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3-*O*-Benzoyl-1,2-*O*-isopropylidene-β-D-fructopyranose

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.041
wR factor = 0.103
Data-to-parameter ratio = 7.0

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

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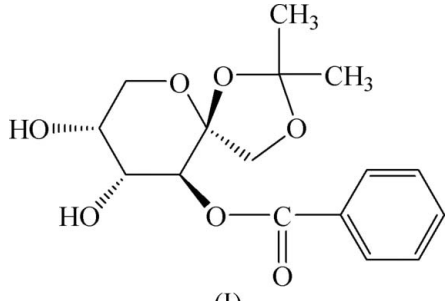
In the structure of the title compound, $C_{16}H_{20}O_7$, the five-membered 1,3-dioxolane ring is disordered with two different positions, *A* and *B* (1/1); it adopts the $^{O}T_4$ conformation slightly distorted towards E_4 for molecule *A*, and the ^{1}E conformation distorted towards $^{1}T_O$ for molecule *B*. The pyranose ring adopts an almost ideal $^{1}C_4$ conformation. The three-dimensional packing is stabilized by strong intermolecular O—H···O interactions and weak C—H···O hydrogen bonds.

Comment

Mono- or di-*O*-isopropylidenated fructopyranoses and fructofuranoses can be suitably modified at unprotected hydroxy groups, affording useful intermediates or starting synthetic blocks for the preparation of various carbohydrate derivatives. Many of them are analogues of significant biologically active compounds (Chery & Murphy, 2004; Izquierdo *et al.*, 2002; Tatibouët *et al.*, 2000; Furneaux *et al.*, 1993) and are also used for detailed structural studies including X-ray analysis (Yu *et al.*, 2005; Ataie *et al.*, 2000; Yu *et al.*, 2002; Ďurík *et al.*, 2001).



(I)

Although the preparation of the title compound, (I), has already been described (Fischer & Noth, 1918; Tian *et al.*, 2001), there is some disagreement regarding its physicochemical data as well as its unambiguous sspectroscopic characterization. For example, Fischer & Noth (1918) give for (I) a melting point of 475–477 K, while Tian *et al.* (2001) describe this compound as an oil. As a part of an investigation of fructopyranose and fructofuranose derivatives, we present here an unambigous structure determination of (I) using X-ray analysis. The fully interpreted NMR spectra are also presented.

The molecular structure of (I) is illustrated in Fig. 1 [the numbering of atoms in the saccharide group corresponds to the numbering according to the IUPAC Nomenclature of Carbohydrates (McNaught, 1996)], and selected bond

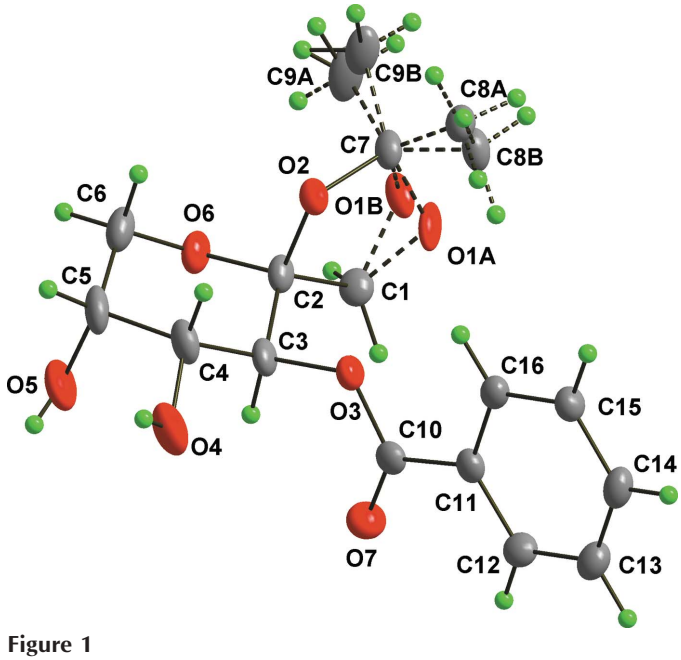


Figure 1
A perspective drawing of (I), showing the atom-numbering scheme. Atomic displacement ellipsoids are shown at the 30% probability level. Both disorder components are shown.

