Bilayer structure of glycolipid crystals. Thermal stability of the crystal and state of the alkyl chain

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The role of alkyl chains in the stabilization of a bilayer structure of glycolipids in the crystalline state has been studied for a series of methyl 6-*O*-acyl-β-D-glucopyranosides and methyl 6-*O*-acyl-α-D-galactopyranosides. Thermal properties and crystal structures of these glycolipids with an odd number of alkyl carbon atoms in the acyl moiety have been investigated by thermal analysis and X-ray methods. The melting temperatures of methyl 6-*O*-acyl-β-D-glucopyranosides, which are lower than those of the corresponding methyl 6-*O*-acyl-α-D-galactopyranosides, decrease with increasing number of alkyl carbon atoms from one to seven, but increase for longer alkyl chains. The α-galactosides show only a monotonic decrease in melting temperature with increasing alkyl chain length. In the crystals, the molecules form a bilayer structure with interdigitated alkyl chains. The arrangement of sugar moieties in the crystals differs between the β-glucosides and the α-galactosides, but they are almost the same among sugar derivatives with various alkyl chain lengths. The packing of the acetyl moiety in a crystal of methyl 6-*O*-α-D-galactoside is different from that of the other α-galactoside derivatives with longer alkyl chains. The carbonyl oxygen atom causes steric hindrance with adjacent alkyl chains, and such unfavorable intermolecular contact explains the relatively low thermal stability of the crystal. On the other hand, the contribution of the β-glucoside to thermal stability is ascribed to the well-ordered packing of the long alkyl chain moiety.

Introduction

Many amphiphiles, such as phospholipids,[1] glycolipids[2–10] or sodium dodecyl sulfate,[11–12] which have alkyl chains as their hydrophobic moieties, form bilayer structures in the crystalline state. In these crystals, hydrophobic and hydrophilic groups are arranged in structures similar to those of cell membranes. We previously reported bilayer structures in the crystals of methyl 6-*O*-acyl-D-glycopyranosides and discussed the characteristics from the viewpoint of the role of sugar moieties in the crystal packing.[8–10] The melting temperatures of methyl 6-*O*-decanoyl-D-glycosides which have a variety of sugar moieties have been observed over a wide range, 59–140 °C, affected by the structure of the sugar moieties.[10,13] Methyl 6-*O*-decanoyl-D-galactopyranoside has the highest melting temperature among acyl sugar derivatives, while 6-*O*-*n*-decanoyl-α-D-mannopyranoside was a syrup.[13] The sugar moieties in these compounds consist of epimers where the orientation of hydroxy groups only differs between the equatorial and axial conformations. Each crystal structure of these acylglycosides shows the characteristic arrangement of sugar moieties and a hydrogen bonding network specific to each type of sugar moiety.[8–10]

The thermal stability of an amphiphile crystal reflects its physicochemical properties. The Kraft point of surfactants has been discussed with no knowledge of their crystal structures because of the difficulty in crystallization. Recently, several crystal structures of surfactants having a sugar component have been reported.[2–10] This type of surfactant has become an important material in biochemistry for dissolving and crystallizing membrane proteins; it has also been used as a commodity detergent,[14] although some of these surfactants are difficult to dissolve in water.[15] The crystal structures of some alkyl α-D-glucopyranosides,[2–5] *N*-alkanoyl-*N*-methylglucamides,[7] *N*-alkylgluconamides[6] and alkyl *O*-alkanoyl-D-glycosides[8–10] have been determined, and the packing structures have been characterized in relation to the structure of sugars and hydrogen bonding systems. These glycolipid molecules often form a liquid crystal phase because they have sugar moieties which play a role in ordering the moieties with hydrogen bonding.[16]

Table 1 Molecular numbering of the methyl acylglycosides

Molecule	No.
Methyl 6-*O*-acetyl-β-D-glucopyranoside[a]	**1**
Methyl 6-*O*-butanoyl-β-D-glucopyranoside	**2**
Methyl 6-*O*-hexanoyl-β-D-glucopyranoside	**3**
Methyl 6-*O*-octanoyl-β-D-glucopyranoside[b]	**4**
Methyl 6-*O*-decanoyl-β-D-glucopyranoside[b]	**5**
Methyl 6-*O*-dodecanoyl-β-D-glucopyranoside[c]	**6**
Methyl 6-*O*-tetradecanoyl-β-D-glucopyranoside	**7**
Methyl 6-*O*-acetyl-α-D-galactopyranoside	**8**
Methyl 6-*O*-butanoyl-α-D-galactopyranoside	**9**
Methyl 6-*O*-hexanoyl-α-D-galactopyranoside	**10**
Methyl 6-*O*-octanoyl-α-D-galactopyranoside[d]	**11**
Methyl 6-*O*-decanoyl-α-D-galactopyranoside[d]	**12**
Methyl 6-*O*-dodecanoyl-α-D-galactopyranoside[c]	**13**

[a] Crystal structure reported in ref. 17. [b] In ref. 8. [c] In ref. 10. [d] In ref. 9.

