organic compounds

Three 1,6-anhydro-β-D-glycopyranose derivatives

C. Foces-Foces

Instituto Rocasolano, CSIC, Departamento de Cristalografía, Serrano 119, E-28006, Madrid, Spain
Correspondence e-mail: cfoces@iqfr.csic.es

Two of the title compounds, 1,6-anhydro-2,3-O-(S)-benzylidene-β-D-mannopyranose, $C_{13}H_{14}O_5$, (I), and 1,6-anhydro-4-O-benzyl-β-D-mannopyranose, $C_{13}H_{16}O_5$, (II), are derived from β-D-mannopyranose, while the third, 1,6-anhydro-3,4-O-(S)-benzylidene-β-D-galactopyranose, $C_{13}H_{14}O_5$, (III), is derived from β-D-galactopyranose. In the crystal packing, each hydroxyl group is involved in O—H···O hydrogen bonds, where the acceptor group is the other hydroxyl group in (II), or the endocyclic O atoms of the dioxolane [in (I)], anhydro [in (II)] or pyranose [in (III)] rings. Differences in the crystal packing arise from the contrasting O—H···O hydrogen-bonding environments.

Comment

The crystal structure determinations of the three title 1,6-anhydro-β-D-glycopyranose derivatives, (I), (II) and (III), were carried out within a project on hydrogen-bonding and cooperativity effects on the assembly of carbohydrates (Lopez de la Paz *et al.*, 1998). Carbohydrates are biomolecules that contain enough hydroxyl groups to form chains and cycles of cooperative O—H···O—H hydrogen bonds, and evidence of this cooperativity in the solid state has been reported previously (Jeffrey & Saenger, 1991; Noltemeyer & Saenger, 1980). The main aim of this report is to explore the ability of the OH group to form intramolecular hydrogen bonds depending on the relative configuration of the OH group and its position on the pyranose ring. Compounds (I), (II) and (III) were selected to study the influence of a second hydroxyl group, as present in (II), on the crystal packing.

(I)   (II)   (III)
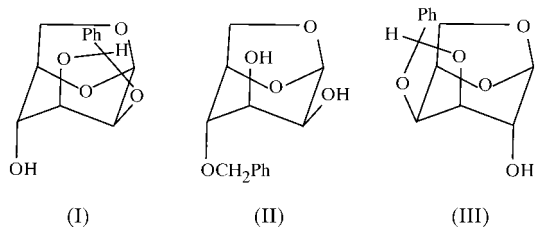
A comparison of the geometrical parameters of the three compounds (Tables 1, 3 and 5) reveals that substitution at positions O3 and/or O2/O4 introduces significant changes in the molecular dimensions, such as in O—C bond distances and in the angles around C2, C3 and C4. These differences can be explained by the dissimilar participation of the O atoms in the hydrogen bonding and by the conformation of the O4R group in (I) and (II), *trans* to C3 *versus gauche*, respectively [H41/C7—O4—C4—C3 = 167 (3) in (I) and 87.1 (3)° in (II)]. Furthermore, the greatest differences between (I) and the previously reported analogue 4-O-acetyl-1,6-anhydro-2,3-O-(S)-benzylidene-β-D-mannopyranose [Cano *et al.*, 1986; Cambridge Structural Database (CSD; Allen & Kennard, 1993) reference FOJMEW] are for the bond distances and angles around O4, where the hydroxyl group is protected with an acetyl one. Similar features are found between (III) and 2-O-acetyl-1,6-anhydro-3,4-O-(S)-benzylidene-β-D-galactopyranose (Cano *et al.*, 1986; CSD reference FOJLUL).

