

2,4-Di-C-methyl- α -L-arabinose mono-hydrate

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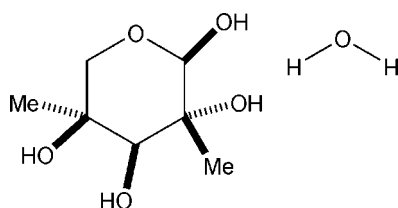
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.029; wR factor = 0.070; data-to-parameter ratio = 10.9.

In aqueous solution, the title compound, $\text{C}_7\text{H}_{14}\text{O}_5 \cdot \text{H}_2\text{O}$, consists of a mixture of the open-chain furanose and pyranose forms; it crystallizes solely as the α -pyranose form. The crystal structure exists as an extensively hydrogen-bonded network, with each molecule acting as a donor and acceptor for seven hydrogen bonds. The absolute configuration of this sugar is determined by the use of 2-*C*-methyl-D-ribo-1,4-lactone as the starting material.

Related literature

For related structures see: Booth, Watkin *et al.* (2007); Booth, Jenkinson *et al.* (2007a,b,c). For background information, see: Mitchell *et al.* (2007); Hotchkiss *et al.* (2006,2007); Soengas *et al.* (2005); Chapleur & Chrétien, (1997); Ho (1978). For related literature, see: Booth, Best *et al.* (2007); Bream *et al.* (2006); Görbitz (1999); Koos & Mosher (1986); Punzo *et al.* (2005).



Experimental

Crystal data

$\text{C}_7\text{H}_{14}\text{O}_5 \cdot \text{H}_2\text{O}$

$M_r = 196.20$

Orthorhombic, $P2_12_12_1$

$a = 6.5700$ (2) Å

$b = 9.1317$ (3) Å

$c = 15.3916$ (4) Å

$V = 923.42$ (5) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.12$ mm⁻¹

$T = 150$ K

$0.40 \times 0.20 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer

Absorption correction: multi-scan (*DENZO/SCALEPACK*;

Otwinowski & Minor, 1997)

$T_{\min} = 0.77$, $T_{\max} = 0.99$

16941 measured reflections

1281 independent reflections

1130 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.070$

$S = 0.94$

1281 reflections

118 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.21$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O8—H4 \cdots O11 ⁱ	0.82	1.99	2.762 (2)	155
O11—H5 \cdots O13 ⁱⁱ	0.83	1.92	2.741 (2)	175
O7—H10 \cdots O8 ⁱⁱⁱ	0.86	1.80	2.658 (2)	176
O10—H13 \cdots O5 ⁱⁱ	0.83	2.02	2.806 (2)	157
O13—H2 \cdots O7	0.87	2.04	2.850 (2)	153
O13—H1 \cdots O7 ^{iv}	0.87	2.37	3.065 (2)	138
O13—H1 \cdots O11 ^{iv}	0.87	2.21	2.976 (2)	147

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

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: LH2460).

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supplementary materials

Acta Cryst. (2007). E63, o3592-o3593 [doi:10.1107/S1600536807035143]

2,4-Di-*C*-methyl- α -*L*-arabinose monohydrate

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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). However, to date, no biological studies have been performed on sugars with more than one branch.

Branching of sugars can be achieved in several ways; the Kiliani reaction of ketoses with cyanide (Hotchkiss *et al.*, 2006; Soengas *et al.*, 2005); calcium oxide treatment of Amadori compounds (Hotchkiss *et al.*, 2006,2007); the Aldol reaction for the introduction of hydroxymethyl branches (Ho, 1978; Koos & Mosher, 1986). Using these techniques, 2-*C*-methyl arabinose derivatives have been reported (Bream *et al.*, 2006; Punzo *et al.*, 2005). Doubly branched sugar derivatives are rare; examples include 2,4-di-*C*-methyl-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 lactones (Booth *et al.*, 2007*a,b,c*).

