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The Crystal and Molecular Structure of β-D-Digitoxose

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β-D-Digitoxose, $C_6H_{12}O_4$, is orthorhombic, space group $P22_12_1$, with $a = 4{\cdot}821$ (2), $b = 11{\cdot}025$ (3), $c = 13{\cdot}807$ (3) Å and $Z = 4$. The structure was solved by direct methods and refined to a final R of 0·043 for 794 counter reflexions. The molecule has the $^4C_1$ pyranoside chair conformation and the equatorial methyl group is in the *anti* position. The three hydroxyl groups are involved in intermolecular hydrogen bonds; two hydroxyl groups, including anomeric O, act as both donor and acceptor and the ring O is an acceptor. Each molecule is linked by six hydrogen bonds to four neighbours to form a two-dimensional network parallel to the *ab* plane.

Introduction

β-D-Digitoxose (2,6-dideoxy-D-ribohexose, or, alternatively, 2,6-dideoxy-D-allose) is a constituent of the cardiac glycosides digitoxin and digoxin. In contrast to many mono- and dideoxy aldoses, β-D-digitoxose is not known to occur in nature in the free state. So far the structures of two members of this class, α-L-fucose (Longchambon, Ohanessian, Avenel & Neuman, 1975) and α-L-rhamnose (Killean, Lawrence & Sharma, 1971), have been reported. Compared with the common aldopyranoses, β-D-digitoxose is missing two hydroxyl groups, at ring C(2) and exocyclic C(6), and this feature led us to determine its structure, mainly to see whether this has any consequences for geometry, conformation and hydrogen-bond pattern.

Experimental

Crystals of β-D-digitoxose were grown at room temperature from a 2% aqueous ethanolic solution of a commercial product obtained through Sigma Corporation.

Photographs showed that the crystal system is orthorhombic with space group $P22_12_1$. Accurate cell dimensions and intensities were measured on an automatic Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation with the 2θ scan technique. The crystal data are summarized in Table 1. From 1007 available reflexions in one octant of the reflexion sphere with $\sin\theta/\lambda = 0{\cdot}65$ Å^{-1}, 213 had $I < 2{\cdot}5\sigma(I)$ and were considered unobserved. Lorentz–polarization corrections were applied, but no correction for absorption was made.

Table 1. *Crystal data for β-D-digitoxose*

Molecular formula	$C_6H_{12}O_4$
Molecular weight	148
Crystal system	Orthorhombic
a (Å)	4·821 (2)
b (Å)	11·025 (3)
c (Å)	13·807 (3)
V (Å^3)	733·86
Z	4
Space group	$P22_12_1$
Calculated density (g cm^{-3})	1·340
λ(Mo $K\alpha$) (Å)	0·71069
μ(Mo $K\alpha$) (cm^{-1})	1·21
Systematic absences	$0k0$, $k = 2n + 1$ $00l$, $l = 2n + 1$

Determination of the structure and refinement

The structure was solved with the *MULTAN* system (Main, Lessinger, Woolfson, Germain & Declercq, 1974). The data were placed on an absolute scale by Wilson's (1942) method. For the structure determination, 100 normalized structure factors ($|E| > 1{\cdot}61$) were used. The first E map revealed all the non-hydrogen atoms. After block-diagonal least-squares refinement with anisotropic thermal parameters, a difference map showed the 12 H atoms with electron densities ranging from 0·2 to 0·6 e Å^{-3}. The positional parameters of the H atoms, with constant isotropic thermal parameters equal to those of the carrier atoms, were included in the refinement. Full-matrix refinement gave a final $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}043$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0{\cdot}026$. The quantity minimized was $\sum w(F_o - F_c)^2$ with weights $w = \sigma^{-2}(F_o)$. The goodness of fit was 0·60, the average shift/error ratio for all parameters was 0·010, the maximum shift/error ratio for C and O parameters was 0·073, and that for H parameters was 0·097. A final difference synthesis showed no maxima above 0·22 e

Table 2. *Fractional atomic coordinates* (×10^4, *for* H × 10^3) *for β-D-digitoxose*