In this report, we discuss the thermal stabilities and X-ray structures of the crystals of methyl acyl-α-D-glucosides and methyl acyl-β-D-galactosides (Table 1) to elucidate the role of the alkyl chain in crystal packing and thermal stability. These acylglycosides have a variety of alkyl chain lengths with a number of alkyl carbon atoms, one to thirteen in the β-glucosides and one to eleven in α-glucosides, and are suitable for investigating the difference in the thermal stability and the alkyl chain packing in the crystalline state. We previously reported the crystal structures of **4**, **5**, **6**, **10**, **11** and **12**,[8–10] the crystal structure of **1** has been reported by Lindberg.[17]

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Table 2 Summary of experimental details for **2**, **3** and **7–10**

Molecule	**2**	**3**	**7**	**8**	**9**	**10**
Molecular formula	$C_{11}H_{20}O_7$	$C_{13}H_{24}O_7$	$C_{21}H_{40}O_7$	$C_9H_{16}O_7$	$C_{11}H_{20}O_7$	$C_{13}H_{24}O_7$
Mol. mass	264.3	292.3	404.5	236.2	264.3	292.3
Solution[a]	A (3:1)	A (1:1)	B (1:1)	B (3:1)	B (4:1)	B (4:1)
Crystal size	0.3 × 0.3 × 0.1	0.3 × 0.4 × 0.1	0.3 × 0.4 × 0.1	0.3 × 0.3 × 0.05	0.3 × 0.4 × 0.05	0.3 × 0.3 × 0.05
a/Å	7.842(1)	7.793(1)	7.713(1)	5.752(2)	5.772(1)	5.784(1)
b/Å	7.389(1)	7.363(1)	7.346(1)	8.082(2)	8.038(1)	8.024(1)
c/Å	11.341(1)	13.534(5)	20.473(1)	12.561(4)	14.686(1)	16.792(1)
β(°)	93.21(1)	99.99(2)	96.76(1)	94.72(1)	94.32(1)	95.40(1)
Z/Å^3	656.1(1)	764.8(3)	1151.9(2)	582.0(3)	679.4(2)	775.8(1)
D_c/g cm^{-3}	1.338	1.269	1.166	1.348	1.292	1.251
F(000)	284	316	444	252	284	316
Radiation	CuKα (40 kV 25 mA)					
μ/cm^{-1}	10.88	8.99	8.10	11.51	10.51	9.76
2θ range (°)	$1 \leq 2\theta \leq 150$					
Data collecting temp.	room temp.					
No. reflections						
measured	1563	1809	2740	1425	1650	1875
observed [$\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$]	1419	1113	2316	1012	1382	1404
Scan mode	$\omega/2\theta$					
$\Delta\omega$	$0.80 + 0.15 \times \tan\theta$					
R-factor	0.086	0.065	0.075	0.061	0.065	0.073
wR	0.122	0.070	0.082	0.061	0.066	0.086
No. parameters refined	163	190	262	154	172	190
$\Delta\rho$ excursions/e Å^{-3}	0.5; −0.6	0.3; −0.3	0.4; −0.3	0.4; −0.3	0.3; −0.4	0.3; −0.3

[a] A; diethyl ether–acetone, B; acetone–methanol, in the ratios given.

Table 3 The torsion angles of connecting domain between pyranoside and alkyl chain moieties

Pyranoside moiety	β-glucoside							α-galactoside					
Compound	**1**[a]	**2**	**3**	**4**[b]	**5**[b]	**6**[c]	**7**	**8**	**9**	**10**	**11**[d]	**12**[d]	**13**[c]
Alkyl chain length	1	3	5	7	9	11	13	1	3	5	7	9	11
Torsion angle (°)													
C(4)–C(5)–C(6)–O(6)	161	158	160	158	158	158	158	−60	−170	−170	−169	−168	−167
O(5)–C(5)–C(6)–O(6)	42	41	43	42	40	39	39	179	68	70	71	71	74
C(5)–C(6)–O(6)–C(8)	72	69	69	69	70	70	69	−179	−139	−132	−131	−129	−131
C(6)–O(6)–C(8)–C(9)	−177	−179	179	179	179	180	1	177	−179	179	180	178	176

[a] Ref. 17. [b] Ref. 8. [c] Ref. 10. [d] Ref. 9.

Experimental

X-Ray analysis

Compounds **2**, **3**, **7**, **9** and **10** were prepared by the reported method with lipase;[18] **8** was prepared by acetylation using acetic anhydride in pyridine. They were purified by column chromatography with the mobile phase, chloroform–methanol [9:1 (v/v)], and were recrystallized several times from acetone–methanol [1:1(v/v)]. Large crystals of **2**, **3**, **7–10** were obtained by slow evaporation from the solution given in Table 2 and were cut to a suitable size for X-ray measurements. Lattice constants and intensity data were measured at room temp. on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu-Kα radiation (40 kV, 25 mA). Crystal data and a summary of experimental details are listed in Table 2.‡ The unit cell parameters were refined with 25 reflections with the 2θ range from 40–50°. Intensity data were collected up to 150° in 2θ. The structures were determined by direct methods using the program XTAL 3.0[19] for **2**, **3** and **8–10** and SIR[20] incorporated in MolEN[21] for **7** and were refined by the full-matrix least-squares method on F_o. The quantity of minimization was $\Sigma w(\lvert F_c\rvert - \lvert F_o\rvert)^2$ with $w = 1$. The positions of hydrogen atoms attached to methylene and methine groups were calculated and included in the least-squares refinement. Those of the hydroxy groups in **3**, **7–10** were identified in difference Fourier maps and were included in the refinement with restraints for geometry between the hydrogen and bonded oxygen atoms. The refinement converged at R values of 0.086, 0.065, 0.075, 0.061, 0.065 and 0.073, for **2**, **3**, **7–10**, respectively.