Unlike the protected lactone **1** (Booth, Watkin *et al.* 2007), which is a twisted boat conformation, the free sugar **2** (compound numbers as in Fig. 3) can be seen to adopt the chair form (Fig. 1). The title compound exists as a three dimensionally hydrogen bonded lattice with each molecule being both a donor and an acceptor for 7 hydrogen bonds. One of the hydrogen bonds, from O13—H1, is bifurcated (Fig.2), it does however slightly exceed the normal range of hydrogen bond length.

Experimental

2,4-Di-*C*-methyl-3,4-*O*-isopropylidene-*L*-arabinono-1,5-lactone **1** (Fig. 3) was treated with diisobutylaluminium hydride, and deprotected with Dowex 50WX8 (H⁺) resin to give the title compound **2** (Booth, Best *et al.*, 2007). 2,4-Di-*C*-methyl- α -*L*-arabinose **2** was crystalized from methanol by slow evaporation: m.p. 405–407 K; $[\alpha]_D^{17} +13$ (*c*, 0.9 in methanol).

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 (1:1.29) 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

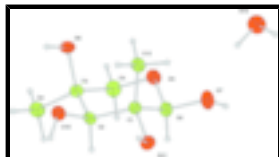


Fig. 1. The title molecular structure with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

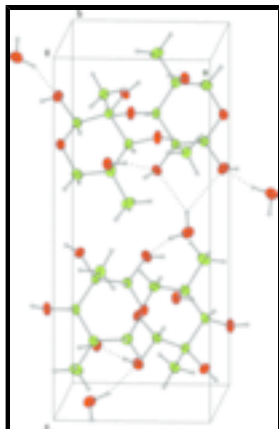


Fig. 2. The packing of the title compound showing the extensive hydrogen bonding as dotted lines and including the bifurcated bond.

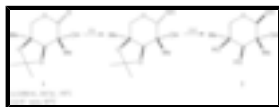


Fig. 3. Synthesis of the title compound **2**.

2,4-Di-C-methyl- α -L-arabinose monohydrate

Crystal data

$C_7H_{14}O_5 \cdot H_2O$

$M_r = 196.20$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 6.5700$ (2) Å

$b = 9.1317$ (3) Å

$c = 15.3916$ (4) Å

$V = 923.42$ (5) Å³

$Z = 4$

$F_{000} = 424$

$D_x = 1.411$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 14290 reflections

$\theta = 5\text{--}28^\circ$

$\mu = 0.12$ mm⁻¹

$T = 150$ K

Plate, colourless

$0.40 \times 0.20 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer

Monochromator: graphite

$T = 150$ K

ω scans

Absorption correction: multi-scan

1130 reflections with $I > 2\sigma(I)$

$R_{int} = 0.033$

$\theta_{max} = 27.9^\circ$

$\theta_{min} = 5.2^\circ$

$h = -8 \rightarrow 8$

(DENZO/SCALEPACK; Otwinowski & Minor, 1997)

