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CRYSTAL STRUCTURE OF β-D-GALACTOPYRANOSYLAMINE

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ABSTRACT

The crystal structure of β-D-galactopyranosylamine ($C_6H_{13}O_5N$) is orthorhombic, with space group $P2_12_12_1$, and cell dimensions a = 7.703(2), b = 7.788(2), c = 12.645(3) Å, V = 757.612 Å^3, Z = 4; D_c and D_m are 1.573 and 1.587 cm^{-3}, respectively. Using MoKα radiation (λ = 0.7107 Å), 2841 reflections were measured on a CAD-4 diffractometer. The structure was solved by using MULTAN-78, and refined anisotropically for the non-hydrogen positional and thermal parameters. Final agreement indices are R(F) = 0.074, wR(F) = 0.086, and S = 2.1523. The conformation is $^4C_1$(D). The orientation of the primary alcohol group is *gauche/trans*. An unexpected feature of the hydrogen bonding is that the amino group accepts a strong O-H---N bond, but has no donor functionality in the crystal structure.

INTRODUCTION

The two amino sugars most widely distributed in Nature are 2-amino-2-deoxy-D-glucose and 2-amino-2-deoxy-D-galactose. The former is found in "mucopolysaccharides" of vertebrate tissue, and as a component of chitin[1], a structural polysaccharide that occurs in abundance in exoskeletons of crustaceans and insects. The latter compound, on the other hand, is mainly found as a component of glycolipids and the glycosaminoglycans of cartilage[2].

Surprisingly, no crystal-structure determinations have hitherto been reported for the simple amino sugars, and only three structures are reported for the amino sugar cations; 2-amino-2-deoxy-β-D-gluco-[3–5] and -galactopyranose hydrochlorides[6] and the D-*gluco* hydrobromide[4,5]. 2-Amino-2-deoxy-α-D-galactopyranosyl phosphate is a zwitterion in the crystal structure of the monohydrate[7].

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TABLE I

SUMMARY OF CRYSTAL DATA FOR β-D-GALACTOPYRANOSYLAMINE

Crystal data

a = 7.703(2), b = 7.788(2), c = 12.645(3) Å
Unit cell volume = 757.612 Å^3
D_c (calculated density) = 1.573, D_m (measured density) = 1.587 g/cm^3
Space group $P2_12_12_1$, Z = 4

Experimental and refinement data

Crystal dimensions, 0.2 × 0.2 × 0.7 mm
Total number of reflections measured, 2841
Number of independent reflections measured, 2650
$2\theta_{max}$ = 80°; data collection mode, $\theta - 2\theta$ step scan with fixed width of 2.6°
Wavelength (MoKα radiation) = 0.7107 Å; temperature, 293 K
Final cycles of refinements:
  No. of reflections, 2117
  No. of variables, 109[a]
  Cut-off for sigma data, $F/\sigma(F) < 2\sigma$ (unit weights and counting statistics used)
  For observed reflections, R(F) = 0.074[b], wR(F) = 0.086, S (goodness of fit) = 2.1523[c]

[a] Refinement of non-hydrogen positional and thermal factors only. [b] Function minimized: $R = \Sigma w(|F_o| - |kF_c|)^2$. [c] S is given by $[R/(n - m)]^{1/2}$, where n is the number of reflections, and m is the number of refinable parameters.

EXPERIMENTAL AND REFINEMENT METHODS

The crystal data for β-D-galactopyranosylamine, $C_6H_{13}O_5N$, are given in Table I. A CAD-4 diffractometer, with MoKα radiation (λ = 0.7107 Å) was used to measure 2841 reflections. The unit-cell dimensions were refined from 40 reflections with 2θ ~40°. Three monitor reflections showed no evidence of radiation damage. No corrections were made for absorption or extinction. The direct-method program[8] MULTAN-78, with 147 reflections with $|E| > 1.20$, revealed the positions of the non-hydrogen atoms, which were refined isotropically to R = 0.10.

