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X-RAY CRYSTAL STRUCTURE OF GALABIOSE, *O*-α-D-GALACTOPYRANOSYL-(1→4)-D-GALACTOPYRANOSE*

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ABSTRACT

O-α-D-Galactopyranosyl-(1→4)-D-galactopyranose, $C_{12}H_{22}O_{11}$, M_r = 342.30, crystallises in the orthorhombic space group $P2_12_12_1$, and has a = 5.826(1), b = 13.904(3), c = 17.772(4) Å, Z = 4, and D_x = 1.579 g.cm^{-3}. Intensity data were collected with a CAD4 diffractometer. The structure was solved by direct methods and refined to R = 0.063 and R_w = 0.084 for 2758 independent reflections. The glycosidic linkage is of the type 1-axial-4-axial with torsion angles $\phi^{O\text{-}5'}$ (O-5′–C-1′–O-1′–C-4) = 98.1(2)°, $\psi^{C\text{-}3}$ (C-3–C-4–O-1′–C-1′) = −81.9(3)°, ϕ^{H} (H-1′–C-1′–O-1′–C-4) = −18°, and ψ^{H} (H-4–C-4–O-1′–C-1′) = 35°. The conformation is stabilised by an O-3 · · · O-5′ intramolecular hydrogen-bond with length 2.787(3) Å and O-3–H · · · O-5′ = 162°. The glycosidic linkage causes a folding of the molecule with an angle of 117° between the least-square planes through the pyranosidic rings. The crystal investigated contained 56(1)% of α- and 44(1)% of β-galabiose as well as ~70% of the *gauche–trans* and ~30% of the *trans–gauche* conformers about the exocyclic C-5′–C-6′ and C-5–C-6 bonds. The crystal packing is governed by hydrogen bonding that engages all oxygen atoms except the intramolecular acceptor O-5′ and the glycosidic O-1′ oxygen atoms.

INTRODUCTION

Galabiose, *O*-α-D-galactopyranosyl-(1→4)-D-galactopyranose, is an integral part of several naturally occurring glycolipids[1]. It constitutes the terminal part of galabiosylceramide and the P^k- and P_1-antigens as well as the internal parts of

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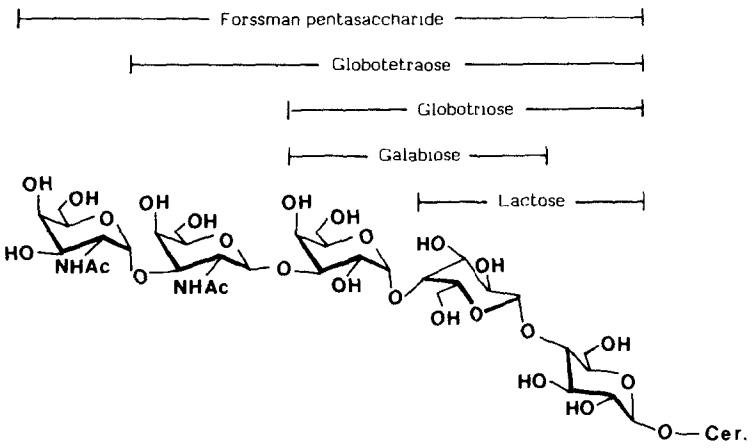

Fig. 1. Galabiose as an internal part of natural glycolipids.

globotetraosylceramide and the Forssman antigen[2] (Fig. 1). These glycolipids function as cell-surface antigens in connection with, *inter alia*, P blood-group specificity[3], Burkitt lymphoma[4], and the attachment of uropathogenic *E. coli*[5] and *Shigella dysenteriae*[6] to mammalian host cells.

Conformational analysis of various oligosaccharidic parts of these compounds has been performed using ^{1}H-n.m.r. spectroscopy[7] and computational methods[7,8]. Crystal structures have been determined for lactose[9] and for 2-acetamido-3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-1,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranose[7], which are both derivatives of the Forssman antigen (Fig. 1). The structural data on galabiose now presented should contribute to an understanding of the conformation of the complete pentasaccharide of the Forssman antigen.