Calorimetry

A Seiko DSC220 differential-scanning calorimeter was used for the thermal analysis. The samples were crystallized from the same solution as used in the preparation of crystals for X-ray analysis. The DSC curves were measured at a scan rate of 2.0 °C min^{-1}. The enthalpy at melting transformation was estimated by the integration of the DSC peak, and the entropy was calculated from the enthalpy and melting temperature. The optical anisotropy of the phases at melting transformation was observed by polarized microscopy.

Results and discussion

Molecular structure

The molecular structures of **2**, **3**, **7–10** are shown in Fig. 1. The conformation of these molecules differ between the different types of sugar moieties, but are not affected by the length of the alkyl chains, except for **8**. The sugar moieties have $^4C_1$ pyranose conformations, and the alkyl chains in the acyl groups have all *trans* conformations. The shapes of the molecules are character-

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‡ Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/106.

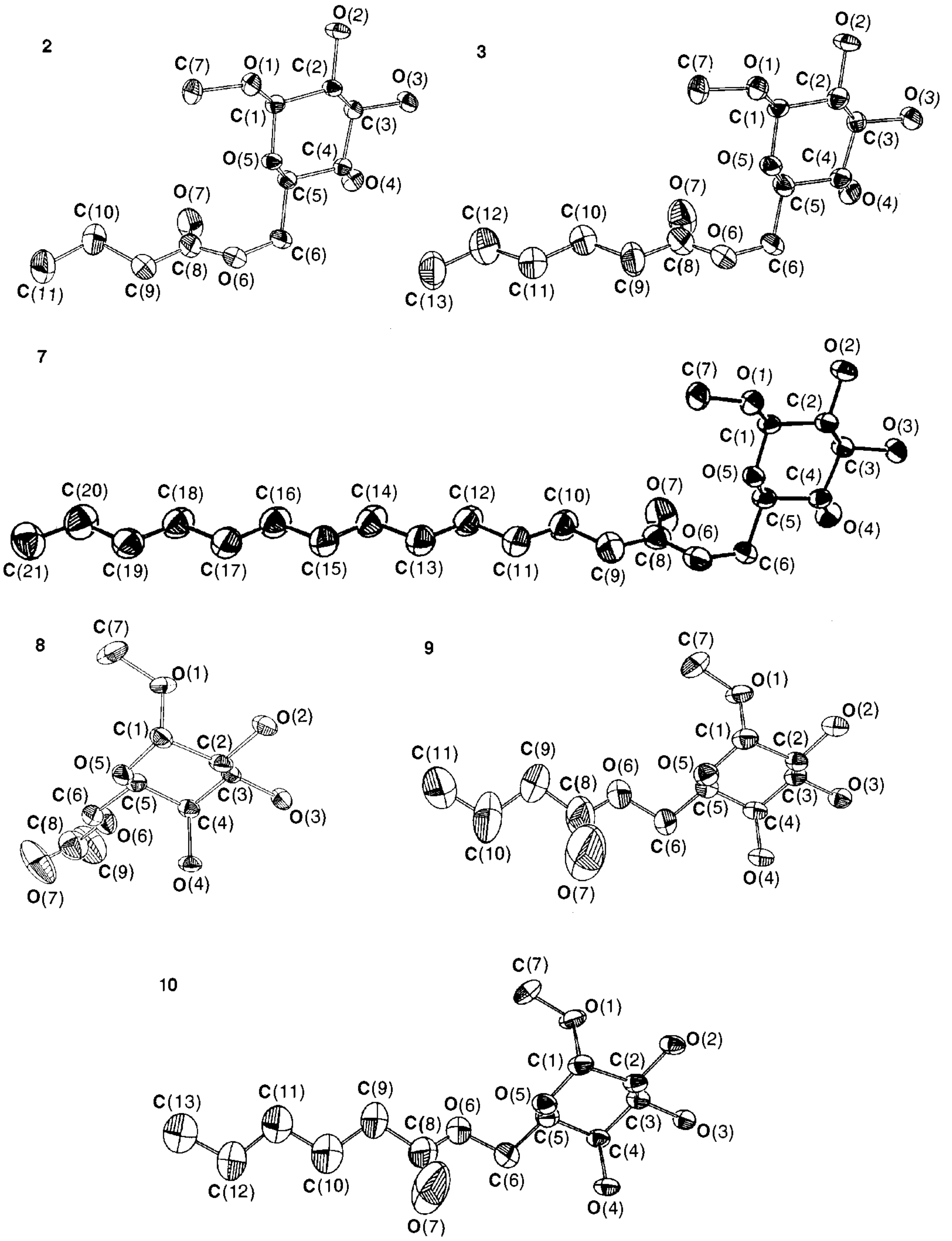


Fig. 1 Structure (ORTEP drawing) and atomic numbering for **2**, **3**, **7**–**10**. Thermal ellipsoids are drawn at 50% probability.