Difference maps revealed the positions of the methylene hydrogen atoms associated with the ring-carbon atoms and the primary alcohol carbon atom (C-6) in stereochemically reasonable positions. For these atoms, the coordinates calculated from the non-hydrogen-atom geometry were used, and were not refined.

The hydroxyl-hydrogen atoms associated with O-2, O-3, O-4, and O-6 were located on sections of the difference map calculated at 0.7 Å from the appropriate oxygen atom and perpendicular to the C–O bond. The coordinates of the four hydroxyl-hydrogen positions obtained in this way were not refined. A similar, difference-map section used to locate the amino-hydrogen atoms showed only a diffuse region of electron density in the plane where H-1–N and H-2–N were expected. The positions of these hydrogen atoms could not be determined, and they were not included in the structure-factor calculations.

The non-hydrogen, atomic parameters were refined by the full-matrix, least-squares program[9] QWKREF, minimizing $R = \Sigma w(|F_o| - |kF_c|)^2$, with $w^{-1} = \sigma_c^2$,

TABLE II

ATOMIC PARAMETERS[a] FOR β-D-GALACTOPYRANOSYLAMINE

Atom	*Fractional coordinates*[b]			U_{eq} *or B*[c]
	x	*y*	*z*	
N	−11961(3)	545(3)	−8697(2)	179(4)
C-1	−10217(3)	707(3)	−8977(2)	191(5)
C-2	−9379(3)	2111(3)	−8313(2)	184(5)
C-3	−7413(3)	2120(3)	−8534(2)	214(5)
C-4	−6644(3)	332(3)	−8398(2)	209(5)
C-5	−7633(3)	−915(4)	−9106(2)	208(5)
C-6	−7019(4)	−2766(4)	−9011(3)	294(6)
O-2	−10054(3)	3747(2)	−8607(2)	260(5)
O-3	−6538(3)	3352(3)	−7896(2)	365(6)
O-4	−6782(3)	−193(3)	−7305(2)	284(5)
O-5	−9429(3)	−913(3)	−8792(2)	227(4)
O-6	−8078(3)	−3873(3)	−9641(2)	328(5)
H-C-1	−1011	103	−981	6
H-C-2	−962	187	−748	6
H-C-3	−723	249	−936	7
H-C-4	−528	35	−863	7
H-C-5	−753	−50	−993	8
H-1-(C-6)	−568	−285	−928	10
H-2-(C-6)	−710	−317	−819	10
H-O-2	−1123	369	−844	10
H-O-3	−732	379	−754	10
H-O-4	−587	3	−702	10
H-O-6	−739	−444	−1032	11

[a] E.s.d. values given in parentheses refer to the least significant digit. [b] Fractional coordinates × 10^4 for non-hydrogen atoms; × 10^3 for hydrogen atoms. [c] $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$; $B = 8\pi^2 \langle U^2 \rangle$.

where σ_c is from counting statistics. The non-hydrogen positional and anisotropic thermal parameters, and an overall scale factor were refined. The final parameters are shown in Table II*. Representation of the atomic structure, using thermal ellipsoids, was obtained by employing the ORTEP-II program[10].

DISCUSSION

The bond distances, and valence and torsion angles are shown in Fig. 1. The conformation is $^4C_1$(D), with puckering parameters[11] $Q = 0.592$ Å, $\theta = 4.89°$, $\varphi = 312.99°$. The C–C bond lengths range from 1.521(4) to 1.540(4) Å, and the exo-cyclic, C–O bond lengths from 1.423(4) to 1.430(4) Å. The two ring C–O bond lengths differ by 0.021 Å, which is significant at 3.5 σ. These data are consistent

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*Lists of observed and calculated structure factors, anisotropic thermal parameters, and bond distances, valence angles, and torsion angles 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/315/*Carbohydr. Res.*, 142 (1985) 39–45.

