Carbohydrate Research, 135 (1984) 47–52
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CRYSTAL STRUCTURE OF 2-DEOXY-β-D-*lyxo*-HEXOSE (2-DEOXY-β-D-GALACTOSE)

RAFFAELLA PULITI,
Istituto per la Chimica di Molecole di Interesse Biologico del C.N.R., Via Toiano 2, 80072 Arco Felice, Napoli (Italy)

CARLO A. MATTIA, AND GUIDO BARONE
Dipartimento di Chimica dell'Università di Napoli, Via Mezzocannone 4, 80134 Napoli (Italy)

(Received April 2nd, 1984; accepted for publication, June 18th, 1984)

ABSTRACT

2-Deoxy-β-D-*lyxo*-hexose (2-deoxy-β-D-galactose, $C_6H_{12}O_5$), M_r = 164.16, is monoclinic, $P2_1$ with a = 9.811(1), b = 6.953(1), c = 5.315(1) Å, β = 91.58(2)°, V = 362.5(1) Å^3, Z = 2, and D_x = 1.504 g.cm^{-3}. The structure was solved by direct methods (MULTAN 79) and refined to R = 0.032 for 800 observed reflections. Each hydroxyl oxygen, acting both as donor and acceptor, is involved in a hydrogen-bonding system, which consists of infinite helical chains around the crystallographic screw axes. Moreover, weak interactions allow the incorporation of the ring-oxygen atoms into an interconnected network.

INTRODUCTION

The crystal structure of 2-deoxy-β-D-galactose is part of a programme on the physico-chemical properties of simple sugars and their derivatives[1–3]. Knowledge of the structure and conformation of these compounds in the solid state may be of value for a better understanding of their behaviour in solution.

EXPERIMENTAL

2-Deoxy-β-D-galactose was crystallised in colourless prisms by slow concentration of an ethanolic solution. The crystals were generally twinned around the (001) axis. A single, non-twinned crystal (0.5 × 0.4 × 0.2 mm) was mounted on an Enraf–Nonius CAD-4 diffractometer (Ni-filtered CuKα) on-line with a PDP-11/34 computer. Accurate cell parameters were determined by least-squares refinement of the setting angles of 24 reflections at medium ϑ ($24° < \vartheta < 31°$) accurately centered. Intensities of 817 independent reflections with $\vartheta \leqslant 76°$ were measured at room temperature using the ω–ϑ scan mode. The equipment and crystal stability were checked by four standard reflections recorded at regular intervals during collection of the data. Intensities were corrected for Lorentz and

0008-6215/84/$ 03.00

TABLE I

POSITIONAL PARAMETERS ($\times 10^4$ FOR THE NON-HYDROGEN ATOMS, $\times 10^3$ FOR THE HYDROGEN ATOMS) AND THERMAL PARAMETERS (Å^2)[a]

	x	y	z	$B_{eq}(B_{iso})^b$
O-1	599(1)	9303(2)	8110(3)	3.61(2)
O-3	4026(1)	8010(2)	2117(2)	3.41(2)
O-4	4538(1)	6424(2)	7059(2)	3.07(2)
O-5	1676(1)	6409	8204(2)	2.85(2)
O-6	1620(1)	2602(2)	10116(3)	3.90(2)
C-1	1151(2)	7890(3)	6581(3)	2.91(3)
C-2	2288(2)	8769(3)	5067(3)	2.97(3)
C-3	2970(2)	7190(3)	3586(3)	2.77(3)
C-4	3514(1)	5640(2)	5375(3)	2.59(2)
C-5	2304(2)	4869(3)	6862(3)	2.66(2)
C-6	2742(2)	3371(3)	8788(3)	3.06(3)
HO-1	−20(3)	885(4)	882(4)	3.61
HO-3	395(2)	747(4)	58(4)	3.41
HO-4	519(2)	545(4)	725(4)	3.07
HO-6	137(2)	147(5)	946(4)	3.90
H-1	50(2)	731(4)	548(4)	2.91
H-2	283(2)	943(3)	620(4)	2.97
H-2′	185(2)	959(3)	402(4)	2.97
H-3	233(2)	674(4)	251(3)	2.77
H-4	394(2)	463(3)	441(4)	2.59
H-5	163(2)	441(3)	564(4)	2.66
H-6	332(2)	392(4)	1014(4)	3.06
H-6′	328(2)	237(4)	803(4)	3.06

[a]Standard deviations in parentheses. [b]$B_{eq} = 4/3\Sigma_i\Sigma_j b_{ij}\mathbf{a}_i\mathbf{a}_j$.