distances and angles are given in Table 1. Note that the dioxolane ring is disordered, with occupancy 50% for both components, denoted *A* and *B*. The puckering parameters (Cremer & Pople, 1975) Q = 0.320 (5) Å and φ = 337.3 (6)°, and the relevant dihedral angles O1*A*—C1—C2—O2 = 8.0 (4)°, C1—C2—O2—C7 = 14.4 (3)°, C2—O2—C7—O1*A* = −30.6 (4)°, O2—C7—O1*A*—C1 = 35.5 (5)°, C7—O1*A*—C1—C2 = −27.5 (5)° are indicative of the $^{O}T_{4}$ ($^{O1A}T_{C7}$) conformation slightly distorted towards the E_4 (E_{C7}) conformation for O1*A*—C1—C2—O2—C7 five-membered 1,3-dioxolane ring in part *A* of (I). Considering the values of the relevant torsion angles O1*B*—C1—C2—O2 = −26.5 (4)°, C1—C2—O2—C7 = 14.4 (3)°, C2—O2—C7—O1*B* = −3.0 (4)°, O2—C7—O1*B*—C1 = −19.8 (5)°, C7—O1*B*—C1—C2 = 28.3 (5)°, and the puckering parameters Q = 0.270 (4) Å and φ = 210.1 (8)°, the analogous O1*B*—C1—C2—O2—C7 five-membered ring in part *B* adopts an ^{1}E (^{C1}E) conformation distorted towards $^{1}T_{O}$ ($^{C1}T_{O1B}$). Although the spiro fusion of the pyranose ring and the 1,3-dioxolane ring at atom C2 (anomeric position of fructopyranose and simultaneously C4-position of 1,3-dioxolane) imposes some rigidity on (I), its influence on the conformation of the O6—C2–C6 pyranose ring is minimal. Considering the values of the puckering parameters Q = 0.554 (4) Å, θ = 177.2 (4)° and φ=180 (7)°, as well as the values of the relevant torsion angles O6—C2—C3—C4 = −55.8 (4)°, C2—C3—C4—C5 = 52.0 (4)°, C3—C4—C5—C6 = −50.8 (5)°, C4—C5—C6—O6 = 55.5 (5)°, C5—C6—O6—C2 = −61.8 (4)° and C6—O6—C2—C3 = 59.7 (4)°, this ring adopts an almost ideal $^{1}C_{4}$($^{C1}C_{C5}$) conformation for both disordered forms of the molecule (*A* and *B*).

There are four strong intermolecular O—H···O hydrogen bonds in the crystal structure of (I), with atoms O4 and O5 as donors, and atoms O4, O5 and O7 as acceptors. Atoms C3 and C9*A* act as donors for weak intramolecular and intermolecular C—H···O interactions. This situation is illustrated in Figs. 2 and 3 and more details of the hydrogen bonding are given in Table 2.

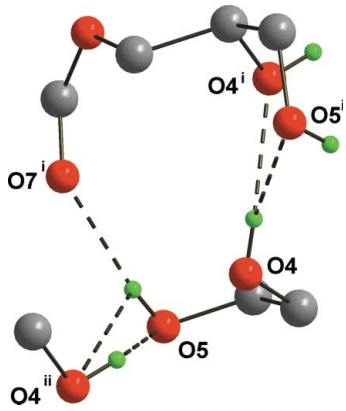


Figure 2
Hydrogen bonding (dashed lines) in (I). Only relevant structural fragments are depicted.

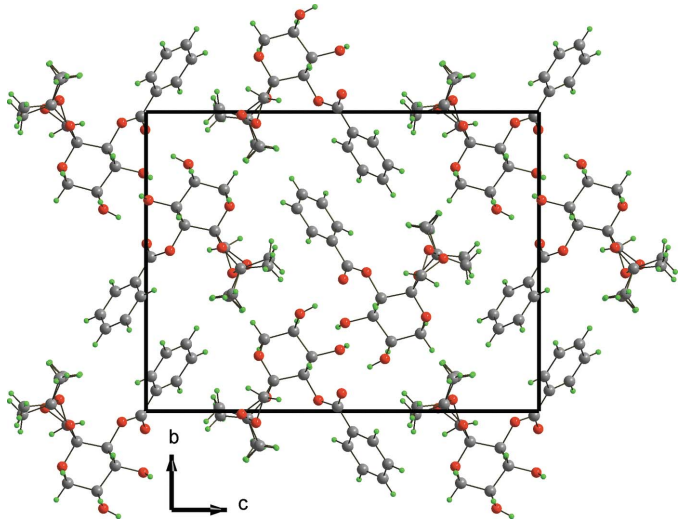


Figure 3
A projection of the structure of (I) along the *a* axis.

