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Crystal structures of methyl 6-*O*-*n*-alkanoyl-*β*-D-glucopyranosides

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Abstract

The crystal structures of methyl 6-*O*-*n*-octanoyl-*β*-D-glucopyranoside **1** and methyl 6-*O*-*n*-decanoyl-*β*-D-glucopyranoside **2**, which are types of glycosurfactants, were determined by X-ray analysis. Anhydrous crystals were obtained from a diethyl ether–acetone solution. The crystals are monoclinic, and the space group is $P2_1$ with $Z = 2$. The cell dimensions are as follows: **1**, $a = 7.760(1)$, $b = 7.373(1)$, $c = 15.514(1)$ Å, $\beta = 102.91(1)°$; **2**, $a = 7.724(1)$, $b = 7.351(1)$, $c = 16.957(2)$ Å, $\beta = 94.81(1)°$. The glucopyranoside moieties are in a $^4C_1$ chair conformation and the conformation of the alkyl chain is the all-*trans* type. The molecules are arranged parallel to the a–c plane in a bilayer structure where alkyl chains are interdigitated. The sugar moieties are stacked to form a hydrophilic zone elongated parallel to the ab plane and arranged with a packing structure similar to that of methyl *β*-D-glucopyranoside in spite of a substituted long alkyl chain. Hydrogen bondings of sugar moieties are found only between the bilayers.

Keywords: Crystal structure; Methyl 6-*O*-*n*-alkanoyl-*β*-D-glucopyranosides; Glycosurfactant; Surfactant; Nonionic surfactant; Interdigitated structure; Hydrogen bond

1. Introduction

Recently some amphiphiles which have sugar moieties as a hydrophilic part have been used for solubilizing proteins or commodity detergents [1]. The solubility of these compounds depends not only on the length of the alkyl chain, but also on the structure

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of the sugar group. For example, *N*-octylgluconamide is difficult to disolve in water at room temperature [2] while *N*-nonanoyl-*N*-methylglucamide is highly soluble [3]. The former forms a gel phase in a specific temperature range [2]. The thermotropic and lyophilic liquid crystals also have been observed in some glycosurfactants [4]. The difference in properties of these compounds are related to the structure of the sugar unit where the intermolecular contacts are important in the overall arrangement of molecules in either liquid or crystalline states. Crystal structures of long chain alkyl glycoside [5–7], thioglycoside [8], and glycoamide [9,10] have already been reported. Alkyl glycosides generally form a bilayer structure with interdigitated alkyl chains while the glycoamide forms two types of monolayer structures depending on the even or odd number of alkyl carbons, where alkyl chains are not interdigitated.

Recently, high yield regioselective routes towards esterifications of sugar derivatives have been developed and these reactions have been applied to the synthesis of glycosurfactants [11–14]. In addition the physicochemical properties of ester derivatives of methyl D-glucopyranoside have been reported [14,15] where the surface tension and area/molecule in the surface layer differ depending on the substituted position of the ester group [15]. Some methyl 6-*O*-decanoyl-D-glycosides exhibit different melting points in the range of 59–137°C [15], depending on the sugar structure and alkyl chain length. In this paper, we deal with the crystal structure of two 6-*O*-*n*-alkanoyl-β-D-glucopyranosides, methyl 6-*O*-*n*-octanoyl-β-D-glucopyranoside **1**, and methyl 6-*O*-*n*-decanoyl-β-D-glucopyranoside **2**.