ized by the dihedral angles of the ester linkage, C(4)–C(5)–C(6)–O(6), O(5)–C(5)–C(6)–O(6), C(5)–C(6)–O(6)–C(8) and C(6)–O(6)–C(8)–C(9) (Table 3). The conformation of the ester group of the β-glucosides, among which the ranges in dihedral angles are within 4°, is not significantly affected by the alkyl chain length. However in the α-galactosides, **8** has a different conformation to the others, and the conformation in **9** is very similar but significantly different from the values of the dihedral angle for **10**–**12**. The conformation of these molecules may be affected by the crystal packing, especially by the alkyl chain packing, as is discussed below. The thermal parameters of alkyl carbon atoms in the α-galactoside derivatives are greater than those of the β-glucosides (Fig. 1). The oxygen atoms of the carbonyl groups in the α-galactoside derivatives, except for the acetyl derivative, have thermal parameters greater than those of the β-glucosides.

General view of molecular arrangement

The molecules are arranged in double layers with interdigitated alkyl chains (Fig. 2). This type of packing has been reported in several glycolipid structures which have pyranose or pyranoside rings.[1–6] The alkyl chain in a crystal is not perpendicular to the layer because the area occupied by the hydrophobic moiety in the layer is larger than that of the alkyl chain. These relations can be explained using eqn. (1) where the angle formed by the

$$S \cos \varphi = 2\Sigma^{1,10} \qquad (1)$$

alkyl chain and the normal to the bilayer is φ, the cross section area of the alkyl chain is Σ, and the occupied area of the layer is S which is estimated as the *ab* area of the unit cell.

S, Σ and φ are listed in Table 4. The β-glucoside has a larger φ angle than the α-galactoside because of the larger occupied area, S, of the β-glucoside than the α-galactoside. The occupied area, S, rapidly decreases in the order **2** to **5** in the derivatives of the β-glucoside, but the α-galactosides show a slight decrease in the order **9** to **13**. The cross sections of **2** and **3** are significantly smaller than those of **4**–**7** which decrease with the increase in