EXPERIMENTAL

Colourless crystals of galabiose were grown by slow evaporation at room temperature from an aqueous methanol solution. A crystal, tabular c, with the

TABLE I

CRYSTAL DATA FOR GALABIOSE

Galabiose	$C_{12}H_{22}O_{11}$	V	1439.8(2) Å^3
M_r	342.30	Z	4
Space group	$P2_12_12_1$ (no. 19)	D_x	1.579 g.cm^{-3}
a	5.826(1) Å	$F(0,0,0)$	728
b	13.905(3) Å	μ(CuKα)	11.88 cm^{-1}
c	17.772(4) Å		

dimensions 0.3 × 0.2 × 0.09 mm^3 was selected for X-ray experiments. The measurements were made on an Enraf–Nonius CAD4 diffractometer with Cu$K\alpha$ radiation and a graphite monochromator ($\lambda K\alpha_1$ = 1.54056 Å). Cell dimensions were determined by least-squares from the θ angles for 44 strong reflections in the range $25° \leq 2\theta \leq 90°$. Reflections $h00$, $0k0$, and $00l$ are systematically extinct, indicating orthorhombic space-group $P2_12_12_1$. Crystal data are given in Table I.

Almost a full hemisphere of reciprocal space, with radius $\sin\theta/\lambda = 0.60$ $Å^{-1}$, was measured with $\omega/2\theta$ scans and $\Delta\omega = 1.10 + 0.50° \tan\theta$. A maximum counting time of 210 s resulted in $\sigma_c(I)/I \leq 0.030$ for the majority of the reflections [$\sigma_c(I)$ is based on counting statistics]. The intensities of three standard reflections were measured every second hour of X-ray exposure time; no significant variation was detected. The quantities I and $\sigma_c(I)$ were corrected for Lorentz, polarisation, and absorption effects. The range of transmission factors was 0.72–0.90. A total of 6339 structure amplitudes was measured. Averaging equivalent reflections and excluding as unobserved those with $I < 3\sigma_c(I)$ gave 2758 observed amplitudes with $R_{int} = \Sigma(F_o^2 - \langle F_o^2 \rangle)/F_o^2 = 0.094$.

STRUCTURE DETERMINATION

The structure was solved by using the MULTAN 80 programme. All non-hydrogen atoms of the α-anomer were located. Subsequent electron-density difference maps showed the presence both of the β-anomer and of two conformations (*gauche–trans* and *trans–gauche*) of the C-6–OH groups. The structure was refined by the full-matrix least-squares method, minimising $\Sigma w(F_o - F_c)^2$ with $w = [\sigma_c^2(F_o) + (0.05F_o)^2]^{-1}$. When this series of refinements had converged, a difference map revealed the location of 15 hydrogen atoms. The positions of the disordered hydrogen atoms bonded to C-1, C-6, and C-6′ were calculated assuming tetrahedral carbon atoms with a C–H bond length of 0.95 Å. Five of the eleven O–H hydrogen atoms were not found in the maps. All hydrogen atoms were assigned fixed isotropic thermal parameters $U_{iso} = 0.076$ $Å^2$ while the other atoms were allowed to vibrate anisotropically within the harmonic approximation. This structural model was refined until the highest shift/error ratio for the positional parameters was 0.06 with an average of 0.016. None of the hydrogen atom parameters were varied. Atomic scattering factors, with corrections for anomalous dispersion, were taken from International Tables for X-ray Crystallography[10]. The absolute configuration for galabiose was known from the starting materials[11]. An attempt to confirm the conformation using anomalous dispersion gave no result of significance. The final, conventional, residual indices are $R = 0.063$ and $R_w = 0.084$, with the standard deviation of an observation of unit weight $S = 1.585$. A difference map calculated at the final stage was featureless, the highest peak being 0.35 $e.Å^{-3}$. No extinction effects were detected.

