de la structure: *SHELXL*93. Graphisme moléculaire: *ORTEP*II (Johnson, 1976). Logiciel utilisé pour préparer le matériel pour publication: *SHELXL*93.

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: CF1182). Les processus d'accès à ces archives est donné au dos de la couverture.

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3-Deoxy-D-fructose

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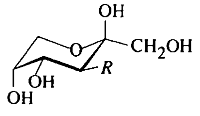
Abstract

The title compound, 3-deoxy-D-*erythro*-hexulose (3-deoxy-D-fructose), $C_6H_{12}O_5$, crystallizes from ethanol as the β-D-pyranose form in the $^2C_5$ conformation. Significant differences from β-D-fructopyranose (D-fructose) are observed in the hydrogen-bonding scheme. The primary hydroxyl group is hydrogen bonded internally to the ring oxygen in D-fructose, while it forms an intermolecular bond to the analogous oxygen of another molecule in the 3-deoxy analog. In both molecules, the hydroxyl group attached to anomeric carbon is a strong hydrogen-bond donor; it is also a hydrogen-bond acceptor in D-fructose, but not in 3-deoxy-D-fructose.

Comment

As part of continuing studies on the origin of the intense sweetness of D-fructose, (1), we have reported the preparation, the solution composition, and an evaluation of the sweet taste of the 3-deoxy analog of D-fructose, namely, 3-deoxy-D-*erythro*-hexulose, (2) (Szarek *et al.*, 1995). Compound (2) was found to be sweet, a result that indicated that the hydroxyl group at C3 is not an essential function of the glycophore of D-fructose. In order to detect structural features such as intramolecular hydrogen bonding (Woods, Szarek & Smith, 1990) that may be responsible for the sweet taste of (2) and to identify possible structural differences with D-fructose, the crystal structure of (2) was also determined.



(1) $1\beta p$; R=OH
(2) $2\beta p$; R=H

3-Deoxy-D-fructose crystallizes from ethanol solution as the β-D-pyranose form ($2\beta p$) in a $^2C_5$ chair conformation (Fig. 1), *i.e.* the same structural entity as the preponderant form of (2) in aqueous solution (Szarek *et al.*, 1995). The Cremer & Pople (1975) puckering parameters for $2\beta p$ [θ = 177.5 (3), φ = 108 (6)°, Q = 0.556 (3), q_2 = 0.026 (3) and q_3 = −0.555 (3) Å] indicate a nearly ideal chair conformation. As shown by the average torsion angle around the ring [55.6° for the title molecule *versus* 55.2° for β-D-fructopyranose (Takagi & Jeffrey, 1977)], the removal of the hydroxyl group at C3 does not change significantly the degree of puckering of the ring. The hydroxymethyl group is oriented +*sc* (*gauche*) with respect to O6, as in $1\beta p$; the torsion angle O1—C1—C2—O6 is −62.4 (3) in (2) and −61.4° in (1).

Comparison of bond lengths and angles between the title molecule and D-fructose [from X-ray (Kanters

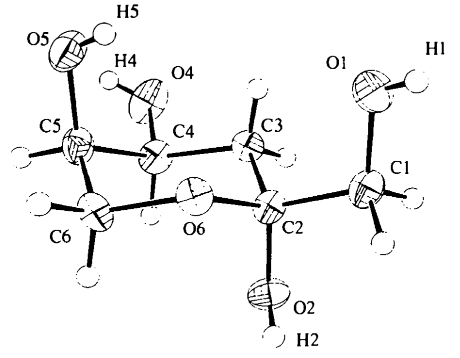


Fig. 1. View of the title molecule showing the labeling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as spheres of arbitrary size.

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et al., 1977) and neutron (Takagi & Jeffrey, 1977) determinations] reveals several differences, the most important ones being the C2—O6 [1.438 (3) in (2) *versus* 1.413 (3) Å in both X-ray and neutron structures of (1)] and C2—C3 [1.522 (4) in (2) *versus* 1.540 (4) (X-ray) and 1.543 (2) Å (neutron) in (1)] distances. Some differences are also observed in bond angles involving the C2 and C5 atoms (smaller endocyclic angles C3—C2—O6 and C4—C5—C6, larger exocyclic angles C1—C2—C3 and C6—C5—O5 in (2), all by at least 7σ). The differences in bond angles may be related to the different arrangements of the O1 and O5 hydroxyl groups in (1) and (2) (see also below).