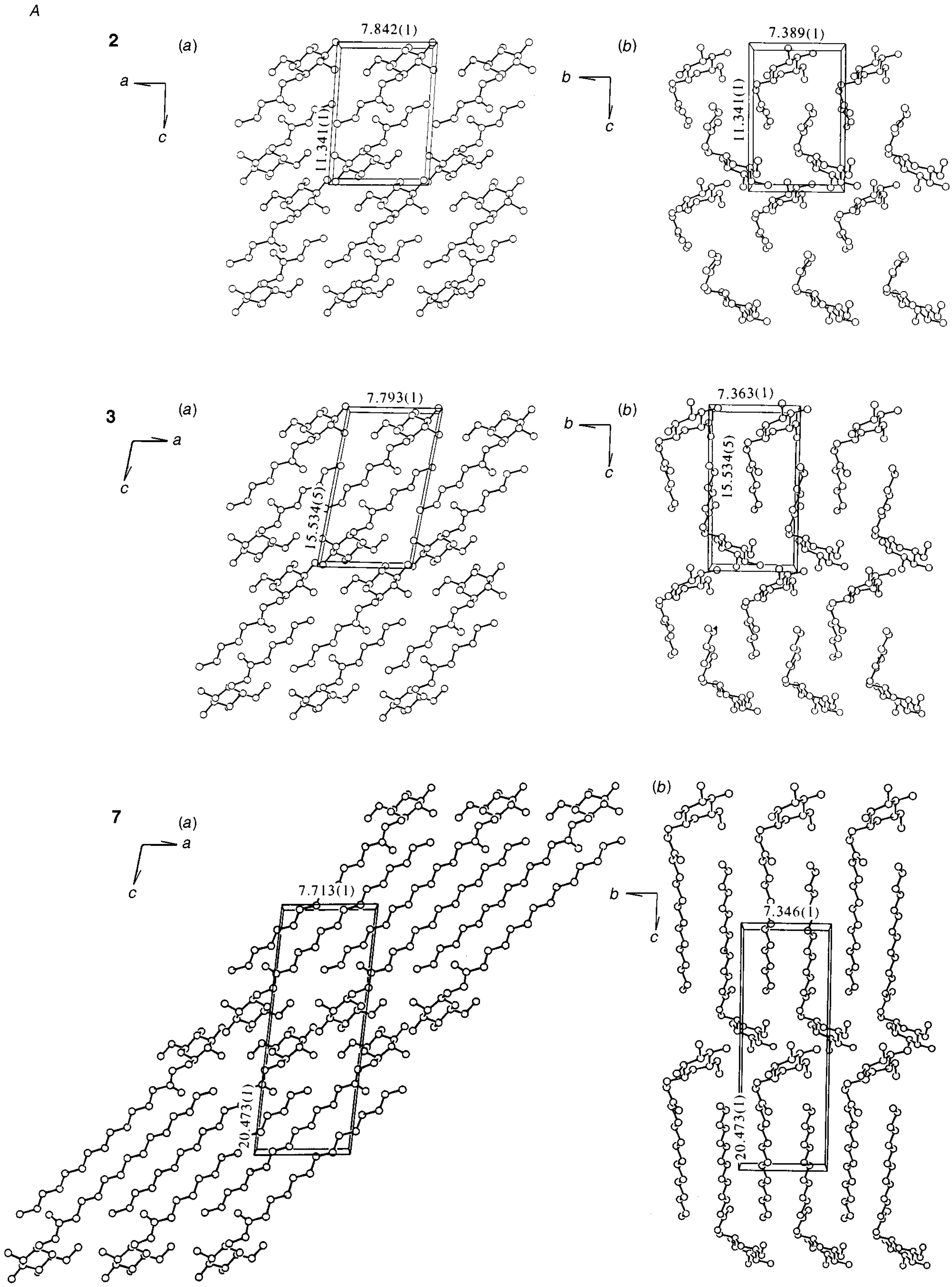
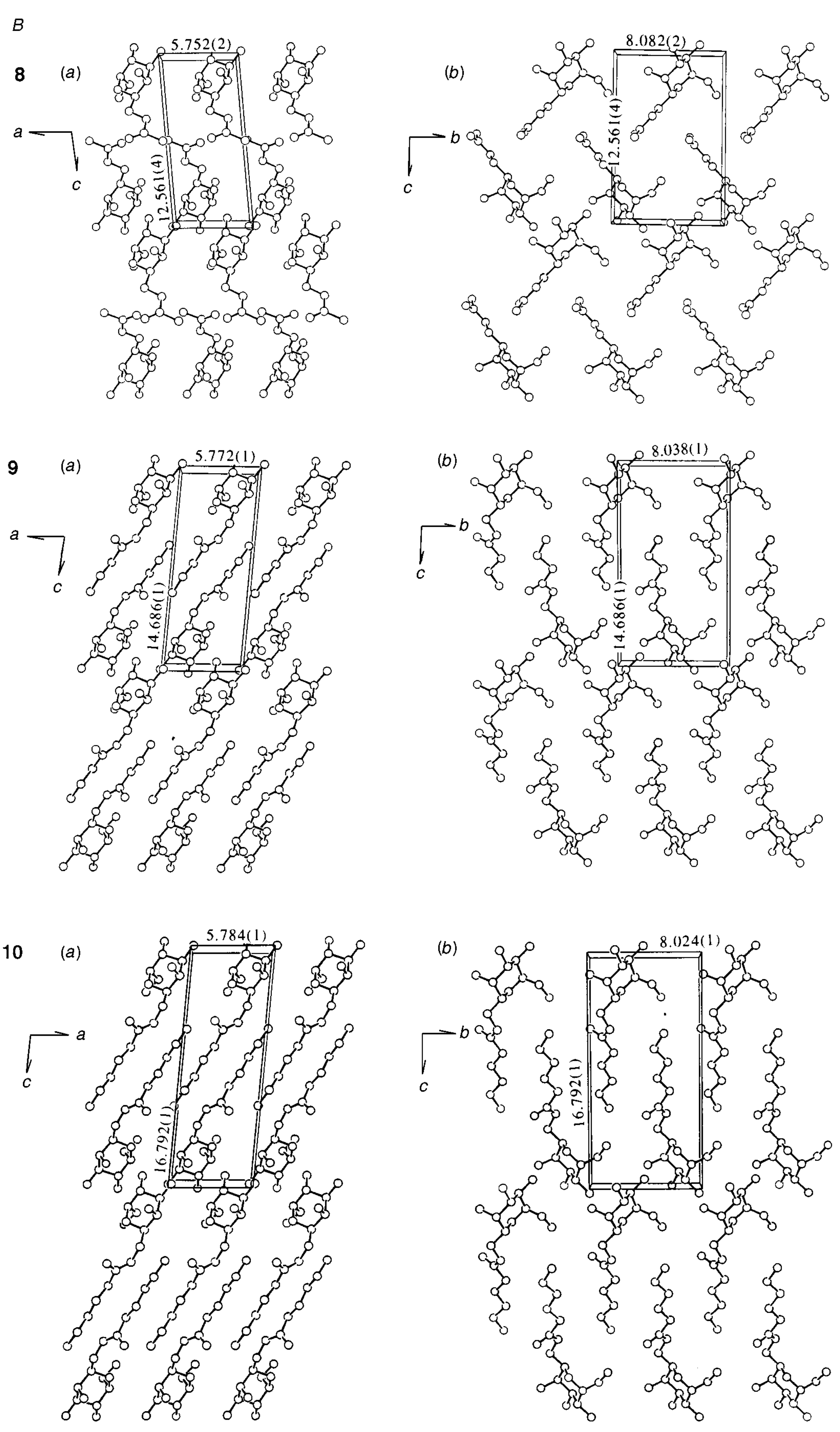


Fig. 2 (*A*) The crystal structures of β-glucoside derivatives, **2**, **3** and **7** projected on the *ac* plane (*a*) and viewed along the *a* axis (*b*). (*B*) (see next page) the crystal structures of α-galactoside derivatives, **8**–**10** projected on the *ac* plane (*a*) and viewed along the *a* axis (*b*).

the alkyl chain length for β-glucosides. On the other hand, the Σ value of the α-galactosides slightly increases in the order **9**–**11** but they decrease for **12**–**13**. In the β-glucoside derivatives, **2** and **3** show larger φ values than **4**–**7** which show the same values, while those of the α-galactoside, **9**–**13**, show similar values *ca.* 33–32°.

