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Schiff bases or glycosylamines: crystal and molecular structures of four derivatives of D-mannose

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Abstract

Crystal and molecular structures of four derivatives of D-mannose are described. Each could exist as either an open-chain Schiff base or as a glycosylamine in the solid state. The derivative formed upon reaction of D-mannose with hydroxylamine is an open-chain oxime, but those formed upon reaction with semicarbazide, aniline, and *p*-chloroaniline are glycosylamines. The oxime, which crystallizes as the syn-(E) isomer, has a fully extended carbon chain. The glycosylamines are all β-pyranoses. The packing arrangement of the oxime involves 'head-to-tail' hydrogen bonding. The semicarbazide derivative, which crystallizes as a dihydrate, features a hydrogen-bonded intramolecular bridge formed by the two water molecules and linking O-6 to the carbonyl oxygen atom. The packing arrangements of the aniline and *p*-chloroaniline derivatives differ from each other but are nevertheless closely related by similar hydrogen-bonding interactions.

Keywords: Schiff bases; Monosaccharide oximes; Monosaccharide semicarbazide derivatives; *N*-arylmannopyranosylamines; X-ray crystallography

1. Introduction

Monosaccharides react with ammonia derivatives to form monosaccharide derivatives that can exist as Schiff bases (open-chain imino compounds) or as glycosylamines. Over the years a variety of experimental techniques have been used to determine which of the two structures is assumed by a given monosaccharide derivative in solution and in the solid state. X-ray crystallography has been used to determine the structures of several of these compounds, and with respect to whether the compound exists as an open chain or as a ring, the results have been mixed. For example, the *p*-bromophenylhydrazone [1,2], tosylhydrazone [3], and oxime [4] of D-glucose have been found to crystallize as cyclic structures, as have the *p*-bromophenylhydrazone of D-arabinose [1,5] and the tosylhydrazones of L-arabinose and D-galactose [3]. In contrast, the phenylhydrazone [6] and *p*-bromophenylhydrazone [7] of D-mannose, the *p*-bromophenylhydrazone of D-ribose [1,8], and the oxime of D-arabinose [4] have been shown to assume acyclic structures in the solid state. The factors that determine which form, Schiff base or glycosylamine, will occur in the solid state are not well known, but are clearly more subtle than simply the chemical identity of the monosaccharide, as is demonstrated by the fact that crystalline arabinose derivatives occur in both acyclic and cyclic forms.

As part of a study of the solid-state structures of monosaccharide derivatives aimed at

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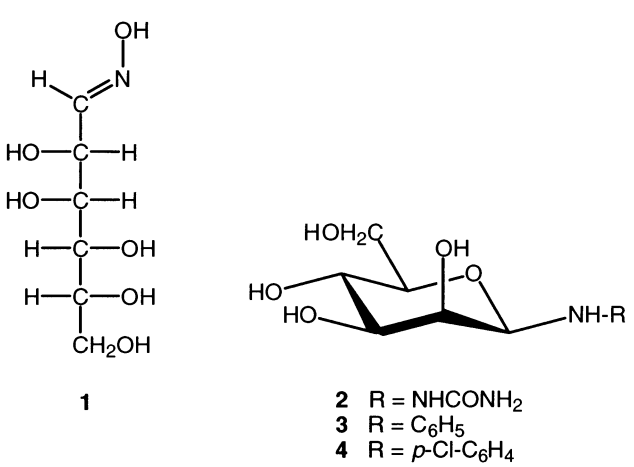
a better understanding of the factors that determine which structural type is formed, we have prepared several derivatives of D-mannose and have determined their crystal structures. We considered D-mannose particularly interesting as a parent monosaccharide because its behavior when treated with hydrazine derivatives, forming crystalline open-chain hydrazones, is different from that of the other aldohexoses D-glucose and D-galactose, which when treated with these reagents form crystalline glycosylamines. We have examined the products of the reaction of D-mannose with hydroxylamine, with semicarbazide, with aniline, and with *p*-chloroaniline. Reaction with hydroxylamine could produce a compound crystallizing as an open-chain oxime or as a cyclic hydroxylamine, although ^{13}C NMR studies have shown that for D-mannose the open-chain form of the derivative is the one assumed in solution [9]. Reaction with semicarbazide could produce a crystalline open-chain semicarbazone or an *N*-mannopyranosylsemicarbazide. Previous workers, obtaining an open-chain pentaacetate in solution (structure determined by solution NMR) upon acetylating D-mannose semicarbazone, have suggested that the predominant form of D-mannose semicarbazone in solution is therefore the open chain as well [10]. Reaction with aniline or *p*-chloroaniline could yield the open-chain Schiff base or the *N*-arylmannopyranosylamine. Studies on acetylated derivatives described in the older literature support the glycosylamine structure for sugar 'anilides' [11], but a subsequent claim that this form had thus been proved conclusively to be the one usually assumed in the normal crystalline state by sugar anilides [12] was not accepted without reservation [13,14]. Subsequent IR spectroscopic studies (samples in KBr discs) support the cyclic structure in the solid state for both the *N*-phenyl- and *N*-*p*-chlorophenylmannosylamines examined here [15]. Recent crystallographic studies performed on acetylated '*p*-nitroanilides' of lyxose and arabinose, compounds of interest as potential model systems for nucleosides, have shown that these compounds assume β-pyranose structures in the solid state as well [16]. On the other hand, given the fact that the phenylhydrazone and *p*-bromophenylhydrazone of D-mannose have been isolated in Schiff base form, we considered the possibility of isolating an open-chain anilide or *p*-chloroanilide of D-mannose to be worth investigating, so we prepared these compounds and determined their crystal structures to establish their molecular configurations conclusively.