$T_{\min} = 0.77$, $T_{\max} = 0.99$

$k = -11 \rightarrow 12$

16941 measured reflections

$l = -20 \rightarrow 20$

1281 independent reflections

Refinement

Refinement on F^2

Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

H-atom parameters constrained

$R[F^2 > 2\sigma(F^2)] = 0.029$

$w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.05P]$,

where $P = [\max(F_o^2, 0) + 2F_c^2]/3$

$wR(F^2) = 0.070$

$(\Delta/\sigma)_{\max} = 0.0004$

$S = 0.94$

$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$

1281 reflections

$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

118 parameters

Extinction correction: none

Primary atom site location: structure-invariant direct methods

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1831 (2)	0.70084 (17)	0.68249 (9)	0.0173
C2	0.0572 (2)	0.69771 (18)	0.76683 (10)	0.0182
C3	0.1773 (3)	0.64940 (16)	0.84777 (10)	0.0196
C4	0.3820 (3)	0.72664 (18)	0.84970 (9)	0.0234
O5	0.48881 (17)	0.71799 (13)	0.76859 (7)	0.0222
C6	0.3753 (3)	0.78939 (18)	0.70095 (9)	0.0197
O7	0.49686 (19)	0.79546 (14)	0.62744 (7)	0.0264
O8	0.21668 (19)	0.49496 (12)	0.84320 (7)	0.0220
C9	0.0617 (3)	0.68310 (19)	0.93123 (10)	0.0283
O10	-0.11528 (18)	0.60444 (12)	0.75668 (7)	0.0242
O11	0.07155 (17)	0.78427 (12)	0.61877 (7)	0.0205
C12	0.2328 (3)	0.55052 (17)	0.64519 (10)	0.0211
O13	0.7830 (2)	0.61191 (13)	0.54079 (7)	0.0308
H21	0.0112	0.8015	0.7754	0.0215*
H41	0.3582	0.8305	0.8620	0.0282*
H42	0.4683	0.6809	0.8955	0.0274*
H61	0.3449	0.8938	0.7173	0.0222*
H91	0.1445	0.6504	0.9804	0.0431*
H92	-0.0729	0.6328	0.9307	0.0421*
H93	0.0428	0.7903	0.9370	0.0427*
H121	0.3029	0.5647	0.5891	0.0336*
H122	0.1090	0.4979	0.6372	0.0331*
H123	0.3215	0.4986	0.6854	0.0327*
H4	0.1094	0.4485	0.8453	0.0343*
H5	-0.0094	0.7306	0.5930	0.0335*

supplementary materials

H10	0.5915	0.8600	0.6343	0.0414*
H13	-0.2163	0.6588	0.7550	0.0382*
H1	0.7733	0.6409	0.4873	0.0480*
H2	0.6683	0.6463	0.5609	0.0480*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0150 (8)	0.0174 (7)	0.0195 (7)	-0.0007 (7)	-0.0003 (6)	0.0009 (6)
C2	0.0139 (8)	0.0182 (7)	0.0226 (7)	0.0018 (7)	0.0017 (6)	0.0002 (6)
C3	0.0195 (9)	0.0165 (7)	0.0228 (7)	0.0016 (7)	0.0018 (7)	0.0012 (6)
C4	0.0241 (9)	0.0251 (7)	0.0210 (7)	-0.0025 (8)	-0.0020 (7)	-0.0021 (6)
O5	0.0163 (6)	0.0261 (6)	0.0241 (6)	-0.0003 (5)	-0.0020 (5)	0.0008 (5)
C6	0.0172 (8)	0.0208 (7)	0.0211 (7)	-0.0018 (8)	0.0006 (7)	0.0011 (6)
O7	0.0221 (7)	0.0305 (6)	0.0267 (6)	-0.0084 (6)	0.0044 (5)	-0.0026 (5)
O8	0.0179 (6)	0.0165 (5)	0.0315 (6)	0.0026 (5)	-0.0010 (6)	0.0023 (4)
C9	0.0323 (10)	0.0284 (8)	0.0240 (8)	0.0071 (9)	0.0060 (8)	0.0029 (7)
O10	0.0130 (5)	0.0237 (6)	0.0358 (6)	-0.0013 (5)	0.0010 (5)	0.0034 (5)
O11	0.0193 (6)	0.0203 (5)	0.0220 (5)	-0.0017 (5)	-0.0048 (5)	0.0018 (4)
C12	0.0200 (8)	0.0191 (7)	0.0241 (7)	-0.0010 (7)	0.0021 (7)	-0.0029 (6)
O13	0.0296 (7)	0.0364 (6)	0.0264 (6)	0.0007 (7)	-0.0047 (6)	-0.0011 (5)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.539 (2)	C6—O7	1.3861 (17)
C1—C6	1.526 (2)	C6—H61	1.006
C1—O11	1.4418 (17)	O7—H10	0.863
C1—C12	1.523 (2)	O8—H4	0.823
C2—C3	1.539 (2)	C9—H91	0.979
C2—O10	1.4261 (19)	C9—H92	0.996
C2—H21	1.003	C9—H93	0.990
C3—C4	1.519 (2)	O10—H13	0.829
C3—O8	1.4355 (18)	O11—H5	0.825
C3—C9	1.524 (2)	C12—H121	0.987
C4—O5	1.4343 (18)	C12—H122	0.952
C4—H41	0.980	C12—H123	0.974
C4—H42	0.996	O13—H1	0.867
O5—C6	1.4371 (18)	O13—H2	0.873
C2—C1—C6	107.29 (12)	C4—O5—C6	110.58 (12)
C2—C1—O11	108.09 (12)	C1—C6—O5	108.90 (12)
C6—C1—O11	105.50 (11)	C1—C6—O7	110.24 (12)
C2—C1—C12	114.59 (13)	O5—C6—O7	108.09 (13)
C6—C1—C12	111.73 (13)	C1—C6—H61	112.6
O11—C1—C12	109.20 (12)	O5—C6—H61	110.6
C1—C2—C3	114.35 (12)	O7—C6—H61	106.3
C1—C2—O10	110.21 (12)	C6—O7—H10	110.0
C3—C2—O10	108.96 (12)	C3—O8—H4	110.5
C1—C2—H21	104.8	C3—C9—H91	108.2