Experimental

Compound (I) was prepared from 3-*O*-benzoyl-1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose synthesized in two steps (isopropylidenation and benzoylation) from D-fructose (Wang *et al.*, 1997; Tian *et al.*, 2001) using selective acid hydrolysis according to the procedure described by Lichtenthaler *et al.* (1985). ^{1}H NMR (300 MHz, CD_3OD): δ 7.38–8.12 (*m*, 5H, aromatics), 5.47 (*d*, 1H, $J_{3,4}$ = 10.1 Hz, H3), 4.07 (*dd*, 1H, $J_{4,5}$ = 3.4 Hz, H4), 4.04 (*dd*, 1H, $J_{5,6a}$ = 1.0 Hz, $J_{6a,6b}$ = 12.5 Hz, H6a), 3.96 (*ddd*, 1H, $J_{5,6b}$ = 1.7 Hz, H5), 3.96 and 3.90 (2*d* of ABq, each 1H, J = 9.2 Hz, H1), 3.75 (*dd*, 1H, H6b), 1.47 and 1.37 (2*s*, each 3H, Me_2C); ^{13}C NMR (75 MHz, CD_3OD): δ 168.0 (CO), 134.5 (C4'), 131.2 (C1′), 130.9 (C2′ and C6′), 129.6 (C3′ and C5′), 113.0 (CMe_2), 106.3 (C2), 73.0 (C1), 71.5 (C5), 71.1 (C3), 70.5 (C4), 66.0 (C6), 26.9 and 26.7 [$(CH_3)_2C$] (the data for the benzoyl group are identified by a prime). Colourless single crystals of adequate quality for diffraction analysis were obtained by slow crystallization from ethanol by cooling in a refrigerator.

Crystal data

$C_{16}H_{20}O_7$	Mo $K\alpha$ radiation
M_r = 324.32	Cell parameters from 5729 reflections
Orthorhombic, $P2_12_12_1$	θ = 1.8–25.4°
a = 5.5771 (1) Å	μ = 0.11 mm^{-1}
b = 14.6164 (3) Å	T = 173 (2) K
c = 19.2112 (4) Å	Needle, colourless
V = 1566.04 (5) Å^3	1.00 × 0.06 × 0.04 mm
Z = 4	
D_x = 1.376 Mg m^{-3}	

Data collection

Siemens SMART CCD area-detector diffractometer	1700 independent reflections
	1306 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.073
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)	θ_{max} = 25.4°
	$h = -6 \rightarrow 6$
T_{min} = 0.766, T_{max} = 0.996	$k = -17 \rightarrow 17$
17488 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.7147P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.041	
$wR(F^2)$ = 0.103	$(\Delta/\sigma)_{max} < 0.001$
S = 0.99	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
1700 reflections	$\Delta\rho_{min}$ = −0.19 e Å^{-3}
244 parameters	Extinction correction: *SHELXTL97*
H-atom parameters constrained	Extinction coefficient: 0.014 (2)

Table 1
Selected geometric parameters (Å, °).

C1—O1*A*	1.400 (5)	O3—C3	1.455 (4)
C1—O1*B*	1.452 (5)	O6—C2	1.417 (4)
C1—C2	1.514 (5)	O7—C10	1.207 (4)
O1*A*—C7	1.438 (5)	C2—C3	1.512 (5)
O1*B*—C7	1.433 (5)	C3—C4	1.501 (5)
O2—C2	1.407 (4)	C4—C5	1.530 (5)
O2—C7	1.441 (4)	C5—C6	1.491 (6)
O3—C10	1.338 (4)	C10—C11	1.481 (5)
C1—O1*A*—C7	107.0 (4)	C2—O6—C6	112.9 (3)
C7—O1*B*—C1	104.6 (3)	O2—C2—C1	103.8 (2)
C2—O2—C7	109.6 (2)	O6—C2—C3	108.7 (3)
C10—O3—C3	119.0 (3)	O3—C10—C11	112.4 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O4^{i}	0.84	2.33	3.093 (5)	151
O4—H4···O5^{i}	0.84	2.29	2.951 (5)	136
O5—H5···O4^{ii}	0.84	2.66	2.951 (5)	102
O5—H5···O7^{i}	0.84	2.05	2.855 (4)	160
C3—H3···O7	1.00	2.29	2.725 (5)	105
C9*A*—H9*A*1···O5^{iii}	0.98	2.47	3.41 (2)	160

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

The absolute configuration at chiral atoms C2, C3, C4 and C5 in (I) was assigned on the basis of the known arrangement in the starting material 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (Takagi *et al.*, 1973), because benzoylation at atom O3 as well as hydrolysis of the isopropylidene group at atoms O4 and O5 does not affect the arrangement of atoms O3, O4 and O5 with respect to the pyranose ring in the reaction product (I). H atoms were constrained to an ideal geometry using an appropriate riding model. The C—H distances were kept fixed at 0.95 Å for aromatic H atoms, 0.99 Å for secondary H atoms and 1.00 Å for tertiary atoms. For the methyl groups, the C—H distances (0.98 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. The U_{iso}(H) values were set at $1.5U_{eq}$(C,O) for methyl and O-bound H atoms, and $1.2U_{eq}$(C) for all other H atoms.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

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