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1,2:4,5-Di-*O*-isopropylidene-*β*-D-*erythro*-hexo-2,3-diulo-2,6-pyranose

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.091
Data-to-parameter ratio = 12.9

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

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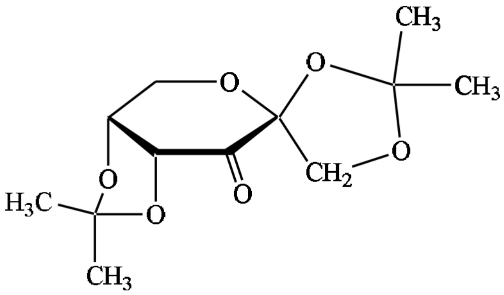
The crystal structure of title compound, $C_{12}H_{18}O_6$, has been determined using single-crystal data. There are two independent molecules in the asymmetric unit. NMR coupling constants, dihedral angles as well as puckering parameters indicate the $^3S_0$ conformation of the pyranose ring in both molecules *A* and *B*. The *cis*-fused 1,3-dioxolane ring in both molecules *A* and *B*, adopts an E_4 conformation. The second five-membered 1,3-dioxolane ring, in molecule *A*, has an E_2 conformation, whereas in molecule *B*, this 1,3-dioxolane ring adopts an E_4 conformation. Molecules *A* form a zigzag infinite chain along the *b* axis with molecules *B* as side chains. This explains why the displacement ellipsoids of atoms of molecule *B* are substantially larger than those of molecule *A*.

Comment

As a continuation of our research on the synthesis and structure determination of selected sugar amino derivatives (Koóš, Steiner, Langer *et al.*, 2000; Koóš, Steiner, Gajdoš *et al.*, 2000; Steiner *et al.*, 1998), we have focused attention on 1,2:4,5-di-*O*-isopropylidene-*β*-D-*erythro*-hexo-2,3-diulo-2,6-pyranose, (I), as a potential starting material. This compound was prepared in two steps from D-fructose according to the procedure of Wang *et al.* (1997). The atom-numbering schemes of both molecules are presented in Fig. 1. The conformation of the pyranose ring of (I) is mentioned only twice in the literature. One proposal, based on a molecular modeling study, favored the $^0S_3$ conformation (McDonald, 1967), whereas a second possibility (more probable), based on the inspection of dihedral angles (from a molecular model) and coupling constants (from NMR), was the $^3S_0$ conformation (Hervé du Penhoat & Perlin, 1979).



(I)

Correlation of dihedral angles associated with coupling constants $J_{5,6}$ = 2.2 Hz and $J_{5,6'}$ = 0.9 Hz with corresponding dihedral angles (H5*A*—C5*A*—C6*A*—H6*A*1 and H5*B*—C5*B*—C6*B*—H6*B*1 about −70°, and H5*A*—C5*A*—C6*A*—H6*A*2 and H5*B*—C5*B*—C6*B*—H6*B*2 about 46°) obtained from X-ray

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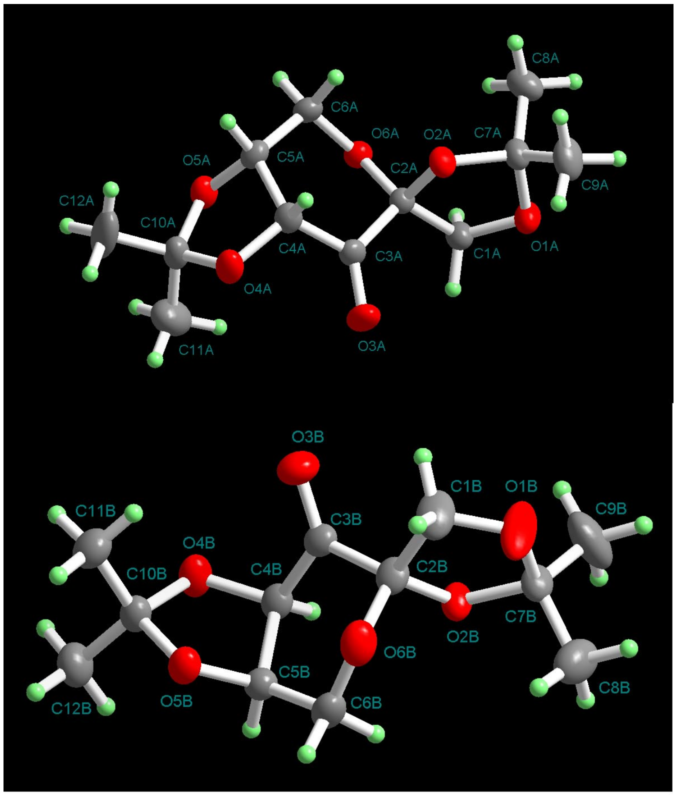