2. Experimental

Compounds **1** and **2** were prepared by esterification of methyl octanoate or methyl decanoate and methyl β-D-glucopyranoside with lipase [12]. The esterification did not involve a change of sugar stereochemistry, and the specific optical rotation of **2** was nearly same as the reported value [14]. These compounds were recrystalized several times from 95:5 diethyl ether–chloroform. Large crystals of **1** and **2** were obtained from 95:5 diethyl ether–acetone. The sample crystal was cut to a suitable size, 0.5 × 0.5 × 0.05 mm for **1** and 0.4 × 0.4 × 0.1 mm for **2**, for X-ray measurement. Lattice constants and intensity data were measured at room temperature on an Enraf-Nonius CAD4 diffractometer with grafite-monochromated CuK_α radiation (40 kV, 20 mA). An empirical absorption correction was made by using the program incorporated in the CAD4 structure determination package. No extinction correction was applied. Crystal data and summary of experimental details are given in Table 1. Reflections with $|F_o| > 3\sigma(|F_o|)$ were considered to be observed for structure analysis purposes. Structures were determined by direct methods using the program Xtal 3.0 [16] and were refined by the least-squares method. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sigma(F)^{-1}$. The hydrogen atoms were located partly on alkyl chain and pyranose ring carbons in a difference Fourier map. Hydrogen atoms attached to methylene and methin groups were calculated and included in the further full matrix least-square refinements. The coordinates and isotropic thermal factor of hydorgen atoms were fixed in the refinement. The refinement converged at *R*-values of 0.084 for **1** and 0.067 for **2**. Maximum values of

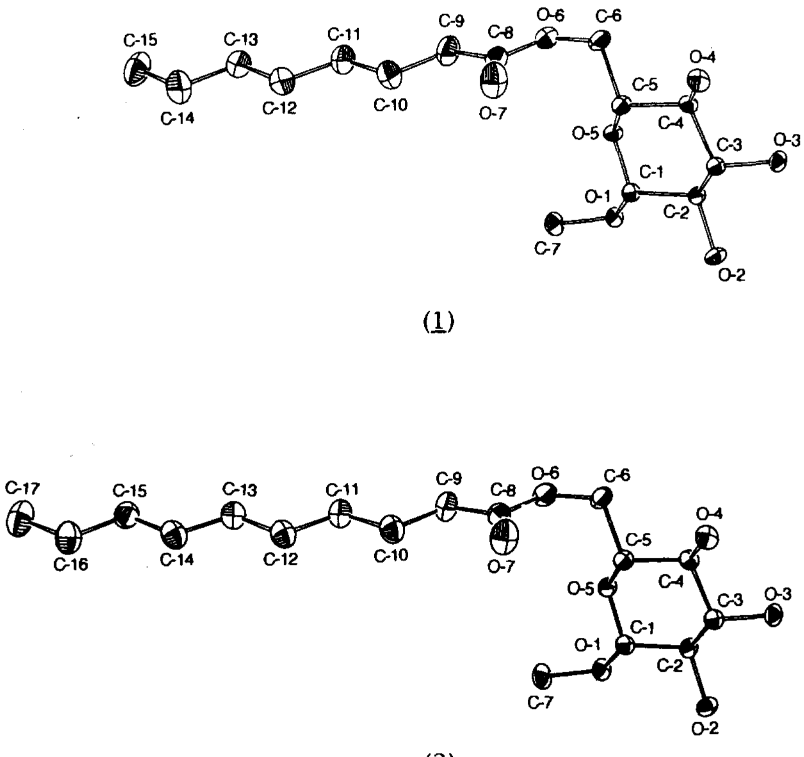
Table 1
Crystal data and summary of experimental details for **1** and **2**

Molecule	1	2
Molecular formula	$C_{15}H_{28}O_7$	$C_{17}H_{32}O_7$
M_w	320.4	348.4
mp [°C]	88	91
$[\alpha]_D^{20}$ [°] (c 1.0, Me_2SO)	−22.5	−20.6 −17.2 [14]
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
Z	2	2
Lattice constant a [Å]	7.760(1)	7.724(1)
b [Å]	7.373(1)	7.351(1)
c [Å]	15.514(1)	16.957(2)
β [°]	102.91(1)	94.81 (1)
Cell volume [Å^3]	865.2(1)	959.4(2)
D_c	1.230	1.206
$F(0\,0\,0)$	348	380
Radiation	CuK_α (40 kV, 20 mA)	
μ [cm^{-1}]	9.26	8.99
Number of reflections for the determination of lattice constants	25	23
and 2θ range [°]	$40 \le \theta \le 50$	
Number of measured reflections	2056	2270
Number of unique reflections	2056	2270
Number of observed reflections ($\|F_O\| > 3\sigma(\|F_O\|)$)	1843	2005
Index range for data collection	$0 \le h \le 9$ $0 \le k \le 9$ $-19 \le l \le 19$	$0 \le h \le 9$ $0 \le k \le 9$ $-21 \le l \le 21$
and 2θ range [°]	$1 \le 2\theta \le 150$	
Scan mode	$\omega/2\theta$	
$\Delta\omega$	$0.80 + 0.15 \times \tan\theta$	
Scan speed [°/min]	4	
R-factor	0.084	0.067
wR	0.115	0.073
S	1.226	0.847
Number of parameters refined	200	218

positive and negative electron densities in the final difference Fourier maps were 0.4 and −0.3, respectively, for **1** and 0.4 and −0.3, respectively, for **2**.