The packing of acetyl derivative **8** is different from that of the other α-galactoside derivatives which have longer alkyl



chains. In the crystal of the α-galactosides, the extension of the alkyl chains with the same conformation of the ester group would result in nonparallel arrangements of the alkyl chains, which would not allow efficient packing. The ester conformations of the α-galactosides change to allow the alkyl chains to arrange in parallel but keep the same arrangement of the sugars. In contrast, there is little change in the dihedral angles of the ester group in β-glucoside derivatives, suggesting that the alkyl chains can be extended without the conformational change of the ester group.

Hydrogen bonds between sugar moieties

Hydrogen bonds are identified from the distance and angle between the hydroxy group and the acceptor oxygen atom (Table 5). Hydrogen bonds link the inter-layer sugar moieties, but are not formed between sugar groups in the same layer. The finite hydrogen bonding chain, O(4)–O(3)–O(2)–O(5), is observed in all the crystals of the β-D-glucosides, while an infinite chain –O(2)–O(3)–O(4)–O(2)– is formed in crystals of the α-D-galactosides. These sugar-specific hydrogen bonding linkages are conserved in spite of the differences in the alkyl chain length.

Table 4 Structural parameters of crystal packing for **2**–**13**

Molecule	Number of carbon atoms in alkyl chain	Occupied area of layer S/Å^2	Cross section of alkyl chain Σ/Å^2	Inclination of alkyl chain φ (°)
2	3	57.9	18.2	51
3	5	57.4	18.3	50
4[a]	7	57.2	19.5	47
5[a]	9	56.8	19.3	47
6[b]	11	56.8	19.2	47
7	13	56.7	19.1	47
9	3	46.4	19.4	33
10	5	46.4	19.4	33
11[c]	7	46.3	19.6	32
12[c]	9	46.1	19.6	32
13[b]	11	46.0	19.5	32

[a] Ref. 8. [b] Ref. 10. [c] Ref. 9.

The mean value and range of hydrogen bonding distances between the donor hydrogen atoms of the hydroxy group and acceptor oxygens at each type of bonding for the glucosides, **3**, **6** and **7** is 1.93 and 1.92–1.93 for O(4)–H(4)···O(3), 1.98 and 1.94–2.04 for O(3)–H(3)···O(2), and 2.04 and 1.94–2.23 Å, respectively. Those of galactosides, **8**–**10** and **13** are 1.83 and 1.80–1.87 Å for O(4)–H(4)···O(3), 1.98 Å and 1.94–2.02 for O(3)–H(3)···O(2), and 1.82 and 1.79–1.82 Å, respectively. The average hydrogen bonding distances of the galactosides are shorter than those of glucosides, and the hydrogen bonding of the galactosides should be stronger than those of the glucosides.

Hydrogen atoms forming hydrogen bonds are not detected for all of the molecules. The hydrogen bonding geometry com-