We have found that, like the arabinose derivatives, the mannose derivatives are not confined to a single structural type (Scheme 1). We have found the hydroxylamine derivative **1** to be a true open-chain oxime, but the derivatives formed on reaction with semicarbazide, aniline, and *p*-chloroaniline, compounds **2**–**4**, to be glycosylamines. The *N*-mannopyranosylsemicarbazide **2** crystallizes as a dihydrate. The *N*-phenylmannopyranosylamine **3** in particular demonstrates the sensitivity of the crystallizing compound to structural influences, the difference of only the –NH– group between aniline and phenylhydrazine being sufficient to produce radically different molecular structures in the corresponding mannose derivatives.



1

2 R = $NHCONH_2$
3 R = C_6H_5
4 R = *p*-Cl-C_6H_4

Scheme 1. Derivatives obtained.

2. Results and discussion

Molecular geometry.—ORTEPII [17] drawings showing the atom numbering scheme and molecular conformation for each compound are presented as Figs. 1–4. Torsional angles for all four structures are listed in Table 1.

The D-mannose oxime **1** is found to possess a fully extended carbon chain. The compound

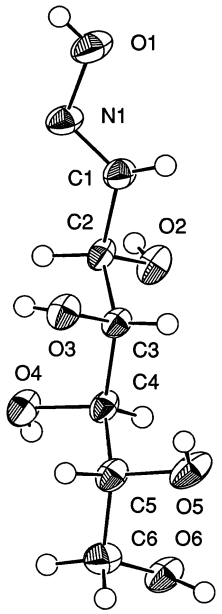


Fig. 1. ORTEPII [17] drawing of **1**, showing atom numbering. The ellipsoids are drawn at the 50% probability level.

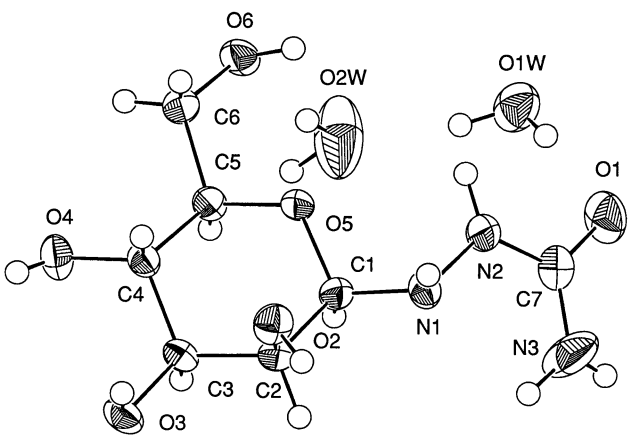


Fig. 2. ORTEPII [17] drawing of **2**, showing atom numbering. The ellipsoids are drawn at the 50% probability level.

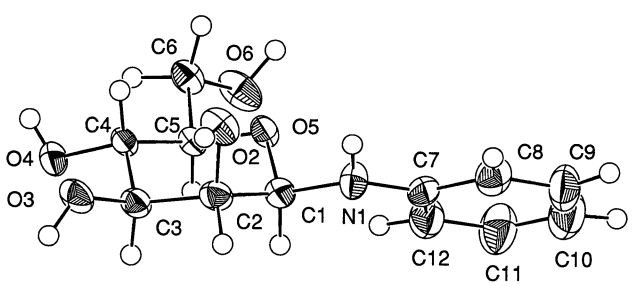


Fig. 3. ORTEPII [17] drawing of **3**, showing atom numbering. The ellipsoids are drawn at the 50% probability level.

is the syn-(E) isomer, the N-1–O-1 bond oriented syn with respect to the C-1–H-1 bond. The C-1–N-1 bond eclipses the C-2–H-2 bond, H-2 being the least sterically demanding of the substituents on C-2. It is interesting that this particular conformation is also found in mannose phenylhydrazone and mannose *p*-bromophenylhydrazone but not in arabinose oxime, an ostensibly more closely related compound. In the anti isomer of arabinose oxime, the C-1–N-1 bond is twisted away from the C-2–H-2 bond so that the C-1–H-1 bond is almost eclipsed by C-2–O-2; in the syn isomer, the C-1–N-1 bond eclipses the C-2–O-2 bond. A similarity shared by **1** and both isomers of arabinose oxime (and with the two arylhydrazones as well) is that the zig-zag of the chain ends with the terminal carbon, the C–C–C–O torsional angle involving the primary hydroxyl assuming a value close to 60° in these structures.