polarisation factors, but not for the absorption effect (μ = 1.09 mm^{-1}). The structure was solved by means of MULTAN 79[4]. The refinement of the positional and anisotropic temperature parameters for all non-hydrogen atoms was carried out by full-matrix (on F) least-squares, yielding a conventional R value of 0.065. At this point, all of the H-atoms were located unambiguously from an electron-density map and were included in the last refinement cycles with isotropic thermal parameters set equal to the B_{eq} of the parent atoms. At convergence, the discrepancy index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.032 for the 800 observed reflections [$I \geq 3\sigma(I)$]. The $R_w = \Sigma[w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ was 0.048, with $w^{-1} = \sigma^2(F_o)$, $\sigma(F_o)$ being obtained from counting statistics. All of the crystallographic work was achieved on the equipment of the "Centro di Metodologie Chimico-fisiche dell' Università di Napoli", using the SDP package and atomic scattering factors of Cromer and Waber[5].

Final atomic parameters are given in Table I*.

*Lists of structure factors and anisotropic thermal parameters have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/299/*Carbohydr. Res.*, 135 (1984) 47–52.

DISCUSSION

Fig. 1 shows a view of the molecule with the thermal ellipsoids (30% probability) and atomic numbering scheme used. The ring substituents are in the configuration 1*e*3*e*4*a*5*e*. The pyranose ring is close to the ideal $^4C_1$ conformation, with ring torsion angles varying from 57.3(2)° to 60.7(2)° (Table II). The Cremer and Pople[6] puckering parameters, for the sequence O-5,C-1,C-2,C-3,C-4,C-5, are $q_2 = 0.0236$, q_3 ($\cong$ Q) = 0.5931, $\vartheta = 2.3°$, and $\varphi_2 = 212.3°$, which show a little distortion towards the twist-boat form ($\varphi_2 = 210°$). This type of distortion is most frequently found in the β anomers[7].

The primary hydroxyl group is in the *gauche* conformation [61.1(2)°] with respect to the C-5–O-5 bond and *trans* [−178.0(3)°] with respect to the C-5–C-4 bond. This *gauche–trans* conformation appears to be energetically preferred and is frequently found in galactosyl derivatives[8].

Bond lengths and angles involving non-hydrogen atoms are given in Table II and are in good agreement with the average values reported for pyranosides[9]. The bond lengths involving hydrogen atoms lie in the range 0.90–0.98 Å. The average lengths for the C–C and C–O bonds are 1.523 and 1.432 Å, respectively, the only marked differences from these average values being C-4–C-5 = 1.540(2) and C-1–O-1 = 1.394(2) Å. The shortness of the last bond is a consequence of the anomeric effect[10,11].

All of the bond angles fall in the accepted range, and the values of 112.9(1)° for C-1–O-5–C-5 and 107.2(1)° for O-1–C-1–O-5 are close to average values (112.0° and 107.3°, respectively) reported[9] for polysaccharides with O-1 equatorial.

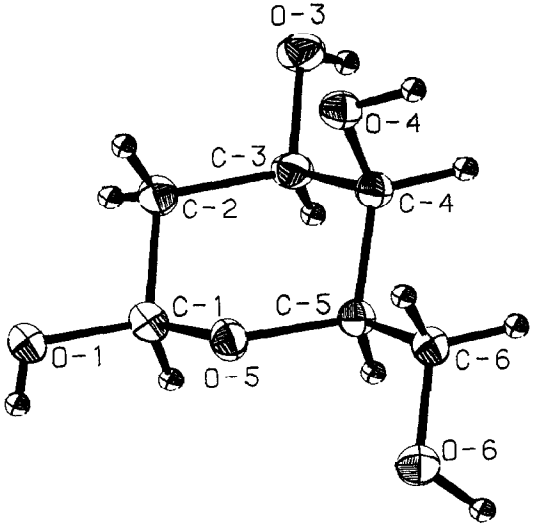

Fig. 1. View of the molecule with numbering scheme. Thermal ellipsoids at 30% probability.