3. Results and discussion

Molecular structures and crystal packings are shown in Figs. 1 and 2, respectively. Atomic coordinates are listed in Table 2. Alkyl chains are in an all-*trans* type conformation, and slightly bent. Atoms belonging to the alkyl chain and the ester group are coplanar within the maximum deviations from the relevant planes of 0.09 Å for **1**



(1)

(2)

Fig. 1. Structure (ORTEP drawing) and atomic numbering for **1** and **2**. Thermal ellipsoids are drawn at 50% probability.

and 0.12 Å for **2**. Puckering [17] and asymmetry [18] parameters in Table 3 show that the pyranose rings have slightly distorted $^4C_1$ chair conformation indicated by $\phi 2$ toward the twist-boat-like methyl 6-*O*-acetyl-β-D-glucopyranoside [19] **3** and methyl β-D-glucopyranoside hemihydrate [20] **4**. The C-6–O-6 bond is *trans* to the C-4–C-5 bond and the conformation of the C-5–C-6–O-6–C-8 angle is gauche with values of 68 and 70° in **1** and **2**, respectively. This conformation seems to be responsible for the stable packing of the pyranose rings and the alkyl chains in the crystal. A similar conformation has been observed in **3** with the corresponding torsion angle of 72°.

Molecules are packed in a bilayer structure with alkyl chains interdigitated and the basic crystal packing does not differ between the two structures in spite of the different alkyl chain lengths. A similar packing structure has been observed in the crystals of long chain alkyl glycosides [5–8]. In the present structures, however, the inclination of alkyl chains against the normal to the bilayer plane (47 and 47° for **1** and **2**, respectively) is larger than that reported for *n*-octyl α-D-glucopyranoside [7] **5** and *n*-decyl α-D-glucopyranoside [5] **6** (26 and 26° for **5** and **6**, respectively). The packing of sugar moieties is affected by the anomeric structure as well as substituents at C-1. The α anomer in *n*-octyl α-D-glucopyranoside **5** and *n*-decyl α-D-glucopyranoside **6** is more closely