Comparison of relevant bond lengths in the *N*-mannopyranosylsemicarbazide **2**, the *N*-phenylmannopyranosylamine **3**, and the *N*-*p*-chlorophenylmannopyranosylamine **4** indicates that the aglycones do not differ greatly in their degree of interaction with the monosaccharide ring. The length of the C-1–N-1 bond in **2**–**4** is the same within experimental uncertainty; in addition, although the O-5–C-1 bond length is greater than the O-5–C-5 bond length in all three structures, the differences in length between these bonds do not vary significantly from structure to structure. Bond angles do differ, with the C-1–N-1–N-2 bond angle of 113.1(2)° in **2** becoming a C-1–N-1–C-7 bond angle of 122.4(2)° in **3** and 123.2(2)° in **4**. These latter two values are comparable with the 122.0(3) and 123.8(2)° values found in *N*-*p*-nitrophenyl-*N*-(2,3,4-tri-*O*-acetyl-β-D-lyxopyranosyl)amine and *N*-*p*-nitrophenyl-*N*-(2,3,4-tri-*O*-acetyl-(α-L-arabinopyranosylamine, respectively [16], in which delocalization of the nitrogen unshared electron

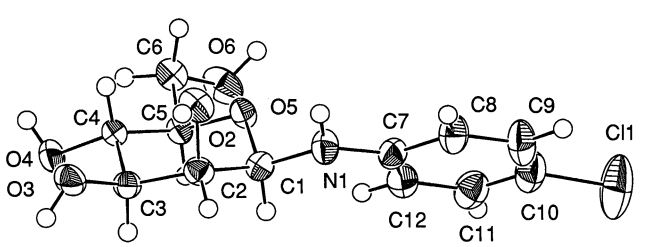


Fig. 4. ORTEPII [17] drawing of **4**, showing atom numbering. The ellipsoids are drawn at the 50% probability level.

Table 1
Selected torsional angles (°)

	1	2	3	4
N-1–C-1–O-5–C-5		177.8(2)	176.8(2)	177.5(2)
N-1–C-1–C-2–C-3	−124.9(2)	177.4(2)	175.6(2)	174.5(2)
N-2–N-1–C-1–C-2		−178.8(2)		
O-1–N-1–C-1–C-2		−178.0(2)		
O-2–C-2–C-1–N-1	115.0(3)	58.0(2)	55.2(3)	53.5(2)
O-2–C-2–C-1–O-5		−62.4(2)	−65.8(3)	−67.3(2)
O-2–C-2–C-3–O-3	180.0(2)	−61.9(2)	−53.6(3)	−52.6(2)
O-2–C-2–C-3–C-4	−56.4(3)	64.2(2)	67.9(3)	69.3(2)
O-3–C-3–C-2–C-1	60.1(2)	177.5(2)	−173.0(2)	−172.4(2)
O-3–C-3–C-4–O-4	67.4(2)	−60.4(2)	−67.8(2)	−67.5(2)
O-3–C-3–C-4–C-5	−52.4(3)	−178.7(2)	172.6(2)	172.4(2)
O-4–C-4–C-3–C-2	−55.1(3)	174.8(2)	171.0(2)	170.8(2)
O-4–C-4–C-5–O-5	−175.7(2)	−179.6(2)	−175.0(2)	−175.3(2)
O-4–C-4–C-5–C-6	63.2(3)	60.9(2)	65.7(2)	65.1(2)
O-5–C-1–N-1–N-2		−58.6(2)		
O-5–C-1–N-1–C-7			−72.1(3)	−73.3(3)
O-5–C-1–C-2–C-3		57.0(2)	54.6(3)	53.7(2)
O-5–C-5–C-4–C-3	−57.0(2)	−58.8(2)	−55.6(2)	−55.6(2)
O-5–C-5–C-6–O-6	−61.0(3)	63.1(2)	73.8(2)	73.6(2)
O-6–C-6–C-5–C-4	60.6(3)	−175.8(2)	−165.0(2)	−165.0(2)
C-1–N-1–N-2–C-7		−115.3(2)		
C-1–N-1–C-7–C-8			178.5(2)	−178.7(2)
C-1–O-5–C-5–C-4		63.1(2)	61.6(2)	61.7(2)
C-1–O-5–C-5–C-6		−174.2(2)	−175.6(2)	−175.7(2)
C-1–C-2–C-3–C-4	−176.2(2)	−56.4(2)	−51.4(3)	−50.5(2)
C-2–C-1–N-1–C-7			166.7(2)	165.4(2)
C-2–C-1–O-5–C-5		−61.7(2)	−61.1(2)	−60.7(2)
C-2–C-3–C-4–C-5	−174.8(2)	56.5(2)	51.4(3)	50.7(2)
C-3–C-4–C-5–C-6	−178.1(3)	−178.3(2)	−175.0(2)	−175.2(2)