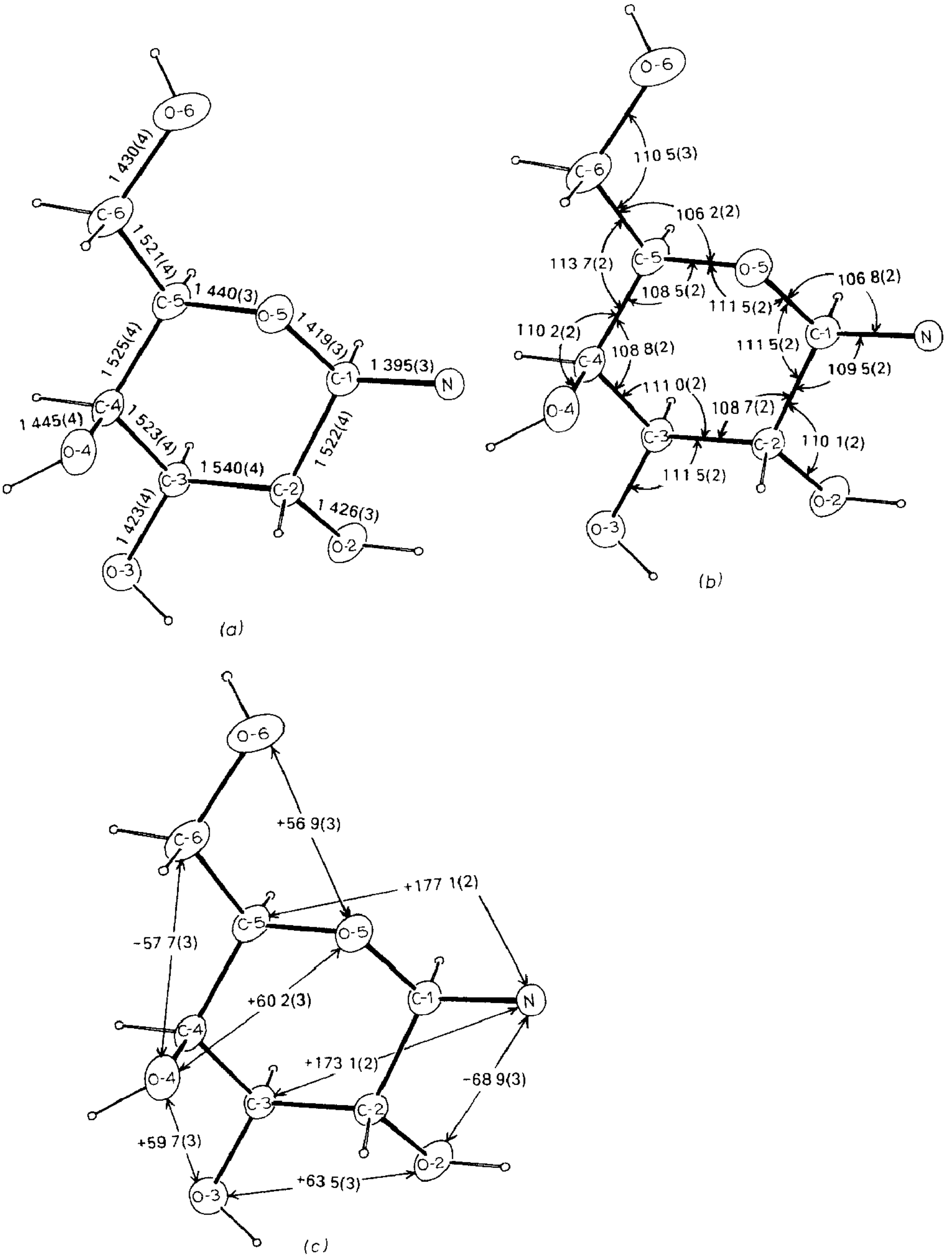


Fig. 1. Selected molecular dimensions for β-D-galactopyranosylamine. (*a*) Bond distances, Å; (*b*) valence angles, degrees; (*c*) torsion angles, degrees. E.s.d. values are given in parentheses.