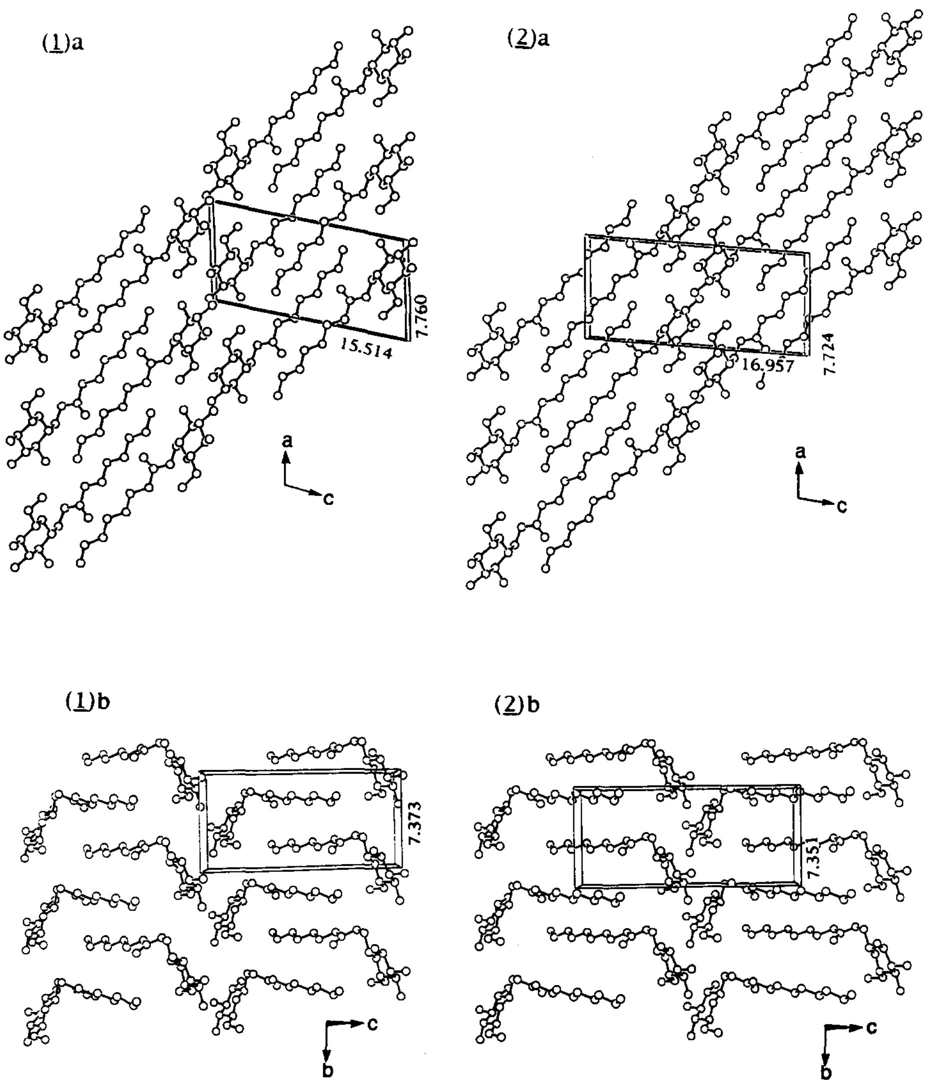


Fig. 2. The crystal structure of **1** and **2**, projected on the *ac* plane (a) and that viewed along the *a* axis (b).

packed as indicated by the unit area of the *ab* plane (57.2, 56.8, 39.0, and 39.3 Å [2] for **1**, **2**, **5**, and **6**, respectively). The pyranose inclination of **1** and **2** against the *ab* plane is smaller than that of **5** and **6** (39, 39, 58, and 57° for **1**, **2**, **5**, and **6**, respectively), therefore the sugar moieties of **1** and **2** require a larger area to arrange in the *ab* plane.

To retain the suitable intermolecular contacts, alkyl chains of **1** and **2** are much more inclined against the *c* axis than those of **5** and **6**. Such a molecular arrangement causes the formation of an intermolecular void near the carboxyl group which is filled with the methyl group bonded to O-1. In the case of 1-*O*-alkyl glycosides, the primary hydroxyl

Table 2
Atomic coordinates and equivalent thermal parameters of *n*-octanoyl and *n*-decanoyl methyl *β*-D-glucopyranoside