C3—C2—H21	108.6	C3—C9—H92	110.1
O10—C2—H21	109.8	H91—C9—H92	111.0
C2—C3—C4	109.68 (12)	C3—C9—H93	109.7
C2—C3—O8	109.53 (13)	H91—C9—H93	107.5
C4—C3—O8	107.33 (13)	H92—C9—H93	110.2
C2—C3—C9	111.63 (13)	C2—O10—H13	106.4
C4—C3—C9	109.34 (13)	C1—O11—H5	109.9
O8—C3—C9	109.23 (12)	C1—C12—H121	108.1
C3—C4—O5	113.00 (12)	C1—C12—H122	108.7
C3—C4—H41	108.2	H121—C12—H122	110.6
O5—C4—H41	107.4	C1—C12—H123	109.2
C3—C4—H42	108.9	H121—C12—H123	109.9
O5—C4—H42	108.3	H122—C12—H123	110.3
H41—C4—H42	111.1	H1—O13—H2	99.4

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O8—H4 \cdots O11 ⁱ	0.82	1.99	2.762 (2)	155
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Fig. 1

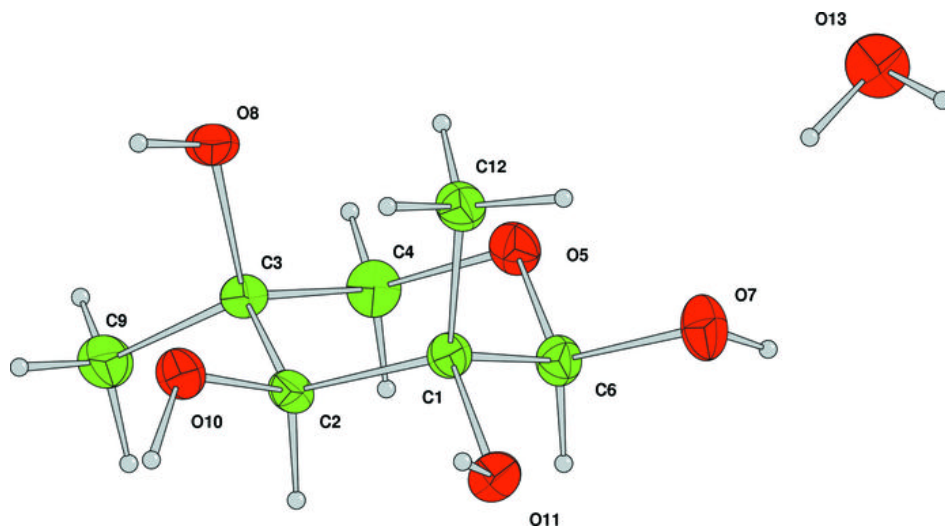


Fig. 2

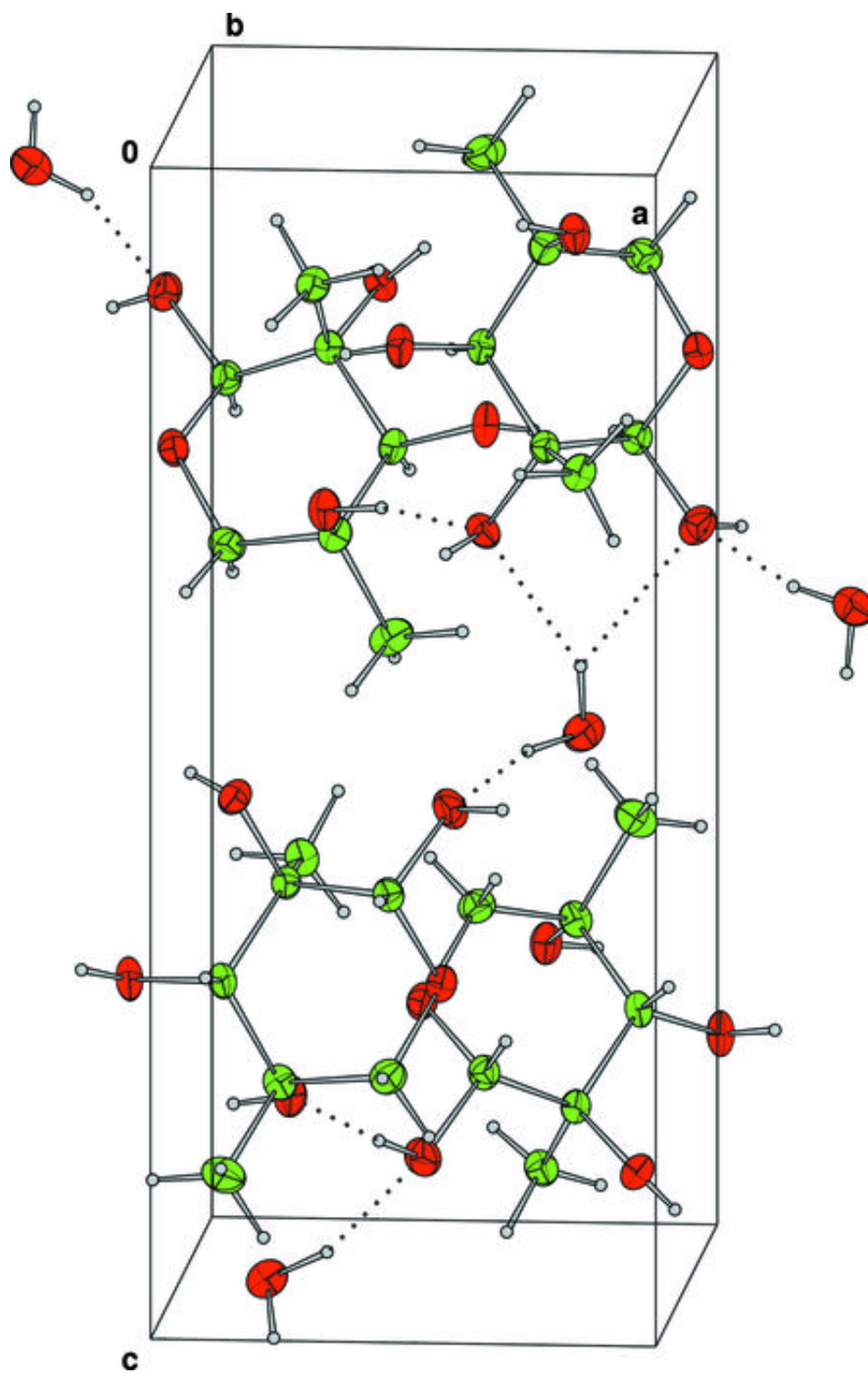


Fig. 3