pair into the aromatic ring is suggested. On the other hand, the N-1–C(aryl) bonds in **3** and **4** are longer than those reported for the nitrophenyl compounds (1.392(3) Å for both **3** and **4** compared with 1.377(5) Å for the lyxose derivative and 1.383(3) Å for the arabinose derivative), indicating that if delocalization does occur in **3** and **4**, it is of lesser importance in these structures than it is in the structures with the powerfully electron-withdrawing nitro substituent.

Compounds **2**–**4** all exist as the β anomer in these solid-state structures, and all assume the $^4C_1$ conformation. Cremer–Pople puckering parameters [18–20] (calculated using the program PLATON-94 [21]) for the three pyranose rings are $Q = 0.595(4)$ Å, $\Theta = 0.0(4)°$, $\Phi = 292.7(248)°$ for **2**; $Q = 0.557(3)$ Å, $\Theta = 3.8(2)°$, $\Phi = 354.5(36)°$ for **3**; and $Q = 0.556(3)$ Å, $\Theta = 4.4(2)°$, $\Phi = 349.0(32)°$ for **4**. Asymmetry parameters ΔC_S [22] for the three rings (also calculated using PLATON-94) are ΔC_S (C-1) = ΔC_S (C-4) = 4.9(3)°, ΔC_S (C-2) = ΔC_S (C-5) = 3.9(3)°, ΔC_S (C-3) = ΔC_S (O-5) = 1.3(3)° for **2**; ΔC_S (C-1) = ΔC_S (C-4) = 7.4(2)°, ΔC_S (C-2) = ΔC_S (C-5) = 6.9(2)°, ΔC_S (C-3) = ΔC_S (O-5) = 0.7(2)° for **3**; and ΔC_S (C-1) = ΔC_S (C-4) = 8.0(2)°, ΔC_S (C-2) = ΔC_S (C-5) = 6.9(2)°, ΔC_S (C-3) = ΔC_S (O-5) = 1.2(2)° for **4**. Although comparison of selected bond lengths (as noted above) would indicate that the aglycones do not differ greatly in their effect on the monosaccharide rings, the puckering and asymmetry parameters show an overall geometric similarity between **3** and **4** that does not extend to **2**. In addition, torsional angles of **3** and **4** resemble each other more closely than those of either structure resemble those of **2**. Replacement of a semicarbazide with an aniline (or substituted aniline) does cause a corresponding adjustment in the monosaccharide ring geometry [23]. On the basis of the observed values of the torsional angles O-5–C-5–C-6–O-6 and C-4–C-5–C-6–O-6, the conformation of the C-6–O-6 side chain in **2**–**4** can be described as *gt* in all three structures [24]. The orientations of the aromatic rings in **3** and **4** (as defined by the torsional angles O-5–C-1–N-1–C-7 and C-1–N-1–C-7–C-8) are closely similar to each other.

Packing arrangements and intermolecular interactions.—Details of the intermolecular hydrogen bonding for all four structures are given in Table 2. The packing arrangements assumed by **1**–**4** are shown in Figs. 5–8.

The packing arrangement assumed by D-mannose oxime **1** (Fig. 5) is different from that assumed by either isomer of arabinose oxime. Both isomers of arabinose oxime crystallize as 'head-to-head' dimers in which hydrogen-bonding interactions link pairs of N–OH groups into six-membered rings, but molecules of **1** are linked by a 'head-to-tail' interaction in which the N–OH group of each molecule forms a hydrogen-bonded bridge across the C-5 and C-6 hydroxyl groups of a neighboring molecule, forming an eight-membered ring in which the O-6 and oxime hydroxyls are H-bond donors and the O-5 hydroxyl and oxime nitrogen are H-bond acceptors. The molecules are linked into chains

by this interaction and are also linked side by side by three H-bonding interactions along the crystallographic **a**-axis and by one H-bonding interaction along the crystallographic **c**-axis. All of the hydroxyl groups serve as H-bond donors; only O-4 does not also serve as a H-bond acceptor.

The semicarbazide derivative **2** (packing shown in Fig. 6) crystallizes as a dihydrate, the water molecules forming a two-molecule hydrogen-bonded bridge linking O-6 intramolecularly to the carbonyl oxygen atom O-1. With both water molecules engaging in hydrogen bonding with O-1, there are no close intermolecular contacts between O-1 and N-2 or between O-1 and N-3, and any hydrogen-bonded interaction of the amide dimer type is precluded. For their part, the N–H hydrogen atoms do not engage in any particularly short hydrogen-bonding interactions.