Molecule	Atom	x/a	y/b	z/c	U_{eq} [a]
1	C-1	0.4881(9)	1.1567(11)	0.1046(5)	3.0(2)
	C-2	0.3252(9)	1.1638(12)	0.0284(5)	3.0(2)
	C-3	0.1727(9)	1.0748(12)	0.0610(5)	3.0(2)
	C-4	0.2261(9)	0.8885(11)	0.0981(5)	2.9(2)
	C-5	0.4034(10)	0.8913(12)	0.1654(5)	3.4(3)
	C-6	0.4637(12)	0.6922(14)	0.1877(7)	5.0(3)
	C-7	0.7848(11)	1.2558(16)	0.1468(6)	4.8(3)
	C-8	0.7150(14)	0.7466(17)	0.3036(7)	5.6(4)
	C-9	0.9113(14)	0.7154(20)	0.3296(8)	6.9(5)
	C-10	0.9964(15)	0.7923(20)	0.4197(8)	6.9(5)
	C-11	1.1930(15)	0.7379(21)	0.4455(8)	7.5(5)
	C-12	1.2859(16)	0.8095(20)	0.5357(8)	7.0(5)
	C-13	1.4812(16)	0.7478(20)	0.5612(8)	6.9(5)
	C-14	1.5785(18)	0.8252(26)	0.6477(8)	8.8(6)
	C-15	1.7721(17)	0.7628(26)	0.6737(9)	9.5(6)
	O-1	0.6314(6)	1.2353(9)	0.0759(4)	3.4(2)
	O-2	0.2772(7)	1.3508(8)	0.0057(4)	3.7(2)
	O-3	0.0266(7)	1.0605(9)	−0.0123(4)	3.7(2)
	O-4	0.0928(7)	0.8244(9)	0.1425(4)	4.0(2)
	O-5	0.5331(6)	0.9721(8)	0.1242(4)	3.0(2)
	O-6	0.6510(9)	0.6765(10)	0.2224(5)	5.1(2)
	O-7	0.6213(10)	0.8204(15)	0.3469(5)	7.7(4)
2	C-1	1.0394(6)	0.4755(8)	0.4062(3)	3.4(2)
	C-2	1.1825(6)	0.4833(8)	0.4738(3)	3.4(2)
	C-3	1.3426(6)	0.3930(8)	0.4454(3)	3.5(2)
	C-4	1.3015(6)	0.2068(8)	0.4115(3)	3.4(2)
	C-5	1.1424(7)	0.2098(8)	0.3518(3)	3.7(2)
	C-6	1.0892(8)	0.0102(9)	0.3303(4)	5.1(2)
	C-7	0.7546(7)	0.5767(11)	0.3676(4)	5.1(2)
	C-8	0.8667(9)	0.0656(10)	0.2272(3)	5.4(2)
	C-9	0.6796(9)	0.0344(12)	0.2041(4)	6.8(3)
	C-10	0.6155(10)	0.1110(12)	0.1234(4)	6.7(3)
	C-11	0.4292(9)	0.0569(12)	0.0991(4)	6.7(3)
	C-12	0.3571(9)	0.1271(12)	0.0200(4)	6.7(3)
	C-13	0.1738(10)	0.0612(12)	−0.0030(4)	6.7(3)
	C-14	0.0948(10)	0.1294(12)	−0.0820(4)	6.9(3)
	C-15	−0.0894(10)	0.0637(12)	−0.1042(4)	6.7(3)
	C-16	−0.1699(11)	0.1388(14)	−0.1800(4)	8.4(3)
	C-17	−0.3549(10)	0.0730(16)	−0.2044(5)	9.3(4)
	O-1	0.8885(4)	0.5554(6)	0.4308(2)	3.9(1)
	O-2	1.2231(4)	0.6699(6)	0.4943(2)	4.1(1)
	O-3	1.4701(4)	0.3792(6)	0.5111(2)	4.3(1)
	O-4	1.4470(4)	0.1417(6)	0.3724(2)	4.4(1)
	O-5	1.0006(4)	0.2914(6)	0.3880(2)	3.5(1)
	O-6	0.9097(6)	−0.0052(7)	0.2993(2)	5.4(1)
	O-7	0.9723(6)	0.1424(10)	0.1895(3)	8.1(2)

[a] $U_{eq} = 100 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 3
Ring-puckering and asymmetry parameters for compounds **1**, **2**, **3**, and **4**

	Molecule			
	1	**2**	**3** [a]	**4** [a]
Ring-puckering parameters				
q_2	0.094	0.100	0.117	0.072
q_3	0.603	0.584	0.577	0.593
ϕ_2	34.2	30.9	36.8	38.8
Q	0.611	0.592	0.588	0.598
θ	9.4	9.7	11.5	7.0
Asymmetry parameters				
ΔC_s(C-1)	6.2	6.0	7.7	5.1
ΔC_s(C-2)	8.7	8.9	9.0	6.6
ΔC_s(C-3)	14.7	14.7	16.6	11.5
ΔC_2(C-1–C-2)	1.8	2.1	1.5	1.4
ΔC_2(C-2–C-3)	16.6	16.7	18.0	12.7
ΔC_2(C-3–C-4)	14.8	14.6	17.2	11.9

[a] All of the parameters of **3** and asymmetry parameters of **4** were calculated from the coordinates of [20] and [21], and the puckering parameters of **4** were quoted from [21].

group is situated at a position similar to that of the methyl group of **1** and **2**, this hydroxyl group forms hydrogen bonds with the adjacent sugar moieties and does not turn to the end of the adjacent long alkyl chain.

