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β-1-Acetamido-4-*O*-β-D-galacto-pyranosyl-D-glucopyranose dihydrate

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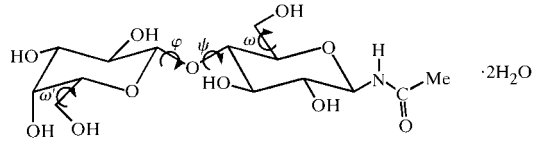
The crystal structure of the title compound, $C_{14}H_{25}NO_{11}\cdot 2H_2O$, has been determined. The glucose and galactose residues are in a $^4C_1$ conformation. The *N*-acetyl group has a *Z-anti* conformation.

Comment

The oligosaccharide components of glycoproteins play an important role in various biological recognition processes, such as protein targeting and cellular recognition (Dwek, 1996). As part of our efforts to unravel the structural aspects of *N*-glycopeptides, we have reported previously the crystal structures of simple model compounds of the linkage region, *viz*. β-1-*N*-acetamido-D-glucopyranose (Sriram *et al.*, 1997) and β-1-*N*-benzamido-D-glucopyranose (Sriram, Srinivasan *et al.*, 1998), and also β-1-*N*-acetamido-2-acetamido-2-deoxy-D-glucopyranose and β-1-*N*-benzamido-2-acetamido-2-deoxy-D-glucopyranose (Sriram, Lakshmanan *et al.*, 1998). For the present study, the title compound (I) was chosen as a disaccharide model.



(I)

The structure of (I) together with the atom-numbering scheme is shown in Fig. 1 (*PLATON*; Spek, 2000). Selected geometrical parameters are listed in Table 1. Both the glucose and galactose residues adopt a $^4C_1$ conformation. The three-dimensional structure of the disaccharide is determined by the glycosidic torsion angles φ(C14—O14—C21—O25) and ψ(C21—O14—C14—C15), the values of which are −89.3 (2) and −157.84 (18)°, respectively. These values compare well with those reported in the literature for the related disaccharides methyl β-lactoside (Stenutz *et al.*, 1999) and methyl β-cellobioside (Ham & Williams, 1970) (Table 2). While there is a good agreement of φ with the corresponding values in *N*-acetyl-α-lactosamine (−88.1°) and α-lactose (−92.60°), the value of ψ differs by about 15–20°. The exocyclic primary hydroxyl group adopts a *gg* and *gt* conformation in glucose and galactose residues, respectively (*gg* is *gauche–gauche* and *gt* is *gauche–trans*). This is indicated by ω(O15—C15—C16—O16) being −59.3 (2)° and ω′(O25—C25—C26—O26) being 58.3 (2)°. In the lactose derivatives shown in Table 3, the glucose hydroxymethyl group is in a *gt* conformation, except for the cases of methyl β-lactoside and *N*-acetyl-α-lactosamine.

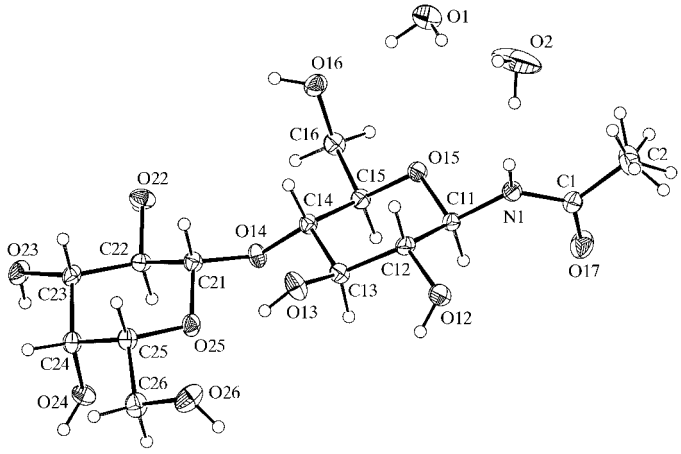


Figure 1
The structure of (I) showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level for C and O atoms. H atoms are shown as spheres of arbitrary radii.

As is observed in the other model compounds reported by us and also in GlcNAc–Asn (Delbaere, 1974), the *N*-acetyl group has a *Z-anti* conformation, as shown by the torsion angles C11—N1—C1—C2 [173.0 (2)°] and C1—N1—C11—O15 [−101.1 (3)°]. When the molecule exists in a fully extended conformation, the angles C14—O14—C21—O25 and C21—O14—C14—C13 should be close to −110 and 110°, respectively (Fries *et al.*, 1971). However, probably to accommodate the intramolecular hydrogen bond observed in most of the β(1(→)4)-linked disaccharides between the O25 and O13 atoms, compound (I) undergoes a symmetrical twist about the bridge glycosidic bonds, with the two torsion angles being −89.3 (2) and 81.5 (3)°, respectively.

Both hydrate molecules are extensively involved in a network of hydrogen bonds which fall into two categories: (i) a finite chain of hydrogen bonds starting from O24—H and ending at O25, passing through the two water molecules, and (ii) a finite chain of hydrogen bonds starting at O24—H and ending at O17, with a hydrogen bond also between N1—H and O17. An infinite chain of hydrogen bonds alternates between O23 and O26 (Table 2).