The estimated standard deviations are given in parentheses and refer to the least significant figure.

	x	*y*	*z*
C(1)	3540 (7)	7643 (3)	6563 (2)
C(2)	2083 (8)	8720 (3)	6139 (3)
C(3)	2487 (7)	9827 (3)	6778 (3)
C(4)	1576 (7)	9516 (3)	7804 (3)
C(5)	2999 (8)	8395 (3)	8186 (3)
C(6)	1874 (11)	7985 (4)	9157 (3)
O(1)	2919 (5)	6590 (2)	6034 (2)
O(3)	5367 (6)	10111 (2)	6735 (2)
O(4)	2218 (5)	10508 (2)	8440 (2)
O(5)	2529 (5)	7401 (2)	7529 (2)
H(C1)	594 (6)	776 (3)	669 (2)
H(C2)	−20 (6)	854 (3)	610 (2)
H′(C2)	305 (6)	881 (2)	551 (2)
H(C3)	154 (7)	1053 (3)	654 (2)
H(C4)	−97 (6)	936 (3)	780 (2)
H(C5)	530 (6)	855 (3)	825 (2)
H(C6)	−67 (7)	790 (3)	911 (2)
H′(C6)	217 (7)	853 (3)	962 (2)
H″(C6)	281 (8)	727 (2)	935 (2)
H(O1)	415 (6)	614 (3)	614 (2)
H(O3)	564 (9)	1066 (3)	696 (2)
H(O4)	104 (7)	1090 (3)	860 (3)

Å^{-3}. Scattering factors for C and O were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Positional parameters are listed in Table 2.* Refinement and subsequent calculations were performed with the XRAY system (Stewart, 1976).

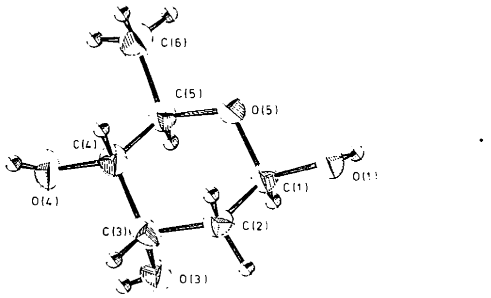

Fig. 1. Molecular conformation and atomic numbering of β-D-digitoxose. C and O atoms are represented at the 50% probability level.

Table 3. *Bond distances* (Å) *for β-D-digitoxose*

The estimated standard deviations are given in parentheses.

C(1)–C(2)	1·499 (5)	C(1)–O(1)	1·404 (4)
C(2)–C(3)	1·520 (5)	C(3)–O(3)	1·424 (5)
C(3)–C(4)	1·522 (5)	C(4)–O(4)	1·435 (4)
C(4)–C(5)	1·509 (5)	C(1)–O(5)	1·445 (4)
C(5)–C(6)	1·516 (5)	C(5)–O(5)	1·440 (4)

Table 4. *Bond angles* (°) *for β-D-digitoxose*

The estimated standard deviations are given in parentheses.

O(1)–C(1)–C(2)	110·6 (3)	C(3)–C(4)–C(5)	112·2 (3)
O(1)–C(1)–O(5)	104·8 (3)	C(3)–C(4)–O(4)	109·6 (3)
C(2)–C(1)–O(5)	110·4 (3)	O(4)–C(4)–C(5)	108·2 (3)
C(1)–C(2)–C(3)	110·5 (3)	C(4)–C(5)–O(5)	109·4 (3)
C(2)–C(3)–C(4)	108·8 (3)	C(4)–C(5)–C(6)	113·0 (3)
C(2)–C(3)–O(3)	106·1 (3)	C(6)–C(5)–O(5)	105·9 (3)
O(3)–C(3)–C(4)	111·7 (3)	C(5)–O(5)–C(1)	112·8 (2)