The packing of the sugar moiety is similar to that observed in **3** [19] and **4** [20]. Two kinds of intermolecular contacts have been observed in the crystal of **3**. One involves water molecules, while the other is in the direct hydrogen bonding contact between sugar groups. The glucoside group of **1** and **2** shows the same type of hydrogen bonding contacts as the latter found in **3** and **4**. The packing of sugar groups reflects the lattice dimensions because the glucoside layer is parallel to the *ab* plane in **1**, **2**, and **4**, and the *ac* plane in **3**. The *a* axis of **1** and **2** are slightly longer than that of **4** [7.433(1) Å], and the *b* axis of **4** [7.433(1) Å] [20] is almost the same. The distances of *a* and *b* axes in **1** and **2** are almost the same as the corresponding axes in **3** [$c = 7.863(2)$ Å, $a = 7.2387(8)$ Å] [19].

The bulkiness of the alkyl chain dose not much affect the packing of the sugar moiety. The slight change in the packing of the sugar moiety between β-D-glucopyranoside and the present compounds may be due to the substitution at the O-6 position. No such relationship has been observed among derivatives of α-D-glucopyranoside [21].

The intermolecular O–O distances in hydrogen bonding contacts are listed in Table 4. The hydroxyl groups form a linear hydrogen bond chain, O-4–O-3–O-2–O-5 (Fig. 3). These intermolecular hydrogen bonds are found only between layers. On the other hand, *n*-octyl and *n*-decyl α-D-glucopyranoside form hydrogen bonds not only between layers but also within the layer [5–8].

Interdigitated alkyl chains projected on the *ac* plane are elongated and almost parallel to each other. The alkyl chain with the all-*trans* conformation is in a planar structure. Adjacent alkyl planes are arranged in the packing of $O'_\perp$ type [22] which have planes at oblique angles to rows. The average angle made by the planes is 69° for **1** and 72° for **2**,

Table 4
O···O Distances of observed hydrogen bonds

O···O	1	2	Distance (Å)	
			3 [19]	4 [20]
(A) O-2–O-5	2.890(9) [a]	2.890(5) [b]	2.932(3) [d]	3.015(2) [c]
(B) O-3–O-2	2.841(8) [e]	2.863(6) [f]	2.840(4) [h]	2.769(2) [g]
(C) O-4–O-3	2.808(9) [e]	2.798(6) [f]	2.806(4) [h]	2.700(2) [g]

The symmetry coordinates are represented by the following: [a] $[-x, +y+1/2, -z]$; [b] $[-x+2, y+1/2, -z+1]$; [c] $[-x+3/2, y-1/2, -z+1/4]$; [d] $[-x, y-2, -z]$; [e] $[-x, y-1/2, -z]$; [f] $[-x+3, y-1/2, -z+1]$; [g] $[-x+5/2, y+1/2, -z+1/4]$; [h] $[-x, y+2, -z]$.

and adjacent alkyl chains are shifted among each other along the *c* axis. These arrangements of alkyl chains are different from the parallel arrangement of alkyl planes found in alkyl α-D-glucoside [5].