Figure 1
The atom-numbering scheme and displacement ellipsoids at the 30% probability level for molecules A and B of (I).

crystallography as well as puckering parameters [Q = 0.476 (2) Å, φ = 193.5 (8)°, θ = 162.0 (2)° for molecule *A*, and Q = 0.511 (2) Å, φ = 218.2 (8)°, θ = 162.8 (2)° for molecule *B*] clearly indicate the $^3S_0$ conformation of the pyranose ring (O6—C2—C3—C4—C5—C6) in both molecules *A* and *B* (Fig. 1). The *cis*-fused 1,3-dioxolane ring (C4—O4—C10—O5—C5 in both molecules *A* and *B*) adopts the E_4 conformation, where the C4, O4, C10 and O5 atoms lie almost in a plane [for molecule *A*, dihedral angle C4—O4—C10—O5 = −3.2 (2)°, and puckering parameters Q = 0.347 (2) Å and φ = 247.7 (4)°; for molecule *B*, dihedral angle C4—O4—C10—O5 = −2.9 (2)°, and puckering parameters Q = 0.367 (2) Å and φ = 248.4 (3)°] and C5 is directed below this plane. The second five-membered 1,3-dioxolane ring (O1—C1—C2—O2—C7 in the molecule *A*) has an E_2 conformation, where the O1, C1, C2, and O2 atoms lie almost in a plane [dihedral angle O1—C1—C2—O2 is 3.4 (2)°, and puckering parameters Q = 0.291 (2) Å and φ = 330.1 (4)°] and C7 faces below this plane. However, in molecule *B*, this 1,3-dioxolane ring adopts the E_4 conformation, where the O2, C7, O1, and C1 atoms lie in a plane [dihedral angle O2—C7—O1—C1 is 0.8 (3)°, and puckering parameters Q = 0.171 (2) Å and φ = 255.7 (9)°] with C2 directed below this plane. It is also noteworthy, that both molecules in the asymmetric unit have the same absolute configuration: *S* on C2, and *R* on C4 and C5.

There are also C6*A*—H6*A*1···O2*B* and C8*A*—H8*A*2···O1A hydrogen bonds (Table 2) which stabilize the