In compounds (I), (II) and (III), the pyranose ring is in a $^1C_4$ conformation distorted towards an E_6 envelope, less puckering at C3 (Boeyens, 1978). The anhydro and dioxolane rings are in an envelope conformation, with flaps at O5 and O3, respectively (Tables 1, 3 and 5, and Fig. 1).
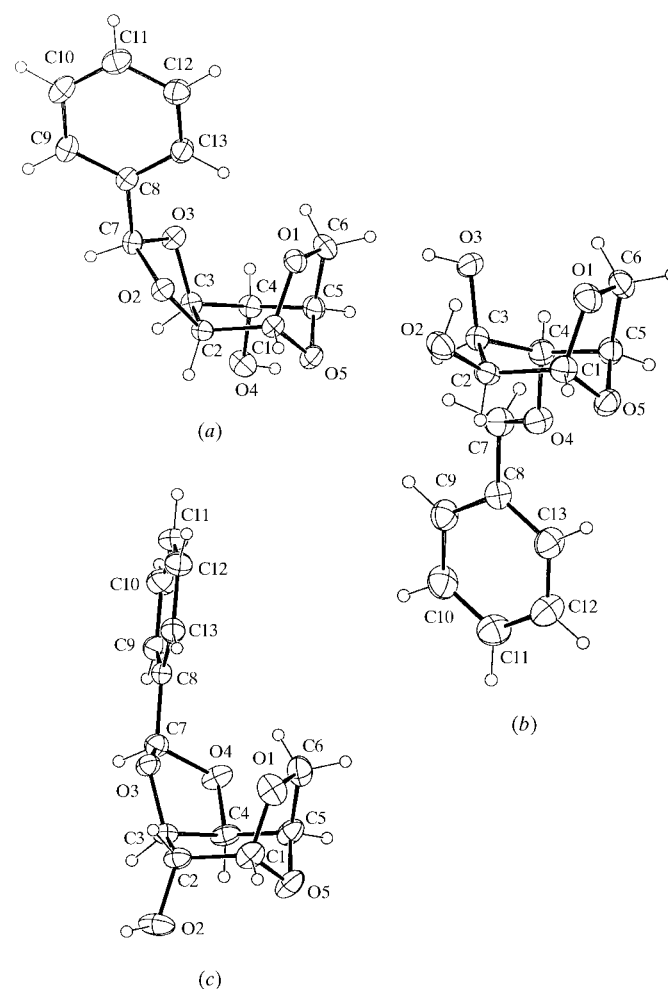

Figure 1
The molecular structures of (*a*) (I), (*b*) (II) and (*c*) (III), displaying the numbering schemes and the conformations of the molecules. The displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

In the crystal packing of 1-6-anhydro-β-D-mannopyranose and 1-6-anhydro-β-D-galactopyranose, the endocyclic O atoms compete with the hydroxyl groups in the formation of hydrogen bonds, and this is also seen in the title compounds (Tables 2, 4 and 6) and those mentioned above. The hydrogen-bond networks have been analysed by means of the graph-set approach (Bernstein *et al.*, 1995), as implemented in the *RPLUTO* program (June 2000 version; Motherwell *et al.*, 1999, 2000).

In (I), the packing can be described as pairs of chains related by a 2_1 axis (Table 2 and Fig. 2*a*). The O4—H···O2 bond is responsible for the formation of each chain [graph set $C(6)$], while C—H···O interactions between atoms O1 and O5 are reinforced by C—H···π contacts.

The hydrogen bonding in (II) differs from that in (I), since molecules of (II) form dimers through three-centre O2—H···O1/O3 hydrogen bonds. Such dimers (Table 4 and Fig. 2*b*) are in turn connected into sheets by O3—H···O2 hydrogen bonds, graph set $C_2^2(8)C(5)[R_2^2(10)]$. The inter- and intramolecular geometry is similar to that reported for 1,6-anhydro-β-D-mannopyranose (Maluszynska *et al.*, 1982; CSD reference BIFTUF). According to the results of a search of the CSD, structure (II) represents an unusual case in pyranoses in which two contiguous hydroxyl groups allow hydrogen bonds, leading to the formation of cyclic dimers. Only one similar cyclic dimer without intermolecular O—H···O hydrogen bonds between them [graph set $R_2^2(10)$, ignoring the D and S patterns] has been previously observed, in 6,7-anhydro-2,3-di-*O*-benzyl-8-deoxy-α-D-*threo*-D-*galacto*-octopyranoside (Engelhardt *et al.*, 1990; CSD reference KIDDEG).

In (III), an O2—H2···O5 hydrogen bond links the molecules into chains (Table 6 and Fig. 2*c*) in a way similar [graph set $C(5)$] to that reported for the analogue 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose (Cano *et al.*, 1984; CSD reference COHJIS). However, when the only hydroxyl group in the molecule is attached at C4, as in 2,3-di-*O*-acetyl-1,6-anhydro-β-D-galactopyranose (Foces-Foces *et al.*, 1976; CSD reference ACHGAL), the hydroxyl group acts as a hydrogen-bond donor to the anhydro O1 atom (O4—H···O1), giving rise to a $C(6)$ motif. Moreover, in 1,6-anhydro-β-D-galactopyranose (Ceccarelli *et al.*, 1980; CSD reference AHGALP), the O5 atoms in the three independent molecules accept hydrogen bonds, whereas only one O1 atom is involved in a hydrogen bond, either in discrete (D) or chain [$C(6)$] first-level motifs.