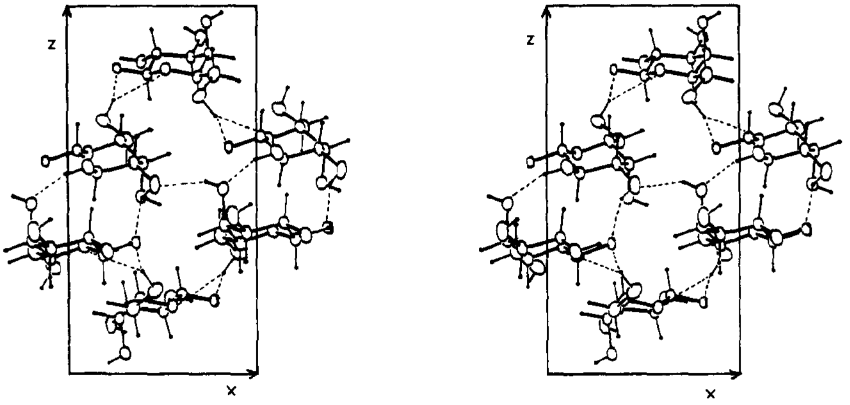
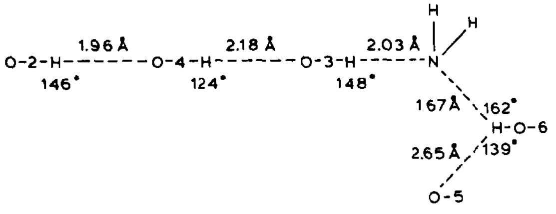


Fig. 2. Stereoview of the unit cell contents in β-D-galactopyranosylamine. The thermal ellipsoids are at 20% probability[10].

with observations on other β-pyranoses. The C–NH_2 bond-length of 1.395(3) Å is shorter than the standard, single-bond length of 1.426 Å; this is consistent with the bond-shortening effect observed in other β-pyranoses. The O-5–C-1–N-1 valence angle of 106.8(2)° is also consistent with the less than tetrahedral angle observed in other β-pyranoses and pyranosides[12]. The orientation of the primary alcohol group is *gauche/trans*, with O-5–C-5–C-6–O-6 = +57°. Fig. 2 is a stereoview of the molecular packing in the unit cell.

Hydrogen bonding

The geometry of the hydrogen bonding is shown in the molecular packing diagram in Fig. 2, and schematically below, with the covalent O–H and N–H bond-distances fixed at the neutron-diffraction values of 0.970 and 1.030 Å, respec-



tively[13]. It consists of a short chain that starts with O-2-H and ends at the nitrogen atom, with a separate, unsymmetrical, three-center bond from O-6-H to the amino nitrogen atoms and the ring-oxygen atom (O-5). It most resembles the hydrogen-bonding of type III observed in methyl β-D-galactopyranoside, except that the chain is finite, rather than infinite[14].

An unexpected feature is that the amino group accepts a strong hydrogen-bond from O-6-H, and a weak bond from O-3-H, but has no donating function.

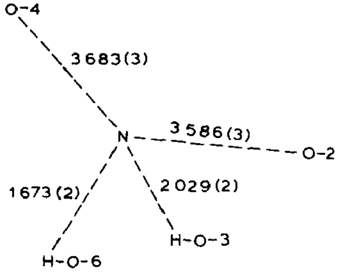


Fig. 3. The environment of the nitrogen atom as viewed along the C-1–N bond. Distances are in Å; e.s.d. values are in parentheses.

The closest intermolecular N---H and N---O separations are shown in Fig. 3. Other than O-3-H and O-6-H, which are hydrogen-bond donor-groups, there are no oxygen atoms closer than 3.5 Å. Because an amine would be expected to accept one hydrogen-bond, in the lone-pair direction, the two O-H---N hydrogen-bond distances may correspond to alternative orientations of the NH_2 group about the C–N bond. The resulting disorder in the hydrogen atoms would account for our inability to locate their positions*. This behaviour of an amino group on the anomeric carbon atom (C-1) is the reverse of that commonly observed with anomeric hydroxyl groups, which generally form strong hydrogen bonds as donors, while being weak hydrogen-bond acceptors[14].

ACKNOWLEDGMENTS

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*Referee's suggestion.

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