In the packing arrangement of aniline derivative **3** (Fig. 7), hydrogen bonding between pyranose rings defines layers lying perpendicular to the **b**-axis. These alternate with layers in which the phenyl rings are packed together, the crystal thereby consisting of alternating hydrophilic and hydrophobic layers. Like the N–H hydrogen atoms in **2**, the N–H hydrogen atom in **3** does not engage in any significant intermolecular interactions. On the other hand, although the ring oxygen O-5 plays no role in the hydrogen bonding in **2**, in **3** it acts as a hydrogen-bond acceptor.

The packing arrangement of the *p*-chloroaniline derivative **4** (Fig. 8) is closely related to that of **3**, the hydrogen-bonding schemes found in the two structures being essentially the same. Both packing arrange-

Table 2
Hydrogen-bond parameters (Å, °) [a]

	D–H···A	D–H	H···A	D···A	D–H···A
1	O-l-H-1O–O-5^{i}	0.74(3)	1.95(3)	2.654(2)	158(4)
	O-2–H-2O–O-l^{ii}	0.80(3)	2.05(3)	2.764(2)	149(3)
	O-3–H-3O–O-2^{iii}	0.72(3)	2.07(3)	2.738(2)	156(4)
	O-4–H-4O–O-3^{ii}	0.71(3)	2.06(3)	2.750(2)	164(4)
	O-5–H-5O–O-6^{iv}	0.76(3)	2.01(3)	2.734(3)	160(4)
	O-6–H-6O–N-1^{v}	0.82(3)	2.04(3)	2.851(3)	173(3)
2	O-lW–H-lW–O-l^{vi}	0.91(4)	1.90(4)	2.794(2)	168(3)
	O-lW–H-2W–O-2W^{vi}	0.88(3)	1.83(3)	2.694(3)	167(3)
	O-2W–H-3W–O-6^{vi}	0.82(3)	2.07(4)	2.880(3)	170(3)
	O-2W–H-4W–O-l^{iv}	1.01(4)	1.87(4)	2.871(4)	176(3)
	O-2–H-2O–O-6^{vii}	0.86(3)	1.86(3)	2.709(2)	172(3)
	O-3–H-3O–O-1^{viii}	0.80(3)	2.20(4)	2.873(2)	142(3)
	O-4–H-4O–O-1W^{viii}	0.79(3)	1.92(3)	2.657(2)	155(3)
	O-6–H-6O–O-3^{ix}	0.90(3)	1.83(3)	2.724(2)	173(3)
	N-l–H-1N–O-4^{ii}	0.88(3)	2.08(3)	2.951(3)	169(3)
	O-4–H-4O–O-6^{ix}	0.79(3)	2.89(3)	3.297(2)	114(3)
	O-4–H-4O–O-2^{iv}	0.79(3)	2.92(3)	3.241(2)	107(3)
	N-3–H-31N–O-2^{x}	0.70(4)	2.91(3)	3.246(3)	113(3)
3	O-2–H-2O–O-4^{ii}	0.79(3)	2.27(3)	2.953(3)	145(3)
	O-3–H-3O–O-5^{iii}	0.84(3)	1.96(3)	2.799(3)	176(3)
	O-4–H-4O–O-3^{xi}	0.82(3)	1.90(3)	2.709(3)	172(3)
	O-6–H-6O–O-4^{x}	0.93(3)	1.84(3)	2.765(2)	175(3)
	N-l–H-1N–O-6^{ii}	0.89(3)	2.27(3)	3.104(3)	155(3)
4	O-2–H-2O–O-4^{ix}	0.82(3)	2.28(3)	3.000(2)	146(3)
	O-3–H-3O–O-5^{iv}	0.85(3)	1.96(3)	2.808(2)	176(3)
	O-4–H-4O–O-3^{xii}	0.83(3)	1.91(3)	2.728(2)	172(3)
	O-6–H-6O–O-4^{ii}	0.90(3)	1.89(3)	2.773(2)	166(3)
	N-l–H-1N–O-6^{ix}	0.88(3)	2.33(3)	3.130(3)	152(3)

[a] Symmetry codes: (i) $-1+x, -1+y, z$; (ii) $1+x, y, z$; (iii) $x, y, 1+z$; (iv) $-1+x, y, z$; (v) $1+x, 1+y, z$; (vi) x, y, z; (vii) $1+x, -1+y, z$; (viii) $x, -1+y, 1+z$; (ix) $x, 1+y, z$; (x) $x, y, -1+z$; (xi) $-1/2+x, 1/2-y, 1-z$; (xii) $-2-x, -1/2+y, -1-z$.