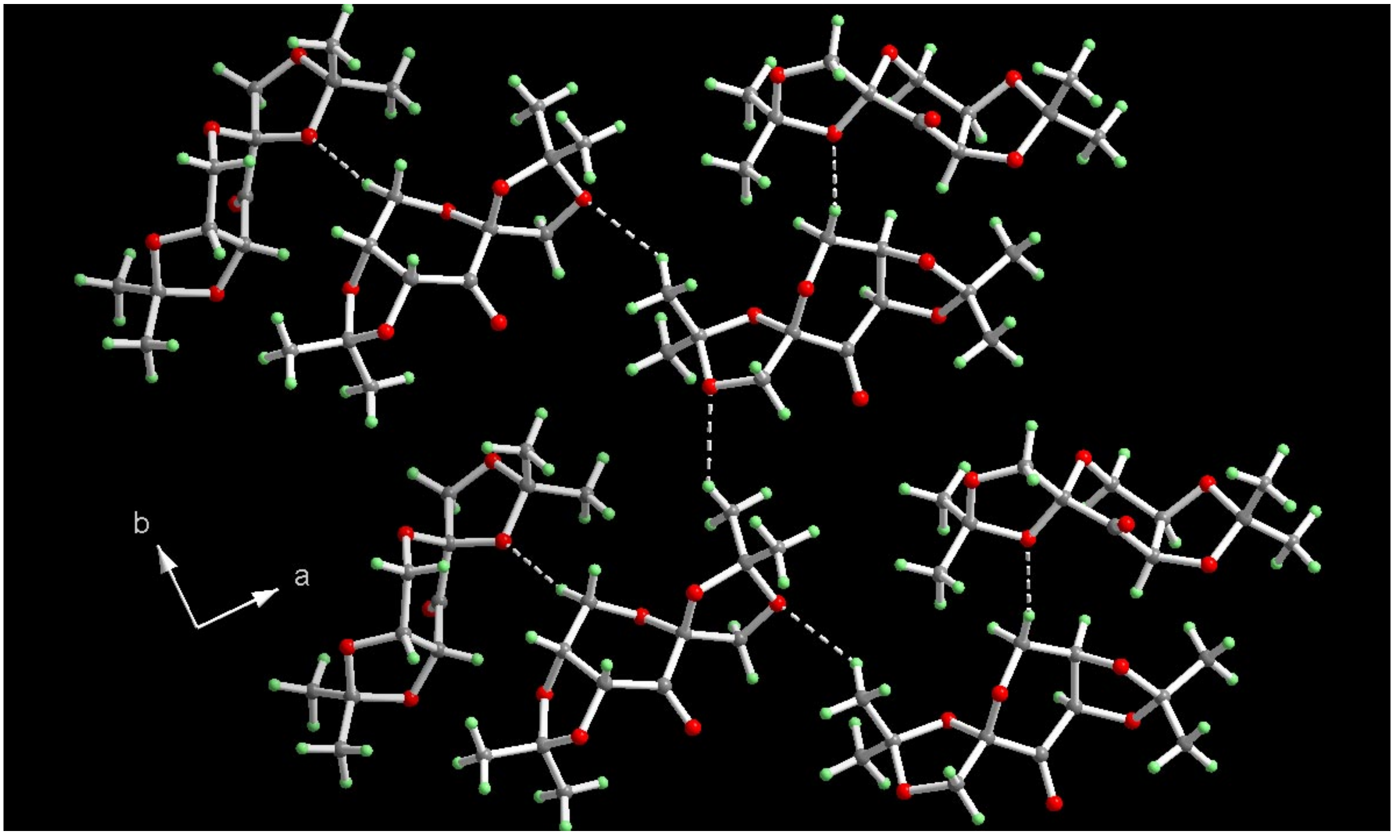

Figure 2
Hydrogen-bond scheme projected along the *c* axis. Molecules *A* form a zigzag infinite chain along the *b* axis with molecules *B* as side chains.

crystal structure of the title compound. Molecules *A* and *B* are connected through hydrogen bonds in such a way that molecules *A* form an infinite zigzag chain along the *b* axis with side chains consisting of molecules *B* (Fig. 2). This could be also an explanation of the slightly larger thermal motion of atoms of molecule *B* in comparison with those of molecule *A*.

Experimental

Compound (I) was prepared in two steps from D-fructose according to the procedure of Wang *et al.* (1997).

Crystal data

$C_{12}H_{18}O_6$
$M_r = 258.27$
Monoclinic, $P2_1$
$a = 10.9909$ (2) Å
$b = 10.5488$ (2) Å
$c = 11.3876$ (2) Å
$\beta = 100.526$ (1)°
$V = 1298.07$ (4) Å^3
$Z = 4$

$D_x = 1.322$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6790 reflections
$\theta = 1.8$–25.5°
$\mu = 0.11$ mm^{-1}
$T = 297$ (2) K
Needle, colorless
0.55 × 0.16 × 0.15 mm

Data collection

Siemens SMART CCD diffractometer
ω scans, 0.30° frames, 30 s each
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.944$, $T_{\max} = 0.984$
13 132 measured reflections
4781 independent reflections

3804 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 25.5°$
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.091$
$S = 1.02$
4781 reflections
370 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.0759P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0159 (17)
Absolute structure: (Flack, 1983)
Flack parameter = −0.2 (8), 2221 Friedel pairs

Table 1
Selected torsion angles (°).

C4*A*—O4*A*—C10*A*—O5*A*	−3.2 (2)	O2*B*—C7*B*—O1*B*—C1*B*	0.8 (3)
C4*B*—O4*B*—C10*B*—O5*B*	−2.9 (2)	H5*A*—C5*A*—C6*A*—H6*A*1	−70
O1*A*—C1*A*—C2*A*—O2*A*	3.4 (2)	H5*B*—C5*B*—C6*B*—H6*B*1	−71
O1*B*—C1*B*—C2*B*—O2*B*	−17.3 (3)	H5*A*—C5*A*—C6*A*—H6*A*2	48
O2*A*—C7*A*—O1*A*—C1*A*	32.5 (2)	H5*B*—C5*B*—C6*B*—H6*B*2	46

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6*A*—H6*A*1···O2*B*$^{\rm i}$	0.97	2.42	3.382 (3)	169
C8*A*—H8*A*2···O1*A*$^{\rm ii}$	0.96	2.57	3.384 (4)	142

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

Data were collected using a Siemens SMART CCD diffractometer at room temperature. A full sphere of reciprocal space was scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm and 30 s per frame. A preliminary orientation matrix was obtained from the first 100 frames using *SMART* (Siemens, 1995). The collected frames were integrated using the preliminary orientation matrix which was updated every 100 frames. Final cell parameters were obtained by refinement on the position of 6826 reflections with $I > 10\sigma(I)$ after integration of all the frames data using *SAINT* (Siemens, 1995). The data were empirically corrected for absorption and other effects using *SADABS* (Sheldrick, 1996) based on the method of Blessing (1995). H atoms were constrained to the ideal geometry using an appropriate riding model. For methyl groups, the C—H distances (0.93 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine with the starting position based on the threefold averaged circular Fourier synthesis.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *XPREP* (Siemens, 1995); program(s) used to solve structure: XFPA98 (Pavelčík, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *PLATON* (Spek, 2001).

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