The data and the final model were compared by probability-plotting of ordered values of $\delta R_1 = (F_{o,1} - F_{c,1})/\sigma(F_{o,1})$ *vs.* those expected for ordered normal

deviates [$\sigma(F_{o,i}) = w^{-1/2}$]. The result was a correlation coefficient of 0.9981, a slope of 1.494(2), and an intercept of 0.154(2). It is concluded, from the correlation coefficient and slope and the related S value, that $\sigma(F_o)$ is, on average, rather well estimated, apart from a scaling factor. The small but non-zero intercept indicates a small systematic error in the intensity measurements (*cf.* the high value of R_{int} given above).

MOLECULAR STRUCTURE

The positional and isotropic thermal parameters of the non-hydrogen atoms are given in Table II. A stereo-view of the molecular structure of galabiose is shown in Fig. 2 together with the labelling of atoms, and Fig. 3 is a view of the molecular packing. Bond lengths are given in Table III, bond angles in Table IV, and torsion angles in Table V. Hydrogen atom coordinates, anisotropic thermal parameters of the non-hydrogen atoms, hydrogen-bond distances and geometries, and a Table of observed and calculated structure factors have been deposited*. The crystal contained 56(1)% of α- and 44(1)% of β-galabiose. Similar proportions of α- and β-forms were found for mannobiose[12].

The bond lengths in galabiose are in good agreement with values encountered in many previous investigations of mono- and di-saccharides[9,13,14]. The ring C–C bonds (range 1.511–1.542 Å) are somewhat shorter than the usual single-bond distance with still shorter C-5–C-6 bonds. The latter involve both primary and secondary carbon atoms, whereas the ring C–C bonds are solely between secondary

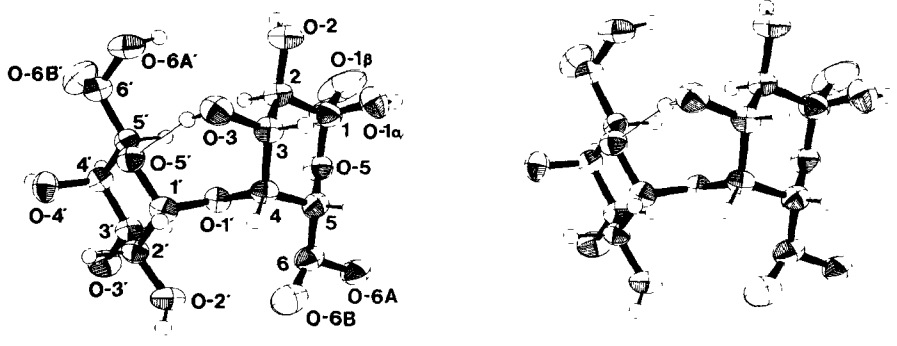

Fig. 2. Stereoscopic view of galabiose. The oxygen atoms O-1β, O-6B', and O-6B are shown as unshaded ellipsoids. The ellipsoids correspond to 50% probability

*Tables of data have been deposited with, and may 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/326/*Carbohydr. Res.*, 146 (1986) 29–38.