Description of the structure

The conformation of the molecule and the numbering of the atoms are shown in Fig. 1. β-D-Digitoxose has the familiar $^4C_1$ (C1) pyranose chair conformation. Bond distances and angles involving C and O atoms are shown in Tables 3 and 4 respectively. The C—C bonds range from 1·499 (5) to 1·522 (5) Å (mean 1·513 Å). The C(1)—C(2) bond (1·499 Å) appears to be shorter (4σ) than corresponding distances in other accurately determined mono- and disaccharides (Arnott & Scott, 1972), though in the structure of α-maltose (Takusagawa & Jacobson, 1978) a C(1)—C(2) distance of 1·498 (4) Å has recently been reported. The exocyclic C—O bonds range from 1·404 (4) to 1·435 (4) Å (mean 1·421 Å). The anomeric C(1)—O(1) distance is short [1·404 (5) Å] and differs by 3·5σ from the mean. The endocyclic C(1)—O(5) and C(5)—O(5) bonds are 1·445 (4) and 1·440 (4) Å respectively. These bond lengths, which relate to the hemiacetal sequence C(5)—O(5)—C(1)—O(1)—H, are consistent with observations on other α- and β-pyranoside structures (Jeffrey & Takagi, 1977; Arnott & Scott, 1972) and with theory (Jeffrey, Pople & Radom, 1972, 1974), in that the anomeric C(1)—O(1) is shortened in both α- and β-pyranosides and the difference in endocyclic C—O bond lengths in β-pyranosides is smaller than in α-pyranosides.

The C—H distances have an average value of 1·07 (4) Å, the O—H distances average 0·74 (5) Å.

The ring bond angles at C atoms range from 108·8 (3) to 113·0 (3)°, the exocyclic C—C—O angles at C atoms range from 105·0 (3) to 111·7 (3)° and the endocyclic C—C—O angles, C(2)—C(1)—O(5) and C(4)—C(5)—O(5), are 110·4 (3) and 109·4 (3)° respectively. The bond angles in the hemiacetal sequence,

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33609 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Endo- and exocyclic torsion angles* (°) *for β-*D*-digitoxose*

The torsion angle *A*(1)–*A*(2)–*A*(3)–*A*(4) is viewed along *A*(2)–*A*(3), with a clockwise rotation of *A*(1) to *A*(4) taken to be positive.

Endocyclic		Exocyclic	
O(5)–C(1)–C(2)–C(3)	57·9	O(1)–C(1)–C(2)–C(3)	173·5
C(1)–C(2)–C(3)–C(4)	−54·1	C(1)–C(2)–C(3)–O(3)	66·2
C(2)–C(3)–C(4)–C(5)	53·6	C(2)–C(3)–C(4)–O(4)	173·8
C(3)–C(4)–C(5)–O(5)	−55·5	O(3)–C(3)–C(4)–C(5)	−63·1
C(4)–C(5)–O(5)–C(1)	58·9	O(3)–C(3)–C(4)–O(4)	57·1
C(5)–O(5)–C(1)–C(2)	−61·0	C(3)–C(4)–C(5)–C(6)	−173·2
		O(4)–C(4)–C(5)–O(5)	−176·5
		O(4)–C(4)–C(5)–C(6)	65·8
		C(6)–C(5)–O(5)–C(1)	−179·0
		C(5)–O(5)–C(1)–O(1)	179·8

O(5)—C(1)—O(1) 104·8 (3) and C(5)—O(5)—C(1) 112·8 (2)°, follow the general trend (Jeffrey & Takagi, 1977) that these valence angles are smaller in β-pyranosides than in α-pyranosides.

The angle O(5)—C(1)—O(1) is exceptional in that it varies with configuration, as was originally noted by Arnott & Scott (1972): when C(1)—O(1) is equatorial the mean value of eight pyranosides is 107·3°, when axial the mean value of 19 pyranosides is 111·6°. The pertinent value in β-D-digitoxose (104·8°) is, in fact, the lowest value so far observed in this class of compounds. The bond angles involving H atoms have mean values distributed as follows over the different classes: H—C—C 110, H—C—O 108, H—O—C 111 and H—C—H 109°.