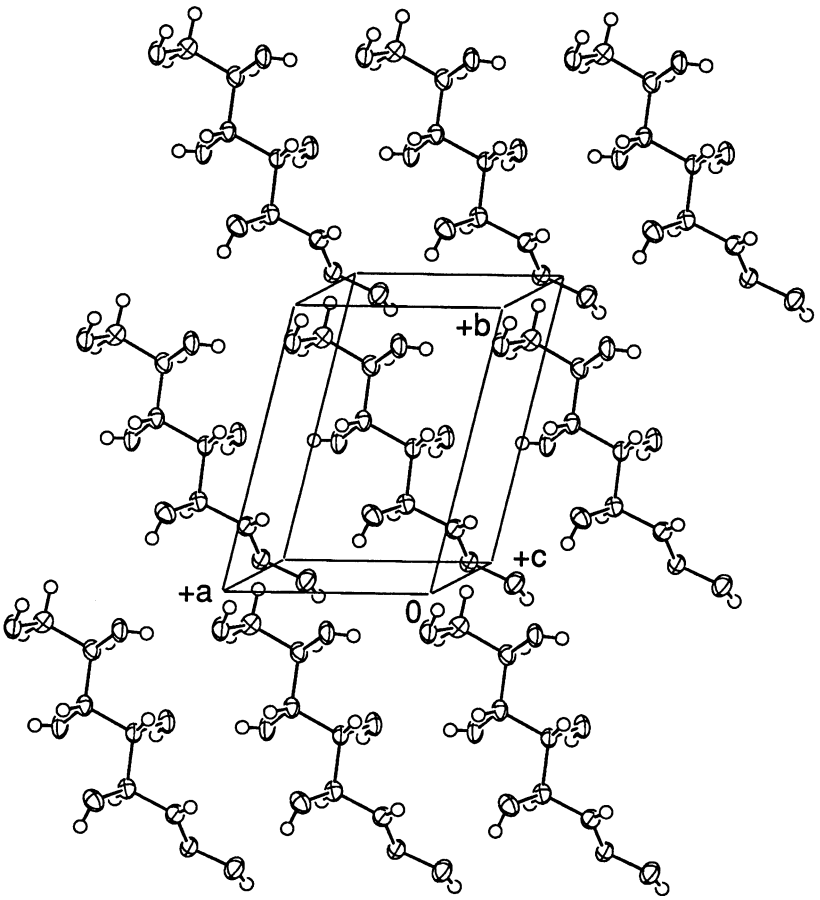


Fig. 5. Molecular packing in **1**.

ments involve a side-by-side interaction in which translationally related pyranosides are linked by a pair of hydrogen bonds, O-3 (donor) to O-5 (acceptor) and O-6 (donor) to O-4 (acceptor). In both structures a hydrogen bond links O-2 (donor) to O-4 (acceptor) of another neighboring translationally related molecule, and another hydrogen bond links O-4 (donor) to O-3 (acceptor) of a neighboring molecule related by a screw axis. The close relationship between the packing arrangements of **3** and **4** can be seen by comparing Figs. 7 and 8, the four-molecule motif shown in Fig. 8 for **4** being embedded in the structure of **3** shown in Fig. 7. The structure of **3** involves a stacking mode in which the motif shown for **4** is turned over and stacked on top of itself such that the phenyl groups define a 'herringbone' pattern. Replacement of a phenyl hydrogen atom by the chlorine atom appears to disrupt this type of interaction between phenyls in **3** and to replace it with a parallel stacking of *p*-chlorophenyl rings in **4**. None of the hydrogen-bonding interactions found in **3** and **4** are found in **2**, in which the presence of the water molecules and their in-

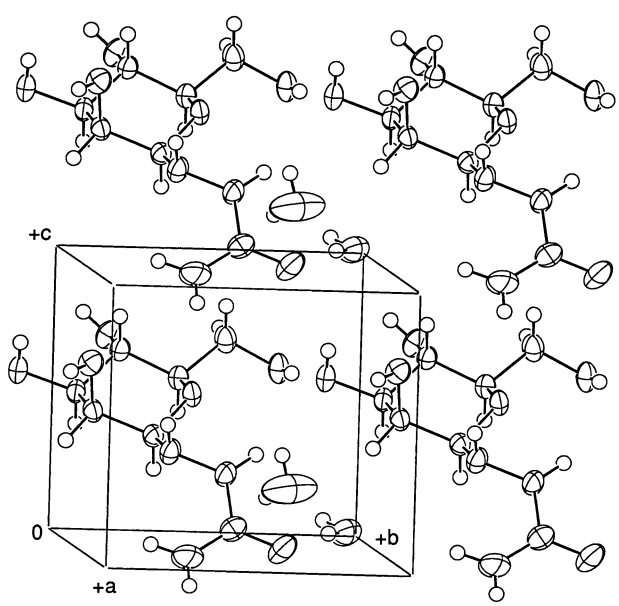


Fig. 6. Molecular packing in **2**.

