005 (5)	−0.0037 (5)
C12	0.0225 (9)	0.0204 (8)	0.0285 (9)	−0.0034 (8)	−0.0001 (8)	−0.0015 (8)
C13	0.0197 (8)	0.0191 (8)	0.0220 (8)	0.0000 (7)	0.0015 (7)	−0.0022 (7)
O14	0.0284 (7)	0.0176 (6)	0.0294 (7)	0.0011 (6)	0.0115 (6)	−0.0030 (5)

Geometric parameters (Å, °)

C1—C2	1.563 (2)	C7—H73	0.996
C1—O5	1.437 (2)	C8—O9	1.434 (2)
C1—C10	1.543 (2)	C8—H81	0.999
C1—C13	1.513 (2)	C8—H82	1.000
C2—O3	1.4439 (19)	O9—C10	1.423 (2)
C2—C8	1.522 (2)	C10—O11	1.400 (2)
C2—C12	1.518 (2)	C10—H101	1.023
O3—C4	1.4240 (19)	O11—H15	0.854
C4—O5	1.4329 (19)	C12—H121	0.998
C4—C6	1.509 (3)	C12—H122	0.996
C4—C7	1.507 (3)	C12—H123	0.989
C6—H61	0.997	C13—O14	1.433 (2)
C6—H62	0.996	C13—H131	1.017
C6—H63	0.978	C13—H132	0.987
C7—H71	1.001	O14—H16	0.861
C7—H72	1.010		
C2—C1—O5	104.58 (13)	H71—C7—H73	111.6
C2—C1—C10	103.22 (14)	H72—C7—H73	111.6
O5—C1—C10	107.11 (13)	C2—C8—O9	105.41 (14)
C2—C1—C13	116.58 (15)	C2—C8—H81	109.6
O5—C1—C13	110.13 (14)	O9—C8—H81	111.5
C10—C1—C13	114.34 (13)	C2—C8—H82	108.6
C1—C2—O3	103.82 (13)	O9—C8—H82	109.6
C1—C2—C8	103.23 (14)	H81—C8—H82	111.9

O3—C2—C8	106.76 (14)	C8—O9—C10	104.90 (12)
C1—C2—C12	117.54 (16)	C1—C10—O9	104.32 (13)
O3—C2—C12	110.00 (14)	C1—C10—O11	107.89 (13)
C8—C2—C12	114.44 (14)	O9—C10—O11	111.21 (14)
C2—O3—C4	110.63 (12)	C1—C10—H101	112.3
O3—C4—O5	105.21 (12)	O9—C10—H101	110.5
O3—C4—C6	110.40 (15)	O11—C10—H101	110.4
O5—C4—C6	111.41 (15)	C10—O11—H15	107.0
O3—C4—C7	108.31 (15)	C2—C12—H121	107.9
O5—C4—C7	108.43 (15)	C2—C12—H122	109.3
C6—C4—C7	112.75 (14)	H121—C12—H122	109.6
C1—O5—C4	110.11 (12)	C2—C12—H123	110.2
C4—C6—H61	110.2	H121—C12—H123	111.2
C4—C6—H62	111.0	H122—C12—H123	108.7
H61—C6—H62	107.5	C1—C13—O14	112.02 (14)
C4—C6—H63	108.6	C1—C13—H131	108.5
H61—C6—H63	110.0	O14—C13—H131	108.8
H62—C6—H63	109.6	C1—C13—H132	110.8
C4—C7—H71	107.5	O14—C13—H132	108.1
C4—C7—H72	107.9	H131—C13—H132	108.5
H71—C7—H72	109.3	C13—O14—H16	109.8
C4—C7—H73	108.8		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H15···O14^{i}	0.85	1.88	2.724 (2)	172
O14—H16···O3^{ii}	0.86	2.07	2.867 (2)	154

Symmetry codes: (i) *x*+1/2, −*y*+3/2, −*z*+2; (ii) −*x*+1, *y*+1/2, −*z*+3/2.