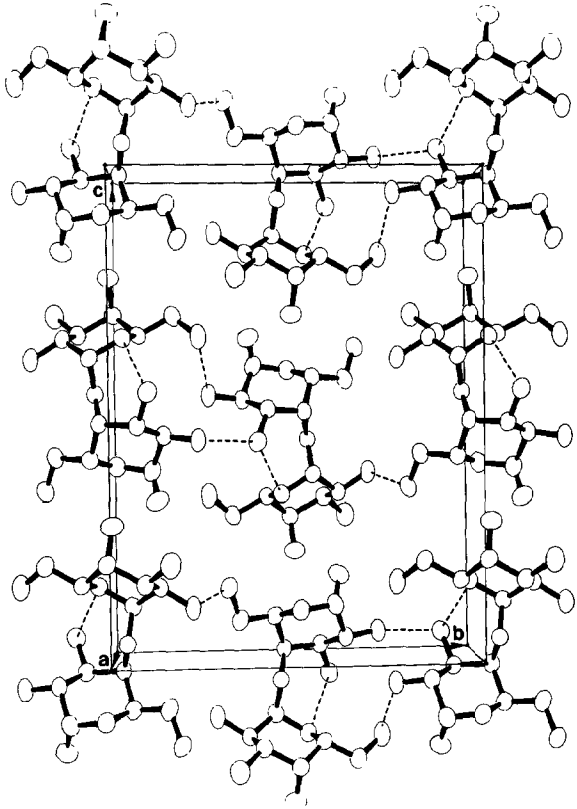

Fig. 3. The molecular packing of α-galabiose. Dashed lines indicate part of the hydrogen bond system.

atoms[9]. The endocyclic C–O bond distances are about the same as the exocyclic ones, the average being 1.434(7)* and 1.417(11)* Å, respectively, excluding the three short distances estimated for the disordered C-1–O-1, C-6′–O-6′, and C-6–O-6 bonds.

As expected, the largest endocyclic bond-angles are those at O-5 and O-5′, C-5′–O-5′–C-1′ = 112.5(2)° and C-5–O-5–C-1 = 114.7(3). These values are about the same as the average calculated from seven α-glycoside linkages, 114.3(9); and eleven methyl α-pyranosides, 113.5(8)[15].

The endocyclic torsion angles in galabiose (Table V) are in good agreement with the mean values for 32 galactose rings[16]. The exocyclic torsion angles O-2–C-2–C-1–O-1(α,β) involving the anomeric oxygen atom O-1 are different in galabiose and methyl D-galactopyranoside[13]: 47.0(4)° in α-galabiose compared to 52.0(2)°, and −44.7(7)° in β-galabiose compared to −67.4(2)°. The differences may be

*Standard deviations of average values $\bar{x}$ are here and below estimated as $[\Sigma(x - \bar{x})^2/(n - 1)]^{1/2}$.

TABLE II

FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS[a] FOR CARBON AND OXYGEN ATOMS

Atom	*x/a*	*y/b*	*z/c*	$U_{iso}/Å^2$
C-1	0.5451(7)	0 1085(2)	0.3920(2)	0.0588(10)
C-2	0.6693(5)	0.1410(2)	0.4636(1)	0 0431(8)
C-3	0.8600(5)	0.0721(2)	0.4842(1)	0.0403(7)
C-4	0.7669(5)	−0.0302(2)	0.4894(1)	0 0382(7)
C-5	0 6440(5)	−0.0566(2)	0.4159(1)	0.0440(8)
C-6	0.5284(6)	−0.1536(2)	0.4208(2)	0.0526(9)
C-1′	0.6834(4)	−0.0561(2)	0.6217(1)	0.0378(7)
C-2′	0.5385(5)	−0.1310(2)	0.6623(1)	0 0406(7)
C-3′	0.2970(5)	−0.0945(2)	0.6743(2)	0.0434(8)
C-4′	0.3020(5)	0.0033(2)	0.7151(1)	0.0436(8)
C-5′	0.4535(5)	0.0719(2)	0.6709(1)	0.0404(7)
C-6′	0.4745(7)	0.1679(2)	0.7098(2)	0.0583(10)
O-1	0.6616(7)	0.1231(3)	0.3318(2)	0.0572(13)
O-1	0.4170(21)	0.1655(5)	0 3600(5)	0.1268(45)
O-2	0.7628(4)	0.2345(1)	0 4543(1)	0.0547(6)
O-3	0.9758(4)	0.1021(1)	0.5514(1)	0.0489(6)
O-5	0.4670(4)	0.0120(1)	0 4005(1)	0 0517(6)
O-6A	0.4402(7)	−0.1848(2)	0.3511(2)	0 0577(11)
O-6B	0.6478(17)	−0.2210(6)	0.4564(4)	0.0754(29)
O-1′	0.6006(3)	−0.0419(1)	0.5484(1)	0.0370(5)
O-2′	0.5365(5)	−0.2174(1)	0.6202(1)	0.0572(7)
O-3′	0.1636(4)	−0.1619(2)	0.7150(1)	0.0630(8)
O-4′	0.3865(4)	−0.0090(2)	0.7897(1)	0.0563(7)
O-5′	0 6815(3)	0.0331(1)	0.6626(1)	0.0427(6)
O-6A′	0.5875(6)	0.2366(2)	0.6653(2)	0 0645(11)
O-6B′	0.3059(26)	0 1997(8)	0 7393(7)	0.0819(45)