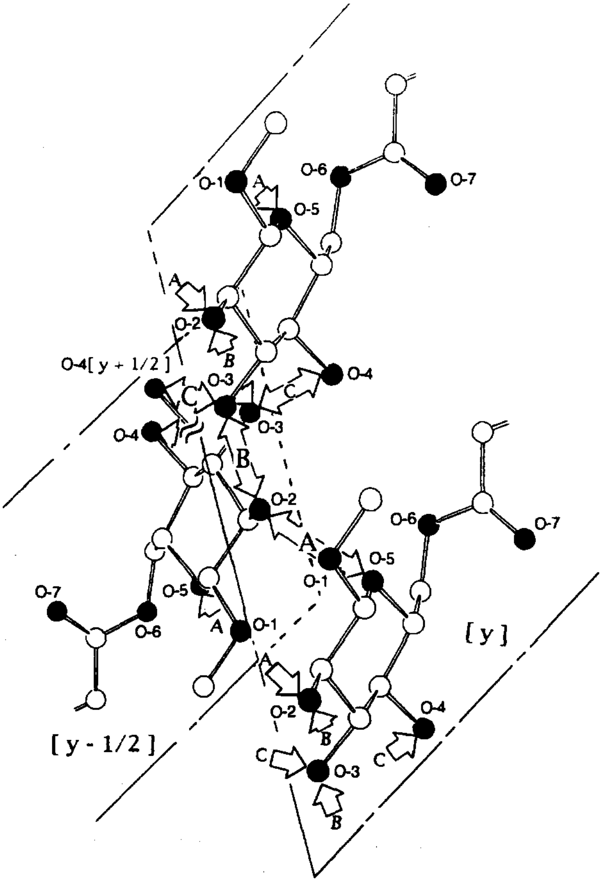


Fig. 3. The hydrogen bonds formed between β-D-glucopyranosides viewed along the *b* axis. Arrows represent the linear hydrogen bond chain, O-5(A)–O-2(B)–O-3(C)–O-4.

References

[1] C. Baron and T.E. Thompson *Biochim. Biophys. Acta*, 382 (1975) 276–285.
[2] B. Pfannemüller and W. Welte, *Chem. Phys. Lipids*, 37 (1985) 227–240.
[3] A. Walter, S.E. Suchy, and P.K. Vinson, *Biochim. Biophys. Acta*, 1029 (1990) 67–74.
[4] G.A. Jeffrey, *Acc. Chem. Res.*, 19 (1986) 168–173.
[5] P.C. Moews and J.R. Knox, *J. Am. Chem. Soc.*, 98 (1976) 6628–6633.
[6] G.A. Jeffrey and Y. Yeon, *Carbohydr. Res.*, 169 (1987) 1–11.
[7] H. v. Koningsveld, J.C. Jansen, and A.J.J. Straathof, *Acta Crystallogr., Sect. C*, 44 (1988) 1054–1057.
[8] S. Bhattacharjee and G.A. Jeffrey, *Mol. Cryst. Liq. Cryst.*, 101 (1983) 247–260.
[9] V. Zabel, A. Müller-Fahrnow, R. Hilgenfeld, W. Saenger, B. Pfannemüller, V. Enkelmann, and W. Welte, *Chem. Phys. Lipids*, 39 (1986) 313–327.
[10] A. Müller-Fahrnow, V. Zabel, M. Steifa, and R. Hilgenfeld, *J. Chem. Soc., Chem. Commun.*, (1986) 1573–1574.
[11] S. Riva, J. Chopineau, A.P.G. Kieboom, and A.M. Klibanov, *J. Am. Chem. Soc.*, 110 (1988) 584–589.
[12] F. Björkling, S.E. Godtfredsen, and O. Kirk, *J. Chem. Soc., Chem. Commun.*, (1989) 934–935.
[13] R. Pulido, F.L. Oriz, and V. Gotor, *J. Chem. Soc., Perkin Trans. 1*, (1992) 2891–2898.
[14] Y. Gama and Y. Kawaguchi, *Yukagaku*, 42 (1993) 685–686.
[15] T. Tamura, S. Shimizu, Y. Sasaki and C. Hirai, *Yukagaku*, 40 (1991) 321–325.
[16] S.R. Hall and J.M. Stwart (Eds.), Xtal 3.0 Reference Manual, University of Western Australia and Maryland, 1990.
[17] D. Cremer and J.A. Pople, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
[18] W.L. Duax, C.M. Weeks, and D.C. Rohrer, *Topics in Stereochemistry*, Vol. 9, 1976, pp 271–383.
[19] K.B. Lindberg, *Acta Crystallogr., Sect. B*, 32 (1976) 642–645.
[20] G.A. Jeffrey and S. Takagi, *Acta Crystallogr., Sect. B*, 33(1977) 738–742.
[21] H.M. Berman and S.H. Kim, *Acta Crystallogr., Sect. B*, 24 (1968) 897–904.
[22] E. Segerman, *Acta Crystallogr.*, 19 (1965) 789–796.