Fig. 1

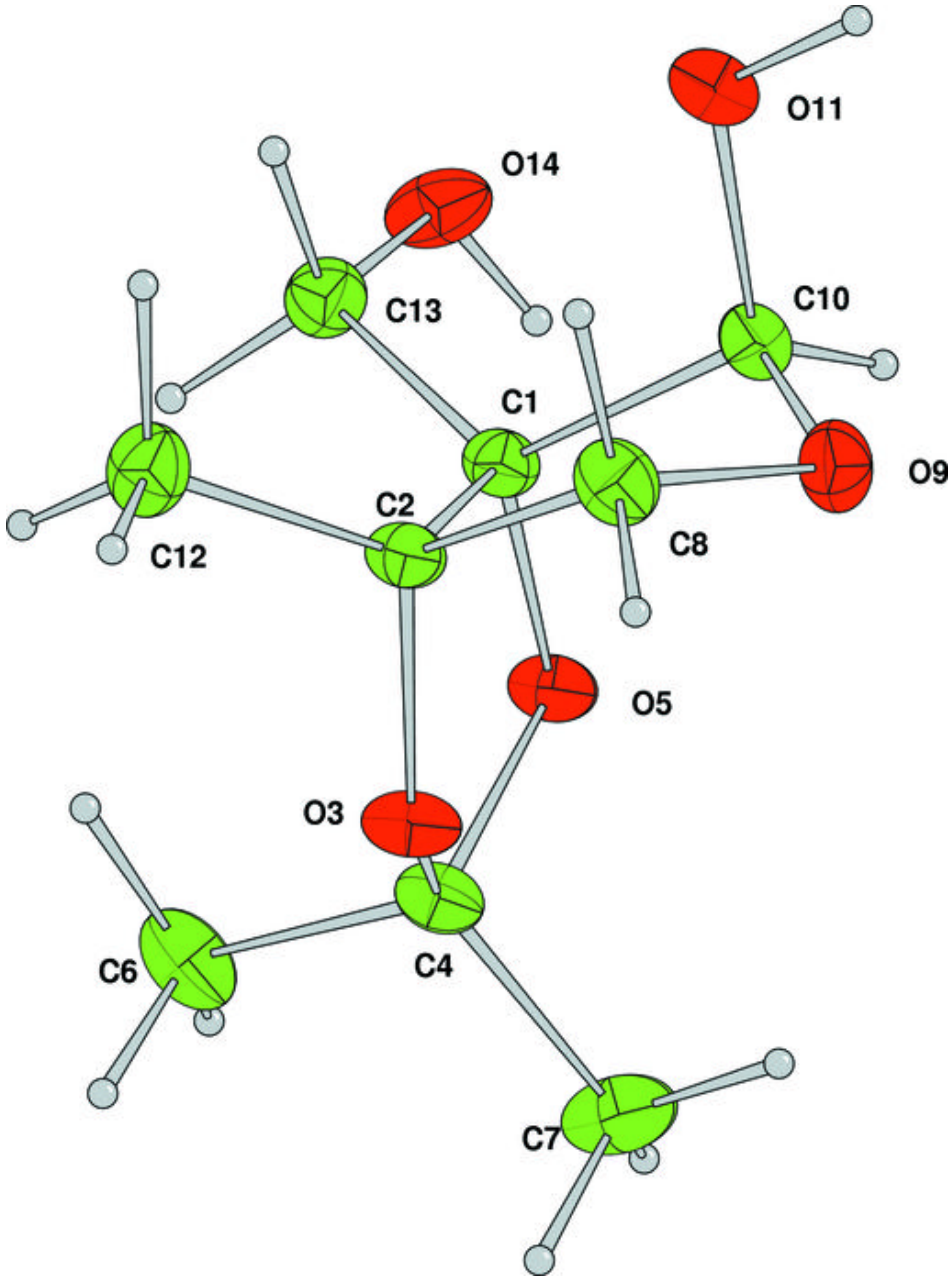


Fig. 2

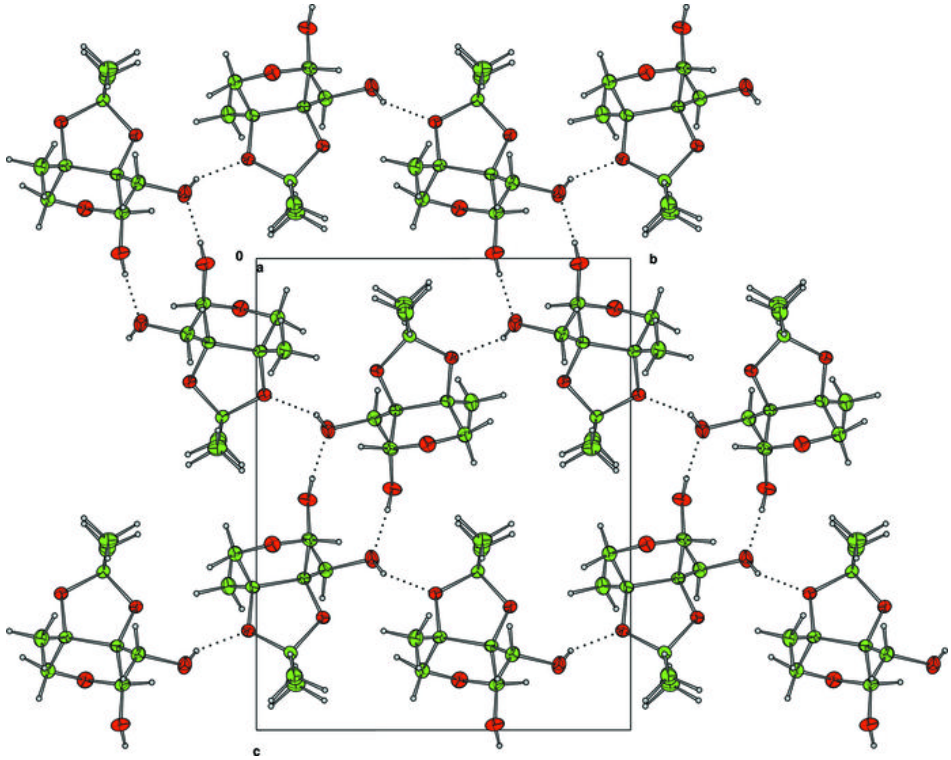
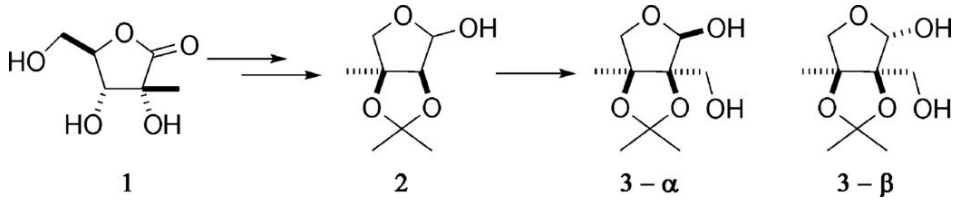


Fig. 3



1 2 3 – α 3 – β