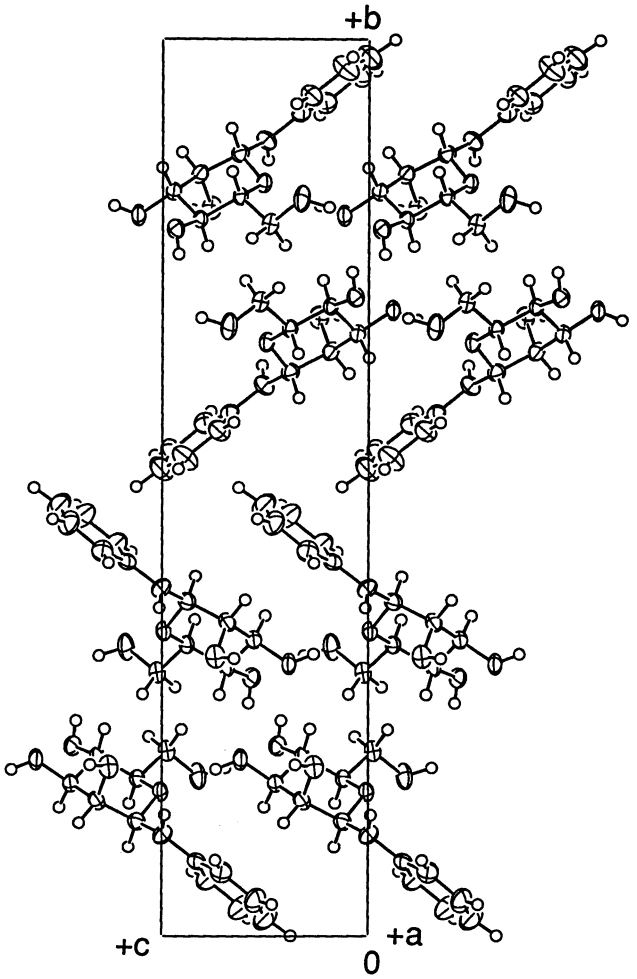


Fig. 7. Molecular packing in **3**.

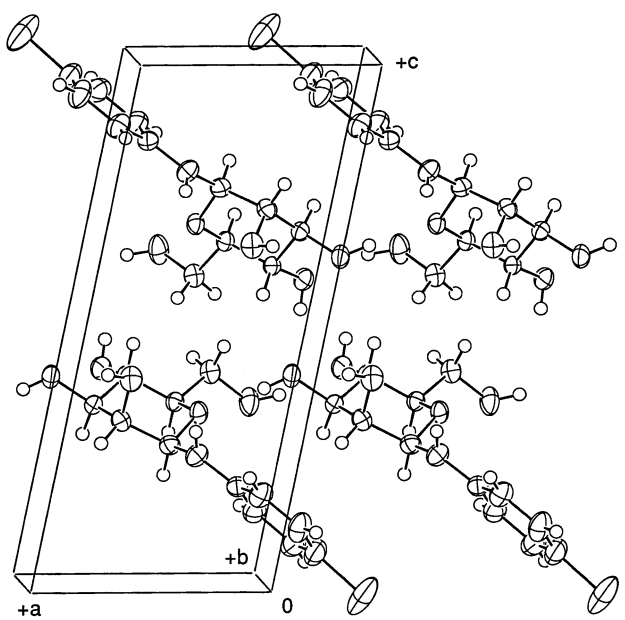


Fig. 8. Molecular packing in **4**. Note the similarity between this view and the bottom half of Fig. 7 (molecular packing in **3**).

teraction with the carbonyl oxygen produce an entirely different hydrogen-bonding pattern.

3. Experimental

Preparation of D-*mannose derivatives.*—The oxime **1** was prepared by combining D-mannose (0.2 g), hydroxylamine hydrochloride (0.5 g), 10% aq NaOH (2 mL), and water (3 mL). Ethanol was added dropwise to clear turbidity. The solution was heated for 15 min and then refrigerated until needle-shaped crystals appeared, mp 188–193 °C (lit. 176–184 °C [25]). The semicarbazide derivative **2** was prepared by combining a solution of D-mannose (0.5 g) in EtOH (5 mL) with a solution of semicarbazide hydrochloride (0.5 g) and NaOAc (0.75 g) in water (5 mL). The resulting solution was heated for 5 min. Crystals of **2** were obtained by means of slow diffusion of EtOH into the reaction mixture, yielding prisms, mp 112 °C (lit. 108 °C [26]). The anilides **3** and **4** were prepared by combining D-mannose (0.3 g) with aniline (0.15 g) and *p*-chloroaniline (0.25 g), respectively, in EtOH (15 mL) and concentrating the solution to a volume of $\sim$8 mL. Recrystallization from EtOH of the powdery solid thus obtained in each case yielded **3** as needles, mp 185–190 °C (lit. 180–181 °C [14]) and **4** as needles, mp 188–192 °C (lit. 171–172 °C [27], 200 °C [15]). Inspection of crystals of **3** under the microscope showed them to contain a narrow channel of solvent extending lengthwise through every crystal examined. Attempts to trim these needles to a size suitable for data collection caused the channel to empty and leave the crystal hollow. An attempt was made to choose the best available untrimmed crystal for the structure determination, but it may have been the existence of a solvent channel through the crystal ultimately chosen that caused the relatively large value for the final unweighted *R* factor for **3**. No such solvent channels were observed in crystals of **4**.