[a]The form of the temperature factor is $\exp[-8\pi^2 U_{iso} \sin^2\theta/\lambda^2]$. U_{iso} is the equivalent isotropic temperature factor coefficient calculated from the average of the anisotropic temperature factor over all directions

TABLE III

BOND LENGTHS (Å) WITH STANDARD DEVIATIONS

	Primed ring	*Unprimed ring*		*Primed ring*	*Unprimed ring*
Endocyclic			*Exocyclic*		
C-1–C-2	1.522(4)	1.532(4)	C-5–C-6	1.508(4)	1.510(4)
C-2–C-3	1.511(4)	1.512(4)	C-2–O-2	1 416(3)	1.420(3)
C-3–C-4	1.542(4)	1.526(3)	C-3–O-3	1.417(4)	1 433(3)
C-4–C-5	1.518(4)	1.534(4)	C-4–O-4	1 425(3)	—
C-5–O-5	1.441(3)	1.431(4)	C-6–O-6A	1.404(5)	1.408(4)
O-5–C-1	1.437(3)	1 425(4)	C-6–O-6B	1.199(15)	1 328(9)
Glycosidic linkage			C-1–O-1α	—	1.283(5)
C-1′–O-1′	1 404(3)	—	C-1–O-1β	—	1.228(10)
C-4–O-1′	—	1 437(3)			

TABLE IV

BOND ANGLES (°) WITH STANDARD DEVIATIONS

	Primed ring	*Unprimed ring*		*Primed ring*	*Unprimed ring*
Endocyclic			*Exocyclic*		
C-1–C-2–C-3	110.7(2)	111.2(2)	O-5–C-1–O-1α	—	114.0(3)
C-2–C-3–C-4	110.2(2)	110.1(2)	O-5–C-1–O-1β	—	117.6(6)
C-3–C-4–C-5	108.8(2)	109.8(2)	C-2–C-1–O-1α		113.3(3)
C-4–C-5–O-5	110.7(2)	109.8(2)	C-2–C-1–O-1β	—	118.8(4)
C-5–O-5–C-1	112.5(2)	114.7(3)	C-1–C-2–O-2	109.6(2)	110.8(2)
O-5–C-1–C-2	110.3(2)	109.9(2)	C-3–C-2–O-2	110.6(2)	109.1(2)
			C-2–C-3–O-3	111.2(2)	111.3(2)
Glycosidic linkage			C-4–C-3–O-3	110.7(2)	112.9(2)
O-5′–C-1′–O-1′	110.2(2)	—	C-3–C-4–O-4	109.8(2)	—
C-2′–C-1′–O-1′	110.1(2)	—	C-5–C-4–O-4	110.8(2)	—
C-1′–O-1′–C-4	117.5(2)	—	C-4–C-5–C-6	111.5(2)	111.9(2)
C-5–C-4–O-1′	106.2(2)	—	O-5–C-5–C-6	107.7(2)	106.6(2)
C-3–C-4–O-1′	112.9(2)	—	C-5–C-6–O-6A	112.5(3)	112.8(3)
			C-5–C-6–O-6B	117.5(7)	115.1(5)