Significant differences are observed in the hydrogen-bonding schemes of $1\beta p$ (Takagi & Jeffrey, 1977) and $2\beta p$ (Table 3). In β-D-fructopyranose, (1), H1 is turned 'inside' and H5 'outside' with respect to the pyranose ring, with an intramolecular hydrogen bond between H1 and O6, and a close contact between H5 and O4 (2.55 Å). In the 3-deoxy analog (2), the situation is reversed, H1 is turned 'outside' and forms an intermolecular hydrogen bond to O6, while H5 points 'inside' the pyranose ring (the close contact of H5 to O6, 2.63 Å, is observed). In both $1\beta p$ and $2\beta p$, the hydroxyl group attached to anomeric carbon atom C2 is a strong hydrogen-bond donor; in $1\beta p$, oxygen atom O2 is also a relatively strong double hydrogen-bond acceptor, while in $2\beta p$, it does not accept any hydrogen bond. It is significant, however, that, in both cases, the H2 and O2 atoms are not involved in an internal hydrogen bond: the 2-OH group would thus be free (in solution) to interact in an *anti-exo*-anomeric orientation with a hydrogen-bond acceptor of the sweet taste receptor (Woods, Szarek & Smith, 1990). In the crystalline state, both (1) and (2) adopt a conformation of the 2-OH group consistent with the *exo*-anomeric effect.

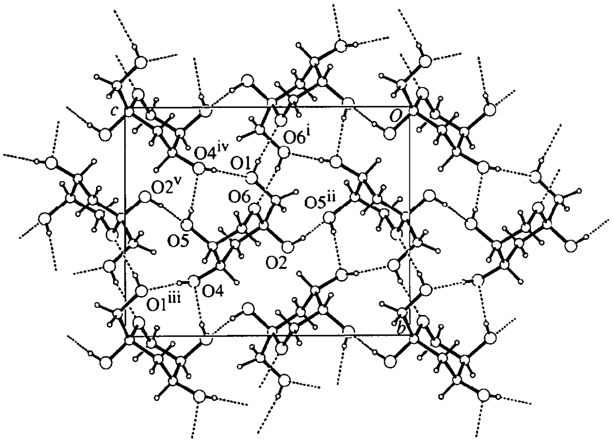

Fig. 2. Crystal packing of (2) projected along the *a* axis with the network of hydrogen bonds represented by dashed lines; the symmetry indicators are as in Table 2, with the addition of (v) $\frac{3}{2} - x, 1 - y, z + \frac{1}{2}$.

The crystal structure of 3-deoxy-D-fructose, (2), is built around a network of hydrogen bonds (see Fig. 2) which consists of finite chains of strong O—H···O bonds (Jeffrey & Takagi, 1978) connecting four molecules which make up the contents of one unit cell. The chain labelled in Fig. 2 starts at atom O2^{v}, goes through atoms O5, O4^{iv} and O1, and terminates at atom O6^{i} (for symmetry codes see Table 3 and Fig. 2 caption). In contrast, molecules of D-fructose, (1), form infinite chains of hydrogen bonds in the crystal lattice.

Experimental

3-Deoxy-D-*erythro*-hexulose was prepared as reported by Szarek *et al.* (1995) and crystallized from ethanol (m.p. 384–385 K).

Crystal data

$C_6H_{12}O_5$
$M_r = 164.16$
Orthorhombic
$P2_12_12_1$
$a = 6.4370\ (7)$ Å
$b = 9.3798\ (12)$ Å
$c = 12.0427\ (9)$ Å
$V = 727.11\ (13)$ Å^3
$Z = 4$
$D_x = 1.500$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 13–17°$
$\mu = 0.131$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.45 × 0.30 × 0.05 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
868 measured reflections
773 independent reflections
636 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.056$, based on standards

$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 11$
$l = -2 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.092$
$S = 0.919$
773 reflections
105 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.211$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.205$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)