Table 5 Hydrogen bonding geometry for **1**–**13**

Molecule	Hydrogen bonding linkage C(A)–O(B)–H(C)···O(D)–C(E)	Symmetry coord.	Distance/Å		Angle (°)			Dihedral angle (°) A–B–D–E
			$\varDelta$(BD)	$\varDelta$(CD)	∠(ABD)	∠(BCD)	∠(BDE)	
β-Glucosides								
1[b]	C(4)–O(4)–H(O4)···O(3)	a[a]	2.806(4)	2.17	92(1)	151	130(1)	−95(1)
2		b	2.79(4)	—	93(1)	—	128(2)	−95(2)
3		c	2.81(3)	1.93	92(1)	152	128(2)	−97(1)
4[c]		d	2.808(9)	—	92(1)	—	127(1)	−97(1)
5[c]		e	2.798(6)	—	93(1)	—	127(1)	−98(1)
6[d]		f	2.80(2)	1.92	93(1)	155	128(1)	−97(1)
7		g	2.82(2)	1.93	92(1)	154	127(1)	−98(1)
1[b]	C(3)–O(3)–H(O3)···O(2)	a	2.840(4)	2.20	122(1)	157	132(1)	−94(1)
2		b	2.85(3)	—	122(1)	—	134(1)	−92(2)
3		c	2.85(2)	1.96	122(1)	155	133(1)	−91(2)
4[c]		d	2.841(8)	—	122(1)	—	133(1)	−92(1)
5[c]		e	2.863(6)	—	123(1)	—	132(1)	−91(1)
6[d]		f	2.84(1)	1.94	122(1)	158	133(1)	−93(1)
7		g	2.83(1)	2.04	123(1)	139	133(1)	−92(1)
1[b]	C(2)–O(2)–H(O2)···O(5)	h	2.932(3)	2.20	107(1)	175	134(1)	1(1)
2		i	2.90(2)	—	107(1)	—	135(2)	−2(1)
3		j	2.91(1)	1.95	108(1)	178	135(2)	−2(1)
4[c]		k	2.890(9)	—	109(1)	—	134(1)	−3(1)
5[c]		l	2.890(5)	—	109(1)	—	134(1)	−4(1)
6[d]		m	2.90(1)	2.23	109(1)	127	133(1)	−4(1)
7		n	2.892(9)	1.94	109(1)	172	134(1)	−5(1)
α-Galactosides								
8	C(2)–O(2)–H(O2)···O(3)	k	2.75(3)	1.80	113(1)	172	114(1)	−142(1)
9		o	2.74(2)	1.81	115(1)	164	116(1)	−141(1)
10		o	2.78(3)	1.83	113(1)	169	115(1)	−141(2)
11[e]		p	2.776(6)	—	113(1)	—	114(1)	−141(1)
12[e]		m	2.771(7)	—	113(1)	—	114(1)	−141(1)
13[d]		m	2.77(2)	1.87	113(1)	156	114(1)	−140(1)
8	C(3)–O(3)–H(O3)···O(4)	k	2.84(3)	2.00	106(2)	146	135(1)	51(1)
9		o	2.85(2)	1.94	108(1)	157	136(1)	47(1)
10		o	2.82(3)	2.01	106(2)	140	135(1)	49(1)
11[e]		p	2.805(6)	—	108(1)	—	134(1)	50(1)
12[e]		m	2.796(7)	—	109(1)	—	134(1)	48(1)
13[d]		m	2.80(3)	1.96	108(1)	146	136(1)	48(1)
8	C(4)–O(4)–H(O4)···O(2)	j	2.738(7)	1.82	123(1)	160	102(1)	−152(1)
9		q	2.701(5)	1.79	121(1)	157	100(1)	−152(1)
10		q	2.752(7)	1.84	122(1)	159	103(1)	−152(1)
11[e]		n	2.750(6)	—	123(1)	—	103(1)	−151(1)
12[e]		m	2.747(7)	—	123(1)	—	103(1)	−150(1)
13[d]		m	2.76(1)	1.83	121(1)	161	103(1)	−151(1)

[a] The symmetry coordinates are represented by the following: a: $[-x, y + 5/2 , -z]$, b: $[-x, y + 1/2, -z + 2]$, c: $[-x + 2, y + 1/2, -z]$, d: $[-x, y - 1/2, -z]$, e: $[-x + 3, y - 1/2, -z]$, f: $[-x - 1, y + 1/2, -z + 1]$, g: $[-x + 3, y + 1/2, -z + 1]$, h: $[-x, y - 5/2, -z]$, i: $[-x + 1, y - 1/2, -z + 2]$, j: $[-x + 1, y - 1/2, -z]$, k: $[-x, y + 1/2, -z]$, l: $[-x + 2, y + 3/2, -z + 1]$, m: $[-x, y - 1/2, -z + 1]$, n: $[-x + 2, y - 1/2, -z + 1]$, o: $[-x, y - 1/2, -z + 2]$, p: $[-x + 3, y + 1/2, -z + 1]$, q: $[-x + 1, y + 1/2, -z + 2]$, [b] Values from ref. 17, in which the positional parameters for the hydrogen atoms were refined. [c] Ref. 8. [d] Ref. 10. [e] Ref. 9.