TABLE V

TORSION ANGLES (°) WITH STANDARD DEVIATIONS

	Primed ring	*Unprimed ring*		*Primed ring*	*Unprimed ring*
Endocyclic			*Exocyclic*		
O-5–C-1–C-2–C-3	56.0(3)	54.3(3)	O-1′–C-1′–C-2′–O-2′	56.4(3)	—
C-1–C-2–C-3–C-4	−54.1(3)	−53.7(3)	O-1α–C-1–C-2–O-2	—	47.0(4)
C-2–C-3–C-4–C-5	54.6(3)	54.4(3)	O-1β–C-1–C-2–O-2	—	−44.7(7)
C-3–C-4–C-5–O-5	−57.6(3)	−56.2(3)	O-2–C-2–C-3–O-3	61.0(3)	57.8(3)
C-4–C-5–O-5–C-1	61.6(3)	60.1(3)	O-3–C-3–C-4–O-4	56.5(3)	—
C-5–O-5–C-1–C-2	−59.8(3)	−58.6(3)	O-4–C-4–C-5–C-6	−56.6(3)	—
			O-5–C-5–C-6–O-6A	66.5(3)	67.6(3)
Glycosidic linkage			O-5–C-5–C-6–O-6B	−160.8(7)	−160.5(4)
O-5′–C-1′–O-1′–C-4′ ($\phi^{O-5'}$)	98.1(2)	—	C-4–C-5–C-6–O-6A	−171.9(3)	−172.3(3)
C-2′–C-1′–O-1′–C-4 (ϕ^{C-2})	−140.0(2)	—	C-4–C-5–C-6–O-6B	−39.2(7)	−40.4(5)
H-1′–C-1′–O-1′–C-4 (ϕ^{H})	−18	—			
C-3–C-4–O-1′–C-1′ (ψ^{C-3})	−81.9(3)	—			
C-5–C-4–O-1′–C-1′ (ψ^{C-5})	157.8(2)	—			
H-4–C-4–O-1′–C-1′ (ψ^{H})	35	—			

caused by the disorder in the galabiose crystal and by additional steric interactions in the methyl D-galactopyranosides.

The observed conformation about the exocyclic C-5–C-6 bond usually falls into two groups, namely, *gauche–trans* where C-6–O-6 is *gauche* to C-5–O-5 and *trans* to C-4–C-5, or *gauche–gauche* where C-6–O-6 is *gauche* to both. There is also the quite rare *trans–gauche* possibility[17]. The conformation about the exocyclic C-5–C-6 and C-5′–C-6′ of galabiose is disordered, showing both the *gauche–trans* and

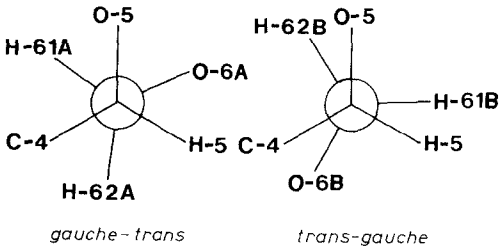

Fig. 4. View down the exocyclic bond C-5–C-6.

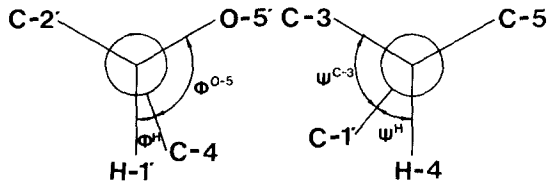

Fig. 5. View down the glycosyl C-1′–O-1′ (left) and C-4–O-1′ (right) bonds

the unusual *trans–gauche* variants (Fig. 4). The most populated is the *gauche–trans* conformation with occupancies 0.77(1) for primed and 0.67(1) for the umprimed atoms. The torsion angles for the *gauche–trans* conformation (Table V) are well within the range for 14 saccharide structures showing the same conformation[9]. The torsion angles of the *trans–gauche* form involving O-6B and O-6B′ atoms agree well with those of the pyranosyl-pyranose structure of ref. 7.