Despite the scarcity of 1,6-anhydrogalactopyranose structures reported in the literature, it seems that when only one hydroxyl group is present in the structure at C2 or C4, the O5 or O1 atom is the acceptor of the corresponding O—H···O hydrogen bond. However, both can be acceptors at the same time when there is more than one hydroxyl group in the molecular structure, as mentioned above and as observed in BIFTUF, where the O5 of one of the two independent molecules and the O1 of the other are involved in discrete (D) first-level motifs.

The volumes per non-H atom of 16.10, 17.00 and 15.93 Å^3 for (I), (II) and (III), respectively, also reflect the differences in the crystal packing. Compound (II) shows the least efficient packing in spite of depicting the shortest O···O distances.

It can be concluded that although these molecules (I) and (III) present similar secondary structure as a whole, the greater number of acceptor groups than donors in the molecular structure allows different linkages of the molecules within it. Several weak interactions (C—H···O and C—
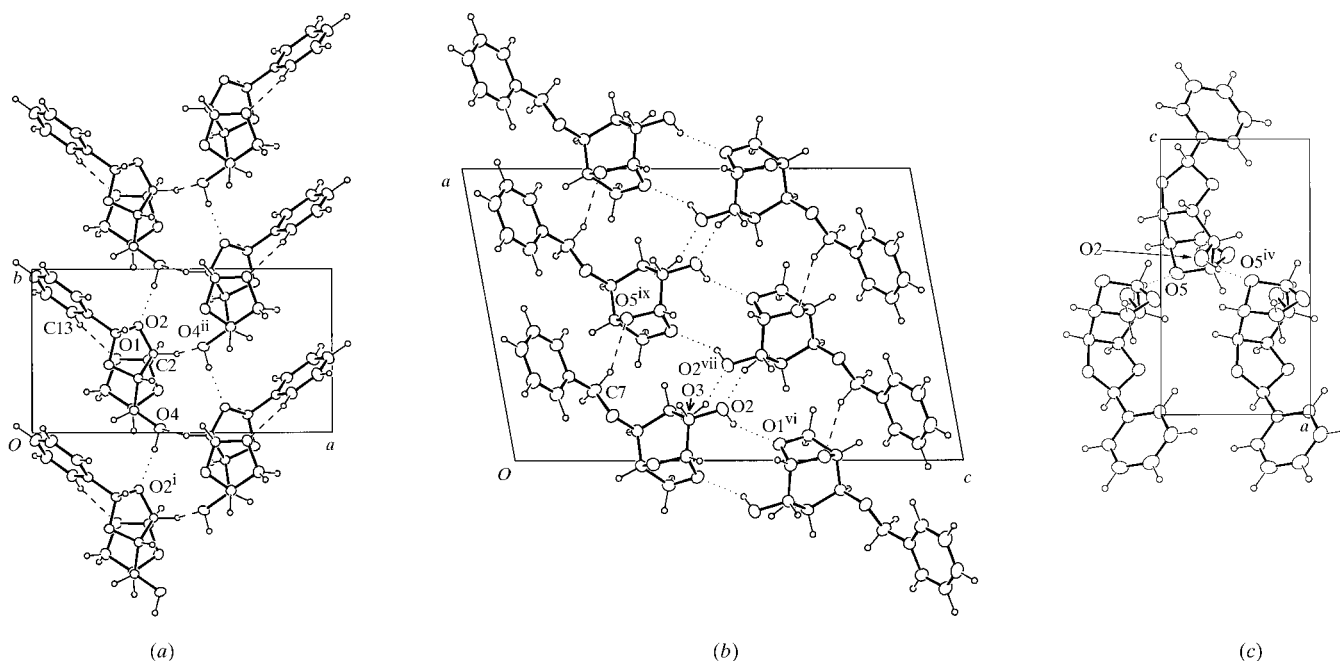
Figure 2
The crystal packing of (*a*) (I), (*b*) (II) and (*c*) (III), showing the secondary structure in the chains. Dotted lines represent hydrogen-bonding interactions; symmetry codes are as in Tables 2, 4 and 6.

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H$\cdots\pi$), other than van der Waals ones, hold the chains together (in Tables 2, 4 and 6, Cg represents the centroid of the phenyl ring).

Experimental

Compounds (I), (II) and (III) were prepared according to the methods of Florent & Monneret (1980), Reeves (1949) and Subero *et al.* (1980), respectively. Crystals of (I), (II) and (III) were obtained by recrystallization from CDCl$_3$.