X-ray crystal structure determinations.—A summary of the crystal data, data collection parameters, and refinement results is given in

Table 3
Crystal data, data collection parameters, and refinement results for **1**–**4** [a]

	1	**2**	**3**	**4**
Formula	$C_6H_{13}NO_6$	$C_7H_{19}N_3O_8$	$C_{12}H_{17}NO_5$	$C_{12}H_{16}ClNO_5$
Formula weight	195.17	273.24	255.27	289.72
Crystal dimensions (mm^3)	$0.24\times0.13\times0.10$	$0.52\times0.24\times0.12$	$0.42\times0.06\times0.05$	$0.48\times0.10\times0.08$
Crystal system	triclinic	triclinic	orthorhombic	monoclinic
Space group	$P1$	$P1$	$P2_12_12_1$	$P2_1$
a (Å)	5.5968(8)	7.0659(7)	6.766(2)	6.518(1)
b (Å)	8.532(1)	7.3383(4)	28.368(2)	6.878(1)
c (Å)	4.9925(8)	6.7234(5)	6.449(2)	14.734(1)
α (°)	94.71(1)	91.500(6)		
β (°)	110.32(1)	104.208(7)		101.42(1)
γ (°)	102.02(1)	67.458(5)		
V ($Å^3$)	215.53(6)	311.23(4)	1237.8(5)	647.6(1)
Z	1	1	4	2
D_c (g cm^{-3})	1.50	1.46	1.37	1.49
$F(000)$	104	146	544	304
μ (Cu K_α) (cm^{-1})	11.31	11.58	9.02	28.04
$2\theta_{max}$ (°)	140.0	140.2	140.2	140.1
No. of measured reflections	1693	2384	2613	2728
No. of unique reflections	765	1094	1308	1247
R_{int}	0.013	0.017	0.035	0.036
No. of observed reflections ($I>0.00\sigma(I)$)	1693	2384	2128	2283
No. of variables	152	215	215	187
Trans. coefficients	0.9452–1.0000	0.6928–1.0000	0.9575–1.0000	0.8977–1.0000
Secondary extinction [28]	5.88165×10^{-5}	1.66301×10^{-4}	1.79468×10^{-6}	2.20998×10^{-5}
Min, max in final difference map (e $Å^{-3}$)	−0.19, 0.22	−0.23, 0.19	−0.31, 0.32	−0.20, 0.29
R; wR	0.030, 0.027	0.036, 0.043	0.074, 0.032	0.042, 0.033

[a] For all four structures: $T=298$ K; diffractometer: Rigaku AFC6S; radiation: Cu K_α; $\lambda=1.54178$ Å; cell determination: 25 reflections (23 for **3**), $30°<2\theta<50°$; data collection: MSC/AFC control software [29]; scan mode: $\omega/2\theta$; structure solution: SHELXS86 [30]; structure refinement: teXsan software package [31]; decay correction: none for **1**; 5.55% for **2**; 2.46% for **3**; 3.27% for **4**; absorption correction: psi scans [32]; figures: ORTEPII [17]; $R=\Sigma\|F_{obs}|-|F_{calc}\|/\Sigma|F_{obs}|$; $wR=[(\Sigma w(|F_{obs}|-|F_{calc}|)^2/\Sigma wF_{obs}^2]^{1/2}$; $w=4F_{obs}^2/\sigma^2(F_{obs}^2)$; $R_{int}=\Sigma\Sigma|<F_i^2>-F_{ij}^2|/\Sigma m<F_i^2>$.

Table 3. For all four structures the non-hydrogen atoms were refined anisotropically. For **1**–**3** the positional parameters of all the hydrogen atoms were refined. An attempt to do the same for **4** led to unreasonable bond lengths for the methylene hydrogens, so in this structure all the C–H hydrogen atoms were placed in calculated positions, while the positional parameters of the O–H and N–H hydrogen atoms were refined.

Supplementary material

Full crystallographic details have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: +44-1223-336408; fax: +44-1223-336033; e-mail: deposit@ ccdc.cam.ac.uk).

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