The pyranose ring is close to the ideal $^4C_1$ chair as shown by the torsion angles (Table 5). The exocyclic torsion angles are close to the values for the ideal *gauche* (60°) or *trans* (180°) arrangements. As already reported (Arnott & Scott, 1972; Jeffrey, McMullan & Takagi, 1977) pyranose rings have approximate mirror symmetry normal to the plane through the ring O and C(3) atoms, with more puckering at O and less puckering at C. From Table 5 it can be inferred that this also applies to β-D-digitoxose and that the mean difference between mirror-related torsion angles is quite small (1°) compared with the values of many pyranosides and methyl pyranosides tabulated by Jeffrey, McMullan & Takagi (1977). Deviations from mirror symmetry in part arise from differences in ring C—O bond lengths (Jeffrey, Pople & Radom, 1974) and as this difference in β-D-digitoxose is negligible (Table 3), the small deviation from mirror symmetry is not unexpected. The regularity of the pyranose chair is further borne out by the small displacements from the three least-squares planes passing through opposite bonds (Table 6) and by the values of the ring-puckering parameters of Cremer & Pople (1975): $q_2 = 0{\cdot}018$ Å, $q_3 = 0{\cdot}568$ Å, $\varphi_2 = 48{\cdot}1°$, $\theta = 1{\cdot}9°$ and $Q = 0{\cdot}569$ Å.

Table 6. *Least-squares planes of β-*D*-digitoxose, with displacements of the atoms from the plane* (Å)

Asterisks indicate atoms not included in the calculation of the plane.

Plane (I)		Plane (II)		Plane (III)	
C(1)	0·008	C(2)	0·009	C(3)	−0·015
C(2)	−0·008	C(3)	−0·008	C(4)	0·015
C(4)	0·008	C(5)	0·009	O(5)	−0·016
C(5)	−0·008	O(5)	−0·009	C(1)	0·016
C(3)*	0·666	C(1)*	0·671	C(2)*	−0·670
O(5)*	−0·650	C(4)*	−0·650	C(5)*	0·660

Table 7. *Torsion angles* (°) *involving hydrogen atoms of β-*D*-digitoxose*

H(C1)–C(1)–C(2)–H(C2)	−176
H(C1)–C(1)–C(2)–H′(C2)	60
H(C2)–C(2)–C(3)–H(C3)	−59
H′(C2)–C(2)–C(3)–H(C3)	70
H(C3)–C(3)–C(4)–H(C4)	57
H(C4)–C(4)–C(5)–H(C5)	176
H(C5)–C(5)–C(6)–H(C6)	176
H(C5)–C(5)–C(6)–H′(C6)	60
H(C5)–C(5)–C(6)–H″(C6)	−59
H(C1)–C(1)–O(1)–H(O1)	27
H(C3)–C(3)–O(3)–H(O3)	51
H(C4)–C(4)–O(4)–H(O4)	−14

The H atoms on neighbouring C atoms of the ring show only slight deviations from the ideal *trans* (180°) or *gauche* (60°) orientations (Table 7). Two of the three H—C—O—H torsion angles (Table 7) are 27 and −14° respectively, and this departure from the ideal value of 60°, which would be favoured by the isolated molecule (Sundaralingam, 1968; Takagi & Jeffrey, 1977), is rather widespread in saccharide structures (Takagi & Jeffrey, 1977; Gress & Jeffrey, 1977; Jeffrey, McMullan & Takagi, 1977; Kanters, Gaykema & Roelofsen, 1978; Fries, Rao & Sundaralingam, 1971). The eclipsing of vicinal H atoms which increases their non-bonding repulsion is to be attributed to the participation of the hydroxyl groups in intermolecular hydrogen bonding and thus illustrates the delicate balance between intramolecular constraints and intermolecular packing forces.

The torsion angles about C(5)—C(6) are 176° [H(C5)—C(5)—C(6)—H(C6)], 178° [C(4)—C(5)—C(6)—H″(C6)] and 177° [O(5)—C(5)—C(6)—H′(C6)], indicating an almost ideal staggered arrangement of the exocyclic methyl group.