Compound (I)

Crystal data

C$_{13}$H$_{14}$O$_5$	$D_x = 1.433$ Mg m^{-3}
$M_r = 250.25$	Cu $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 71
$a = 13.0265 (7)$ Å	reflections
$b = 7.0672 (3)$ Å	$\theta = 2$–$45°$
$c = 6.3376 (2)$ Å	$\mu = 0.930$ mm^{-1}
$\beta = 96.432 (4)°$	$T = 293$ K
$V = 579.77 (4)$ Å^3	Rectangular prism, colourless
$Z = 2$	$0.43 \times 0.33 \times 0.17$ mm

Data collection

Philips PW1100 four-circle diffractometer	$R_{int} = 0.016$
$\omega/2\theta$ scans	$\theta_{max} = 67.49°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -15 \rightarrow 15$
	$k = -8 \rightarrow 8$
$T_{min} = 0.776$, $T_{max} = 0.854$	$l = -7 \rightarrow 7$
2488 measured reflections	2 standard reflections
1148 independent reflections	frequency: 90 min
1148 reflections with $I > 0$	intensity decay: none

Refinement

Refinement on F	H atoms treated by a mixture of independent and constrained refinement
$R = 0.029$	
$wR = 0.032$	
$S = 1.001$	Weighting scheme: see below
1148 reflections	$(\Delta/\sigma)_{max} = 0.001$
167 parameters	$\Delta\rho_{max} = 0.18$ e Å^{-3}
	$\Delta\rho_{min} = -0.13$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O2—C2	1.436 (3)	O3—C3	1.437 (3)
O2—C2—C3	103.8 (2)	O4—C4—C5	110.76 (19)
O3—C3—C2	102.5 (2)	O4—C4—C3	106.22 (17)
O3—C3—C4	110.2 (2)		
C7—O2—C2—C3	−1.4 (2)	C3—O3—C7—O2	40.3 (2)
C2—O2—C7—O3	−23.7 (2)	O2—C2—C3—O3	25.2 (2)
C7—O3—C3—C2	−40.1 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H41$\cdots$O2^i	0.96 (5)	1.86 (5)	2.803 (3)	167 (4)
C2—H2$\cdots$O4^{ii}	1.04	2.59	3.317 (2)	126
C7—H7$\cdots$O1^{iii}	1.04	2.54	3.316 (2)	131
C13—H13$\cdots$O1	1.04	2.40	3.353 (3)	152
C1—H1$\cdots$O5^{iv}	1.04	2.54	3.317 (3)	131
C4—H4$\cdots Cg^i$	1.04	2.83	3.843 (3)	165
C10—H10$\cdots Cg^v$	1.04	2.90	3.752 (4)	140

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

Compound (II)

Crystal data

C$_{13}$H$_{16}$O$_5$	$D_x = 1.369$ Mg m^{-3}
$M_r = 252.27$	Cu $K\alpha$ radiation
Monoclinic, $C2$	Cell parameters from 48
$a = 11.9752 (5)$ Å	reflections
$b = 5.7487 (2)$ Å	$\theta = 2$–$45°$
$c = 18.0759 (14)$ Å	$\mu = 0.882$ mm^{-1}
$\beta = 100.295 (6)°$	$T = 293$ K
$V = 1224.34 (12)$ Å^3	Rectangular plate, colourless
$Z = 4$	$0.43 \times 0.33 \times 0.05$ mm

Data collection

Philips PW1100 four-circle diffractometer	$R_{int} = 0.033$
$\omega/2\theta$ scans	$\theta_{max} = 67.42°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -14 \rightarrow 14$
	$k = -6 \rightarrow 6$
$T_{min} = 0.794$, $T_{max} = 0.957$	$l = -21 \rightarrow 21$
2496 measured reflections	2 standard reflections
1208 independent reflections	frequency: 90 min
1208 reflections with $I > 0$	intensity decay: none

Refinement

Refinement on F	H atoms treated by a mixture of independent and constrained refinement
$R = 0.032$	
$wR = 0.040$	
$S = 1.081$	Weighting scheme: see below
1208 reflections	$(\Delta/\sigma)_{max} < 0.001$
171 parameters	$\Delta\rho_{max} = 0.13$ e Å^{-3}
	$\Delta\rho_{min} = -0.13$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