Experimental

The title compound was prepared by peracetylation followed by selective de-*O*-acetylation of β-lactosylamine. Lactose dissolved in a saturated aqueous ammonium bicarbonate solution was allowed to react for five days to obtain β-lactosylamine (Likhosherstov *et al.*, 1986). The amine obtained after lypophilization was extracted with methanol and treated with pyridine and acetic anhydride to obtain the peracetylated product, which on subsequent de-*O*-acetylation

with sodium methoxide gave compound (I) in an overall yield of 30% [m.p. 515 K (decomposition); literature: 519–521 K (Kuhn & Kruger, 1954)]. Crystals suitable for analysis were obtained from an aqueous methanol solution by slow evaporation.

Crystal data

$C_{14}H_{25}NO_{11}\cdot 2H_2O$
$M_r = 419.38$
Triclinic, $P1$
$a = 4.860\ (6)$ Å
$b = 7.603\ (10)$ Å
$c = 13.242\ (2)$ Å
$\alpha = 85.47\ (1)^\circ$
$\beta = 84.06\ (2)^\circ$
$\gamma = 75.19\ (1)^\circ$
$V = 469.8\ (9)$ Å^3
$Z = 1$
$D_x = 1.482$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15$–25°
$\mu = 0.13$ mm^{-1}
$T = 293\ (2)$ K
Prismatic, colourless
0.35 × 0.35 × 0.34 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{min} = 0.92$, $T_{max} = 0.96$
1650 measured reflections
1650 independent reflections
1592 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.0^\circ$
$h = -5 \rightarrow 5$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 15$
2 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.072$
$S = 1.04$
1650 reflections
274 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.0587P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O14—C21	1.384 (3)	N1—C1	1.334 (3)
O14—C14	1.432 (3)	N1—C11	1.434 (3)
O15—C11	1.417 (3)	C15—C16	1.512 (4)
O25—C21	1.422 (3)	C25—C26	1.506 (4)
C21—O14—C14	117.37 (18)	C1—N1—C11	122.7 (2)
C11—O15—C15	111.98 (18)	O15—C11—N1	107.11 (19)
C21—O25—C25	113.61 (18)		
C11—N1—C1—O17	−7.5 (4)	C21—O14—C14—C13	81.5 (3)
C11—N1—C1—C2	173.0 (2)	O15—C15—C16—O16	−59.3 (2)
C1—N1—C11—O15	−101.1 (3)	C14—O14—C21—O25	−89.3 (2)
C21—O14—C14—C15	−157.80 (18)	O25—C25—C26—O26	58.3 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O22^{i}	0.82	1.93	2.721 (3)	162
O13—H13···O25	0.82	2.06	2.767 (3)	144
O16—H16···O12^{ii}	0.82	1.93	2.749 (4)	172
O22—H22···O13^{iii}	0.82	1.96	2.767 (4)	170
O23—H23···O26^{iii}	0.82	1.97	2.753 (4)	159
O24—H24···O2^{iv}	0.82	1.86	2.675 (3)	171
O26—H26···O23^{i}	0.82	1.90	2.716 (5)	173
N1—H1···O17^{v}	0.86	2.10	2.849 (4)	146
O1—H111···O17^{v}	0.82 (4)	2.08 (4)	2.872 (5)	161 (5)
O1—H112···O16	0.88 (4)	1.91 (4)	2.782 (3)	168 (4)
O2—H211···O1^{vi}	0.85 (4)	1.91 (4)	2.758 (4)	170 (5)
O2—H212···O1	0.82 (4)	2.07 (4)	2.804 (5)	148 (5)

Symmetry codes: (i) $x-1, 1+y, z$; (ii) $1+x, y-1, z$; (iii) $x, y-1, z$; (iv) $x, y, z-1$; (v) $1+x, y, z$; (vi) $x-1, y, z$.

Table 3
Comparison of selected torsion angles of lactosyl acetamide, (I), with those of related disaccharides (°).

Compound	φ	ψ	ω	ω'
Lactosyl acetamide·H_2O[a]	−89.3	−157.8	−59.5	58.1
Methyl β-lactoside·CH_3OH[b]	−88.4	−161.3	−54.6	57.3
Methyl β-cellobioside·CH_3OH[c]	−91.1	−160.7	−55.1	52.4
β-Lactose[d]	−70.9	−131.5	72.6	50.5
α-Lactose·H_2O[e]	−92.6	−143.0	63.2	59.4
N-Acetyl-α-lactosamine·H_2O[f]	−88.1	−139.5	−56.0	66.8
α-Lactose·$CaCl_2\cdot 7H_2O$[g]	−76.9	−136.9	63.8	59.8
α-Lactose·$CaBr_2\cdot 7H_2O$[h]	−76.0	−134.9	61.9	62.4

Notes: (*a*) this report; (*b*) Stenutz *et al.* (1999); (*c*) Ham & Williams (1970); (*d*) Hiroustu & Shimada (1974); (*e*) Fries *et al.* (1971); (*f*) Longchambon *et al.* (1981); (*g*) Cook & Bugg (1973); (*h*) Bugg (1973).

The water H atoms were located from the difference Fourier map and were refined isotropically. All other H atoms were treated as riding (N—H = 0.86 Å and C—H = 0.96–0.98 Å).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1160). Services for accessing these data are described at the back of the journal.

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