TABLE II

BOND LENGTHS, BOND ANGLES AND TORSION ANGLES[a]

Bonds			
O-1–C-1	1.394(2)	C-1–C-2	1.522(2)
O-3–C-3	1.432(2)	C-2–C-3	1 517(2)
O-4–C-4	1.435(2)	C-3–C-4	1.524(2)
O-5–C-1	1.430(2)	C-4–C-5	1.540(2)
O-5–C-5	1.435(2)	C-5–C-6	1.514(2)
O-6–C-6	1.428(2)		
Angles			
C-1–O-5–C-5	112.9(1)	O-4–C-4–C-3	110.3(1)
O-1–C-1–O-5	107 2(1)	O-4–C-4–C-5	110.4(1)
O-1–C-1–C-2	109.1(1)	C-3–C-4–C-5	107.7(1)
O-5–C-1–C-2	110.6(1)	O-5–C-5–C-4	110.1(1)
C-1–C-2–C-3	108.9(1)	O-5–C-5–C-6	107.1(1)
O-3–C-3–C-2	109.3(1)	C-4–C-5–C-6	112.2(1)
O-3–C-3–C-4	112.1(1)	O-6–C-6–C-5	112.5(1)
C-2–C-3–C-4	109.9(1)		
Torsion angles			
C-5–O-5–C-1–O-1	−178.8(2)	O-3–C-3–C-4–C-5	179.7(2)
C-5–O-5–C-1–C-2	−60.0(2)	C-2–C-3–C-4–O-4	−62.6(2)
C-1–O-5–C-5–C-4	60.7(2)	C-2–C-3–C-4–C-5	57.9(2)
C-1–O-5–C-5–C-6	−177.1(3)	O-4–C-4–C-5–O-5	62.2(2)
O-1–C-1–C-2–C-3	174.9(3)	O-4–C-4–C-5–C-6	−57.0(2)
O-5–C-1–C-2–C-3	57.3(2)	C-3–C-4–C-5–O-5	−58.3(2)
C-1–C-2–C-3–O-3	178.9(3)	C-3–C-4–C-5–C-6	−177.5(3)
C-1–C-2–C-3–C-4	−57.7(2)	O-5–C-5–C-6–O-6	61.1(2)
O-3–C-3–C-4–O-4	59 1(2)	C-4–C-5–C-6–O-6	−178.0(3)

[a]Bond lengths in Å, bond and torsion angles in degrees; standard deviations in parentheses

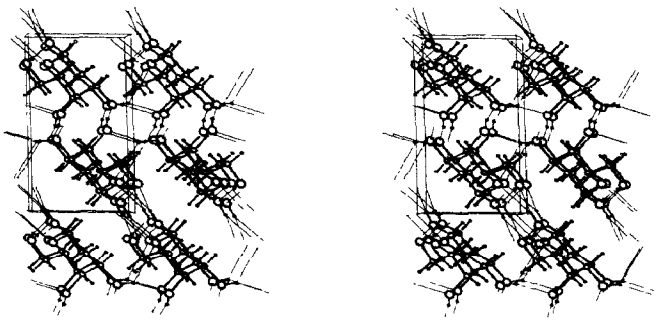

Fig. 2 Stereoview of crystal packing.

TABLE III

GEOMETRY OF THE O-H · · · O INTERMOLECULAR INTERACTIONS

D–H · · · A	*Symmetry code*	*D · · · A (Å)*	*D–H (Å)*	*H · · · A (Å)*	*∠D–H · · · A (°)*
Hydrogen bonds					
O-1–H · · · O-6	$-x, \frac{1}{2}+y, 2-z$	2.672(2)	0.93(2)	1.75(2)	169.3(1)
O-3–H · · · O-4	$x, y, -1+z$	2.962(1)	0.90(2)	2.10(2)	159.4(1)
O-4–H · · · O-3	$1-x, -\frac{1}{2}+y, 1-z$	2.789(2)	0.93(2)	1.89(2)	161.1(1)
O-6–H · · · O-1	$x, -1+y, z$	2.710(2)	0.90(3)	1.82(3)	171.6(1)
Weak interactions					
O-1–H · · · O-5	$-x, \frac{1}{2}+y, 2-z$	3.347(2)	0.93(2)	2.81(2)	117.9(1)
O-3–H · · · O-5	$x, y, -1+z$	3.258(2)	0.90(2)	2.64(2)	126.4(1)