O2—C2	1.420 (3)	O3—C3	1.412 (4)
O2—C2—C3	111.4 (2)	O4—C4—C5	105.6 (2)
O3—C3—C2	112.3 (2)	O4—C4—C3	111.1 (2)
O3—C3—C4	107.1 (2)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H21$\cdots$O1^{vi}	0.94 (4)	2.03 (2)	2.761 (3)	134 (3)
O3—H31$\cdots$O2^{vii}	0.93 (3)	1.85 (3)	2.741 (2)	159 (4)
C2—H2$\cdots$O3^{viii}	1.04	2.60	3.305 (4)	125
C7—H7$b\cdots$O5^{ix}	1.04	2.43	3.409 (4)	157
C5—H5$\cdots Cg^x$	1.04	2.71	3.635 (3)	148

Symmetry codes: (vi) $-x, y, 1 - z$; (vii) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$; (viii) $x, 1 + y, z$; (ix) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (x) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

Compound (III)

Crystal data

C$_{13}$H$_{14}$O$_5$	$D_x = 1.45$ Mg m^{-3}
$M_r = 250.25$	Cu $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 76
$a = 9.0956 (3)$ Å	reflections
$b = 5.8461 (2)$ Å	$\theta = 2$–$45°$
$c = 11.0603 (5)$ Å	$\mu = 0.941$ mm^{-1}
$\beta = 102.871 (4)°$	$T = 293$ K
$V = 573.34 (4)$ Å^3	Rectangular prism, colourless
$Z = 2$	$0.43 \times 0.30 \times 0.17$ mm

Data collection

Philips PW1100 four-circle diffract-ometer	$R_{int} = 0.049$
$\omega/2\theta$ scans	$\theta_{max} = 67.46°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -10 \rightarrow 10$
	$k = -7 \rightarrow 7$
$T_{min} = 0.760$, $T_{max} = 0.850$	$l = -13 \rightarrow 13$
2368 measured reflections	2 standard reflections
1127 independent reflections	frequency: 90 min
1127 reflections with $I > 0$	intensity decay: none

Refinement

Refinement on F	H atoms treated by a mixture of independent and constrained refinement
$R = 0.034$	
$wR = 0.043$	
$S = 1.046$	Weighting scheme: see below
1127 reflections	$(\Delta/\sigma)_{max} < 0.001$
167 parameters	$\Delta\rho_{max} = 0.15$ e Å^{-3}
	$\Delta\rho_{min} = -0.12$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

O2—C2	1.421 (4)	O3—C3	1.431 (4)
O2—C2—C3	107.7 (3)	O4—C4—C5	110.3 (2)
O3—C3—C2	110.8 (3)	O4—C4—C3	104.1 (2)
O3—C3—C4	102.2 (2)		
C7—O3—C3—C4	39.9 (2)	C4—O4—C7—O3	26.4 (3)
C3—O3—C7—O4	−42.0 (2)	O3—C3—C4—O4	−23.5 (3)
C7—O4—C4—C3	−1.3 (3)		

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H21$\cdots$O5^{iv}	0.91 (6)	2.06 (5)	2.950 (4)	161 (4)
C1—H1$\cdots$O2^{iv}	1.04	2.52	3.224 (5)	125
C9—H9$\cdots$O3^{xi}	1.04	2.55	3.381 (4)	136
C3—H3$\cdots$Cg^{xi}	1.04	2.98	3.971 (3)	160

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

In all three compounds, the Friedel pairs were merged as no significant information could be extracted (Flack, 1983). The enantiomers considered in this study (Fig. 1) correspond to those known from the syntheses [Florent & Monneret (1980), Reeves (1949) and Subero *et al.* (1980), respectively] and were checked by means of the configurational angles using the torsion angles (Cano *et al.*, 1985). All H atoms were located on the corresponding difference Fourier map. Nevertheless, all H atoms, except hydroxyl-H, were generated in idealized positions and were kept fixed during refinement (C—H = 1.04 Å). Attempts to refine the secondary extinction parameters resulted in insignificant values (Zachariasen, 1967). The weighting scheme was established in an empirical way so as to give no trends in $<w\Delta^2F>$ versus $<F_o>$ or $<\sin\theta/\lambda>$: $w = K/\{[(a + b)F_o]^2\}[(c + d)\sin\theta/\lambda]$. The parameters a, b, c and d were adjusted to flatten the initial trends (*PESOS*; Martínez-Ripoll & Cano, 1975). Details of a, b, c, d and K for the range of F for each compound are available in the deposited CIF.

For all compounds, data collection: Philips PW1100 software (Hornstra & Vossers, 1973); cell refinement: *LSUCRE* (Appleman, 1984); data reduction: *Xtal*3.6 (Hall *et al.*, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *CRYLSQ* in *Xtal*3.6; molecular graphics: *Xtal*3.6; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.6.

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