Extinction coefficient: 0.009 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: absolute structure cannot be determined reliably from the X-ray data (Flack, 1983), however, it is known from the stereospecific synthesis (Szarek *et al.*, 1995).
Flack parameter = −1 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	1.1717 (5)	0.4038 (3)	0.4717 (2)	0.0283 (7)
C2	1.0257 (5)	0.5179 (3)	0.5150 (2)	0.0221 (6)
C3	1.1089 (4)	0.6005 (3)	0.6143 (2)	0.0224 (7)
C4	0.9445 (5)	0.6944 (3)	0.6659 (2)	0.0246 (7)
C5	0.7488 (5)	0.6099 (3)	0.6939 (2)	0.0269 (7)
C6	0.6782 (5)	0.5328 (3)	0.5906 (2)	0.0275 (7)
O1	1.2212 (4)	0.3049 (2)	0.5570 (2)	0.0359 (6)
O2	0.9834 (4)	0.6152 (2)	0.4303 (2)	0.0284 (6)
O4	1.0342 (4)	0.7627 (2)	0.7595 (2)	0.0397 (7)
O5	0.7820 (4)	0.5146 (2)	0.7834 (2)	0.0345 (6)
O6	0.8403 (3)	0.4428 (2)	0.5469 (2)	0.0243 (5)

Table 2. *Selected geometric parameters* (Å, °)

C1—C2	1.516 (4)	C2—O6	1.438 (3)
C2—C3	1.522 (4)	C1—O1	1.421 (4)
C3—C4	1.511 (4)	C2—O2	1.396 (3)
C4—C5	1.526 (4)	C4—O4	1.419 (4)
C5—C6	1.509 (4)	C5—O5	1.416 (4)
C6—O6	1.441 (3)		
O1—C1—C2	110.6 (2)	C3—C2—O6	109.3 (2)
C1—C2—O2	109.3 (2)	C4—C5—O5	111.8 (2)
C1—C2—C3	114.3 (3)	C4—C5—C6	108.4 (2)
C1—C2—O6	105.1 (2)	C6—C5—O5	111.7 (2)
O2—C2—C3	108.0 (2)	C2—O6—C6	114.3 (2)
O2—C2—O6	110.7 (2)		
O6—C2—C3—C4	−52.8 (3)	C6—O6—C2—C3	57.1 (3)
C2—C3—C4—C5	53.1 (3)	O1—C1—C2—O2	178.7 (2)
C3—C4—C5—C6	−53.7 (3)	O1—C1—C2—C3	57.5 (3)
C4—C5—C6—O6	56.4 (3)	O1—C1—C2—O6	−62.4 (3)
C5—C6—O6—C2	−60.8 (3)		

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O6^{i}	0.71 (4)	2.04	2.748 (3)	175
O2—H2···O5^{ii}	0.82 (4)	1.95	2.744 (3)	164
O4—H4···O1^{iii}	0.77 (4)	2.03	2.783 (3)	168
O5—H5···O4^{iv}	0.74 (4)	1.98	2.692 (2)	162

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

All H atoms were located in the ΔF maps but due to the low reflection-to-parameter ratio they were allowed for as riding atoms using the appropriate *SHELXL*93 *AFIX* (Sheldrick, 1993) commands (*AFIX* 13 C—H 0.98, *AFIX* 23 C—H 0.97 and *AFIX* 144 with O—H distances refined).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTON* (Spek, 1992). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1300). Services for accessing these data are described at the back of the journal.

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α,α-Difluoro-β-lactone and its Non-Fluorinated Analog

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Abstract

The structures of 4,4-dibenzyloxetan-2-one, $C_{17}H_{16}O_2$, (1), and 4,4-dibenzyl-3,3-difluorooxetan-2-one, $C_{17}H_{14}F_2O_2$, (2), were determined in order to relate their structures to differences in their reactivities towards nucleophiles and thermal decarboxylation. The lactone rings in the two compounds are different, with the former exhibiting a planar ring, while the latter has a bent ring and an average endocyclic torsion angle of 6.8 (2)°. Bond distances of the CO_2 fragment are shorter in compound (2) than in their counterparts in (1).

Comment

Although β-lactones (oxetan-2-one) have been known for more than 100 years (Einhorn, 1883; Pommier &

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