The three hydrogen bonds are intermolecular (Table 8). Two O—H groups, O(1)—H and O(4)—H, function as donor and acceptor; O(2)—H is a donor only and ring O(5) acts as an acceptor. When corrected for the shortening of O—H bond lengths characteristic of X-ray data, as compared with neutron diffraction O—H distances (Jeffrey & Takagi, 1977), the H···O dis-

Table 8. *Hydrogen-bond distances* (Å) *and angles* (°) *of β-*D*-digitoxose*

	O–H	H···O	H···O*	O···O	∠O–H···O	Symmetry operation†
O(1)–H(O1)···O(4′)	0·78 (3)	1·97 (3)	1·81	2·729 (4)	162 (2)	646.4
O(3)–H(O3)···O(5′)	0·69 (3)	2·23 (3)	1·97	2·905 (3)	166 (4)	656.4
O(4)–H(O4)···O(1′)	0·75 (3)	2·12 (3)	1·91	2·843 (3)	164 (3)	556.4
O(4)···H(O1″)–O(1″)						656.4
O(5)···H(O3″)–O(3″)						646.4
O(1)···H(O4″)–O(4″)						546.4

* Corrected by expanding the covalent O–H bond distances to the neutron diffraction value of 0·96 Å in the direction of the bond.

† The symmetry operation is performed on the O′ (acceptors) and O″ atoms (donors). The first three digits specify the lattice translations. The last digit indicates one of the following symmetry operations: (1) x,y,z; (2) $x,-y,-z$; (3) $-x, \frac{1}{2}-y, \frac{1}{2}+z$; (4) $-x, \frac{1}{2}+y, \frac{1}{2}-z$ (*e.g.* 546.4 is $-b+c$ from 555.4).

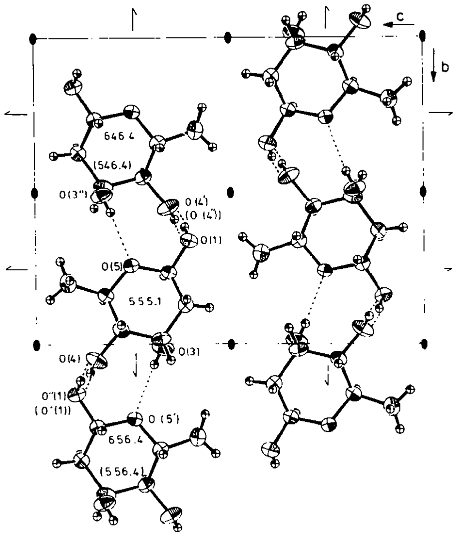

Fig. 2. Projection of the structure along −**a**. The hydrogen bonds are indicated by dashed lines. The superscripts of the O atoms refer to the symmetry operations defined in Table 8. The O atoms in parentheses relate to molecules generated by the symmetry operations shown in parentheses.

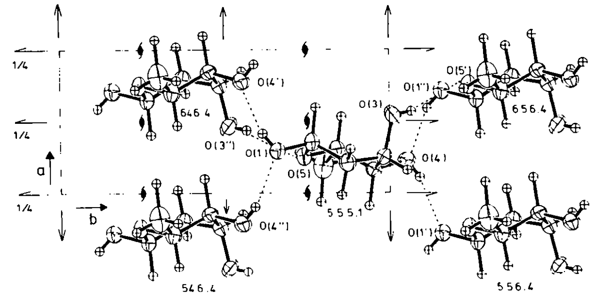

Fig. 3. Projection of the structure along −**c**. The hydrogen bonds are indicated by dashed lines. The superscripts of the O atoms refer to the symmetry operations defined in Table 8.

tances show a similar distribution to that reported from neutron diffraction studies of carbohydrate structures (Jeffrey, Gress & Takagi, 1977) in that the donor–acceptor O–H···O–H bonds are shorter than the O–H···O bonds to a ring O atom (Table 8). The shortest of the O–H···O–H-type bonds in β-D-digitoxose is that from anomeric O(1)–H, which is in agreement with the prediction of Tse & Newton (1977) that anomeric O–H groups form stronger bonds because of the electronic structure of the hemiacetal group. From theory it has also been shown (Tse & Newton, 1977) that anomeric O is a relatively poor acceptor, due to an appreciable depletion of charge at the anomeric proton by the anomeric effect. Accordingly, the pertinent H(O4)···O(1′) distance is indicative of a weaker interaction.