The most notable structural feature of galabiose is the conformation of the glycosidic bond. The bond is of the type 1-axial-4-axial of ref. 17. Information about the relative arrangements of the two galactose rings is provided by the torsion angles $\phi^{O-5'}$ = O-5′–C-1′–O-1′–C-4, ψ^{C-3} = C-3–C-4–O-1′–C-1′, ϕ^{H} = H-1′–C-1′–O-1′–C-4, and ψ^{H} = H-4–C-4–O-1′–C-1′. These angles are given in Table V and shown in Fig. 5. The geometry of the glycosidic linkage causes a folding of the disaccharide, which might also be a characteristic folding in different oligosaccharides shown in Fig. 1. The angle between the least-square planes through the pyranosidic rings is 116.8(1)°.

The conformation of galabiose is stabilised by an O-3–H · · · O-5′ intramolecular hydrogen-bond. A similar bond was found in β-cellobiose[18] and α-lactose[9]. The bond is of medium strength with O-3 · · · O-5′ distances of 2.787(3), 2.80(2), and 2.811(4) Å in the three structures.

The conformations of the two pyranoid rings are slightly twisted chairs, as expected. The puckering parameters and distances from the least-squares planes, based on $^4C_1$ conformations, are given in Table VI. The ring formed by the internal O-3 · · · O-5′ hydrogen bond (O-5′, C-1′, O-1′, C-4, C-3, O-3) is also a twisted chair.

TABLE VI

DEVIATIONS (Å) FROM LEAST-SQUARE PLANES AND PUCKERING PARAMETERS FOR GALABIOSE[a]

	Primed ring	*Unprimed ring*
C-1	0.670(2)	0.652(3)
C-2*	0.016(3)	0.012(3)
C-3*	−0.018(3)	−0.011(3)
C-4	−0.695(3)	−0.680(3)
C-5*	0.016(3)	0.013(3)
O-5*	−0.008(2)	−0.007(2)
Puckering parameters[20,21]		
Q (Å)	0.577(3)	0.563(3)
ϕ (°)	62(8)	27(9)
θ (°)	178.2(3)	178.3(3)
q_2 (Å)	0.018(3)	0.016(3)

[a]Starred atoms were used to calculate the least-squares planes.

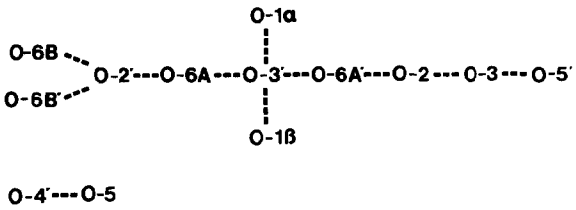

Fig. 6. Patterns of hydrogen bonding in the galabiose crystal.

MOLECULAR PACKING

The galabiose molecules are interconnected by a complex system of hydrogen bonds. Part of the system is shown in Fig. 3. The only oxygen atom that is not involved in a hydrogen bond is the glycosidic O-1′ atom. Carbohydrate molecules appear to maximise the hydrogen-bond energy by forming infinite or long finite chains of hydrogen bonds[19]. The hydrogen-bonding pattern in the galabiose crystal is shown in Fig. 6. The oxygen atom O-3′ may act as an acceptor for the proton of either of the anomeric oxygen atoms O-1α or O-1β and for O-6A. This means that both the anomers can be accommodated in the crystal structure with no apparent sacrifice in the number of hydrogen bonds. The same is true for the *trans–gauche* conformer with atoms O-6B and O-6B′.

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