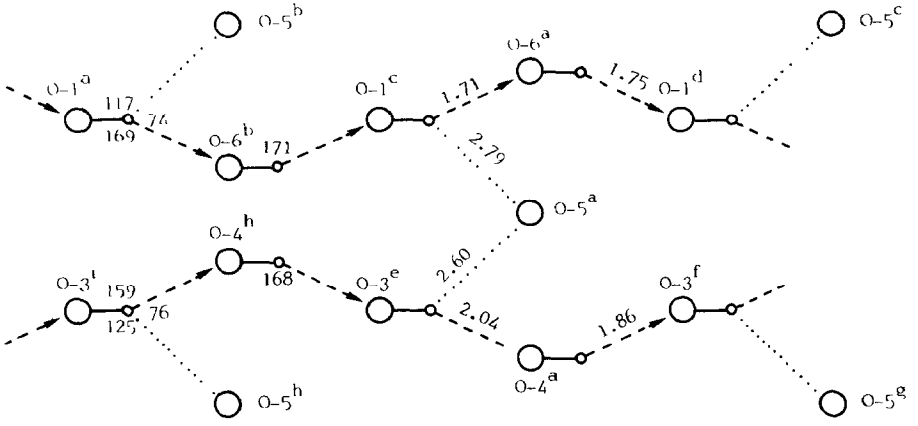

Fig. 3. Hydrogen-bonding (– – –) and weak interactions (· · · · ·) with O–H covalent bonds normalised at the neutron diffraction value of 0.97 Å. The distances are in Å, angles in degrees. Symmetry codes: a, x, y, z; b, $-x, \frac{1}{2}+y, 2-z$; c, $-x, -\frac{1}{2}+y, 2-z$; d, $x, -1+y, z$; e, $x, y, 1+z$; f, $1-x, -\frac{1}{2}+y, 1-z$; g, $1-x, -\frac{1}{2}+y, 2-z$; h, $1-x, \frac{1}{2}+y, 2-z$; i, $1-x, \frac{1}{2}+y, 1-z$.

A stereoview of the molecular packing is shown in Fig. 2. All hydroxyl oxygens, each acting both as donor and acceptor, are involved in a complex network of intermolecular hydrogen-bonds (Table III). This network can be described in terms of two helices, each winding round a screw axis, and formed by the infinite sequences ---→O-1–H---→O-6–H---→O-1–H---→ and ---→O-3–H---→O-4–H---→O-3–H---→, respectively.

The ring oxygen, which is not involved in the previously described sequences of hydrogen bonds, is located between the helices with the hydrogens HO-1 and HO-3 approximately set along its free tetrahedral positions (Fig. 3). The distances O-1 · · · O-5 and O-3 · · · O-5 are at the outer limits normally accepted for hydrogen bonds. However, for the system formed by O-3, HO-3, O-4, and O-5, the overall geometry indicates that O-5 can be considered as an acceptor in the weak component of an asymmetric, *three-center* hydrogen bond[12]. On the other

hand, for the system formed by O-1, HO-1, O-6, and O-5, which has a substantially similar geometry, the higher values of the contact distances HO-3 · · · O-5 and O-3 · · · O-5 rules out the presence of a *three-center* hydrogen bond. The interactions involving the ring oxygen and the neighbouring hydrogen atoms probably contribute to the stability of the packing, without disrupting the cooperative advantage of the infinite chains of hydrogen bonds. The pattern of these intermolecular interactions falls in the type IV of the classification given by Jeffrey and Mitra[13].

ACKNOWLEDGMENTS

This work was supported by the Italian C.N.R. and the Ministry of Public Education.

REFERENCES

1 G. BARONE, P. CACACE, G. CASTRONUOVO, AND V. ELIA, *Carbohydr. Res.*, 91 (1981) 101–111.
2 G. BARONE, P. CACACE, G. CASTRONUOVO, V. ELIA, AND U. LEPORE, *Carbohydr. Res.*, 115 (1983) 15–22.
3 G. BARONE, G. CASTRONUOVO, D. DOUCAS, V. ELIA, AND C. A. MATTIA, *J. Phys. Chem.*, 87 (1983) 1931–1937.
4 P. MAIN, M. M. WOOLFSON, AND G. GERMAIN, *MULTAN 79, A Computer Program for the Automatic Solution of Crystal Structures,* Department of Physics, University of York, U.K., 1979.
5 D. T. CROMER AND J. T. WABER, in *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974.
6 D. CREMER AND J. A. POPLE, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
7 G. A. JEFFREY AND S. TAKAGI, *Acta Crystallogr., Sect. B,* 33 (1977) 738–742.
8 J. OHANESSIAN AND H. GILLIER-PANDRAUD, *Acta Crystallogr., Sect. B,* 32 (1976) 2810–2813.
9 S. ARNOTT AND W. E. SCOTT, *J. Chem. Soc., Perkin Trans. 2,* (1972) 324–335.
10 R. U. LEMIEUX, *Pure Appl. Chem.*, 25 (1971) 527–548.
11 G. A. JEFFREY, J. A. POPLE, J. S. BINKLEY, AND S. VISHVESHWARA, *J. Am. Chem. Soc.*, 100 (1978) 373–379.
12 C. CECCARELLI, G. A. JEFFREY, AND R. TAYLOR, *J. Mol. Struct.*, 70 (1981) 255–271.
13 G. A. JEFFREY AND J. MITRA, *Acta Crystallogr., Sect. B,* 39 (1983) 469–480.