The hydrogen-bond scheme (Fig. 2) consists of an O(1)–H···O(4′)–H···O(1′)–H infinite chain propagating along **a** and a single-link branch from O(3) to ring O(5′). Each molecule of β-D-digitoxose is connected to four neighbours by six hydrogen bonds to form a two-dimensional network roughly parallel to the *ab* plane (Fig. 3). The molecules in one network unit are symmetry related by the 2_1 axis along **b**. Sheets of this network are loosely stacked along **c**, as may be inferred from the fact that the shortest contact distances in the **c** direction are those between H″(C6) of the methyl group and H(O1) (2·77 Å) and H(C2) and H′(C2) of the ring methylene group (2·82 and 2·86 Å). The very weak interactions in the **c** direction, evidently due to the absence of two potential hydrogen-bond donors at C(2) and C(6), are also reflected in the low density of β-D-digitoxose (1·340 g cm^{-3}) compared with the density range of 1·50 to 1·60 g cm^{-3} commonly observed in normal aldohexoses.

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Preparation and X-ray Analysis of a 1:1 Adduct of Hexamethylenetetramine Oxide and Thiourea

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A 1:1 adduct of hexamethylenetetramine oxide and thiourea ($C_6H_{12}N_4O.CH_4N_2S$) has been prepared and subjected to crystal-structure analysis. The crystals are orthorhombic, space group *Pbca*, with $a = 7{\cdot}698$ (5), $b = 12{\cdot}03$ (1), $c = 23{\cdot}09$ (2) Å and $Z = 8$. The structure was solved by direct methods and refined with 1426 observed Cu $K\alpha$ film data to $R = 0{\cdot}099$. In the crystal lattice each $(CH_2)_6N_4O$ molecule is linked by O···H–N hydrogen bonds to three thiourea molecules and *vice versa*, giving rise to corrugated layers normal to **c**. Neighboring layers, related by the *c* glide, pack with protruding $(CH_2)_6N_4$ groups fitting into hollows between the layers.

Introduction

X-ray analysis of the 1:2 adduct of hexamethylenetetramine with thiourea, $(CH_2)_6N_4.2(NH_2)_2CS$, has shown that the two molecular components are linked by N···H–N and S···H–N hydrogen bonds in a three-dimensional network (Mak, Lau, Ladd & Povey, 1978). Recently we isolated hexamethylenetetramine oxide, $(CH_2)_6N_4O$, and a number of its acid adducts (Lam & Mak, 1978*a*). The title compound was prepared and studied as part of our current structural investigation of hydrogen-bonded molecular complexes of hexamethylenetetramine (Mak, Tse, Chong & Mok, 1977; Mak, Yu & Lam, 1978) and its *N*-oxide (Lam & Mak, 1978*b*; Mak & Lam, 1978).

Experimental

Preparation of the hexamethylenetetramine oxide–thiourea 1:1 *adduct*

Hexamethylenetetramine oxide (I) was prepared by the reaction of hexamethylenetetramine with 30% aqueous hydrogen peroxide (Lam & Mak, 1978*a*) and recrystallized from chloroform. Thiourea (II) was recrystallized from ethanol. Compounds (I) (0·8 g, 5 mmol) and (II) (0·4 g, 5 mmol) were dissolved separately in the minimum amount of ethanol. The solutions were mixed at room temperature and set aside for crystallization; these yielded colorless, air-stable crystals (III) of stoichiometry $C_7H_{16}N_6OS$† [m.p. 153–

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† Elemental analysis performed by the Australian Microanalytical Service, CSIRO, Parkville, Victoria, Australia.