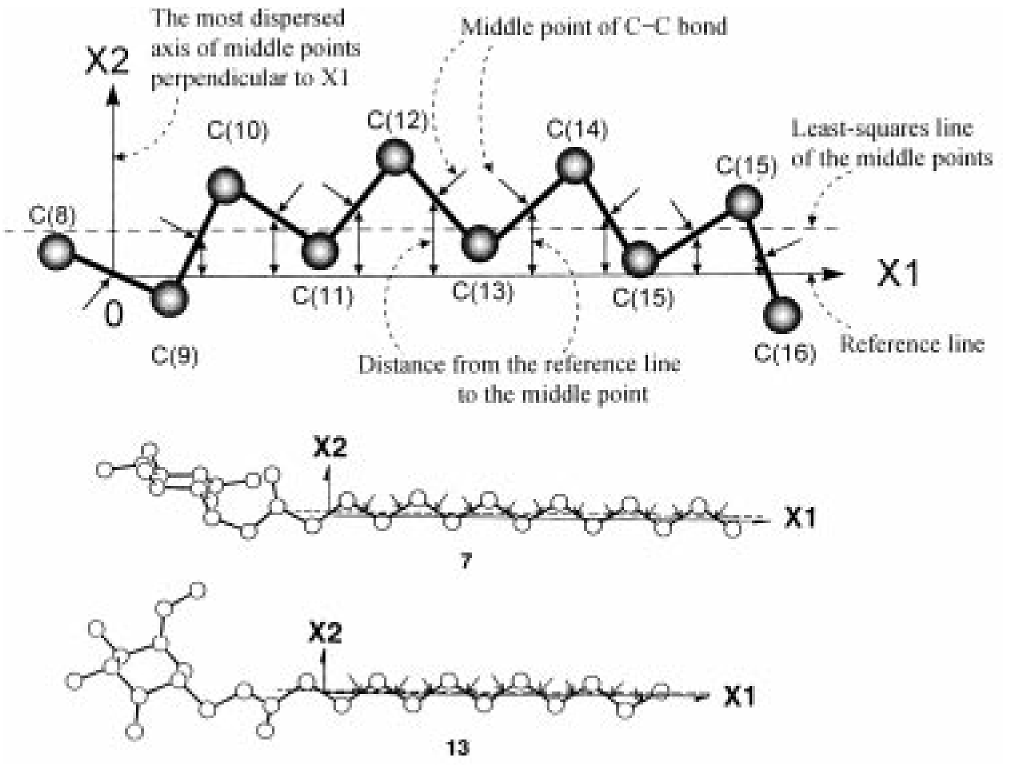


Fig. 3 A schematic drawing of the model for the measurement of the degree of distortion of the alkyl chain and its application to **7** and **13**. The arrows indicate the mid-points of the C–C bond in the alkyl chain. The dotted line is the least-squares line through the mid-points. The reference line, X1, is defined as that which passes through the mid-point between C(8) and C(9). X2 is the axis which is pointed to the most dispersed direction of mid-points perpendicular to X1.

pared with the lengths between O(B) and O(D), the angles, O(A)–O(B) · · · C(D), O(B) · · · O(D)–C(E) and the dihedral angles C(A)–O(B) · · · O(D)–C(E) related to the hydrogen bonding without the hydrogen atoms of hydroxy groups has a similar value for each type of hydrogen bonding for the molecules with different lengths of alkyl chain (Table 5). The differences are within 0.04 and 0.06 Å [distances of O(B) · · · O(D)], 3 and 4° [angles of C(A)–O(B) · · · O(D) or O(B) · · · O(D)–C(E)] and 6 and 4° [dihedral angles of C(A)–O(B) · · · O(D)–C(E)] for the β-glucosides and the α-galactosides, respectively.

In the β-glucosides, the structures of the hydrogen bonding linkage are the same as those of the methyl β-D-glucopyranoside hemihydrate,[22] having the hydrogen bond chain, O(6) · · · O(water) · · · O(4) · · · O(3) · · · O(2) · · · O(5), which is not affected by the acylation of the 6-position. In contrast, the α-galactosides have arrangements of the sugar moiety and hydrogen bond linkage which are different from those in the crystals of methyl α-D-galactopyranosides hydrate.[23]

Alkyl chain packing

The packing of the alkyl chain may be characterized in relation to the structure of the sugar moieties. The adjacent two alkyl planes are nearly perpendicular in crystals of β-D-glucosides, but parallel packing is observed in crystals of α-galactosides. The former is categorized as $O'_\perp$ and the latter as $O'_\parallel$, according to Vand.[24] These types of packing are not affected by the length of the alkyl chain. All of the alkyl chains are somewhat bent. The adjacent two alkyl chains are not parallel (Fig. 2); the difference in the angles made by a pair of interdigitated alkyl chains is shown in Table 6. The degree of distortion of the alkyl chain is measured as the distance from the reference line to the mid-point of each C–C bond. The reference line is defined as a line passing the mid-point of the C(8)–C(9) bond parallel to the least-squares line and through the mid-points of the C–C bonds in the alkyl chain, as shown Fig. 3. The distance between the mid-points of the C–C bond and the reference line is plotted in Fig. 4. The alkyl chains of **2**–**4** and **9**–**13** are bent in an arc and those of **5**–**7** form a 'meander'. The distortion of the alkyl chain is caused by contact with adjacent molecules. This contact is observed between O(7) and the adjacent alkyl chain in the β-glucosides. Since this unfavorable contact disturbs the packing between adjacent alkyl chains, the line of the alkyl chain causes the 'meander' (Fig. 5). The bending of the alkyl chains is more prominent in **5**–**7** than in **2**–**4**. The steric hindrance of O(7) with the alkyl chains in **2**–**4** produces larger angles between pairs of interdigitated alkyl chains than those of **5**–**7**, because the alkyl chain is too short to bend. The steric hindrance of O(7) with the end of the adjacent alkyl chain bends the alkyl chains in derivatives **5**–**7**. The alkyl chains of the α-galactosides are bent by the contact with the adjacent oxygen O(7) at the end of the chain, while those of the β-glucosides are bent at the position of contact with O(7) [Table 6, Fig. 3 and 4(*b*)]. The larger angles made by a pair of interdigitated alkyl chains and less distinctive bending for **8**–**10** than **11**–**13** should be caused by the same effect as found in the β-glucosides, where the steric hindrance of O(7) affects the structure of the whole alkyl chain in **8**–**10**.

Table 6 Angles made by a pair of interdigitated alkyl chain directions

Molecule	Difference in angles (°)	Molecule	Difference in angles (°)
2	27.7	**9**	11.0
3	10.1	**10**	10.1
4	5.9	**11**	5.9
5	1.8	**12**	4.6
6	0.3	**13**	2.1
7	0.0		

Atomic thermal parameters

The values of the thermal parameters are shown in Fig. 6. The sugar moiety has thermal parameters lower than those of the alkyl chain moiety. The thermal parameters of carbon atoms in

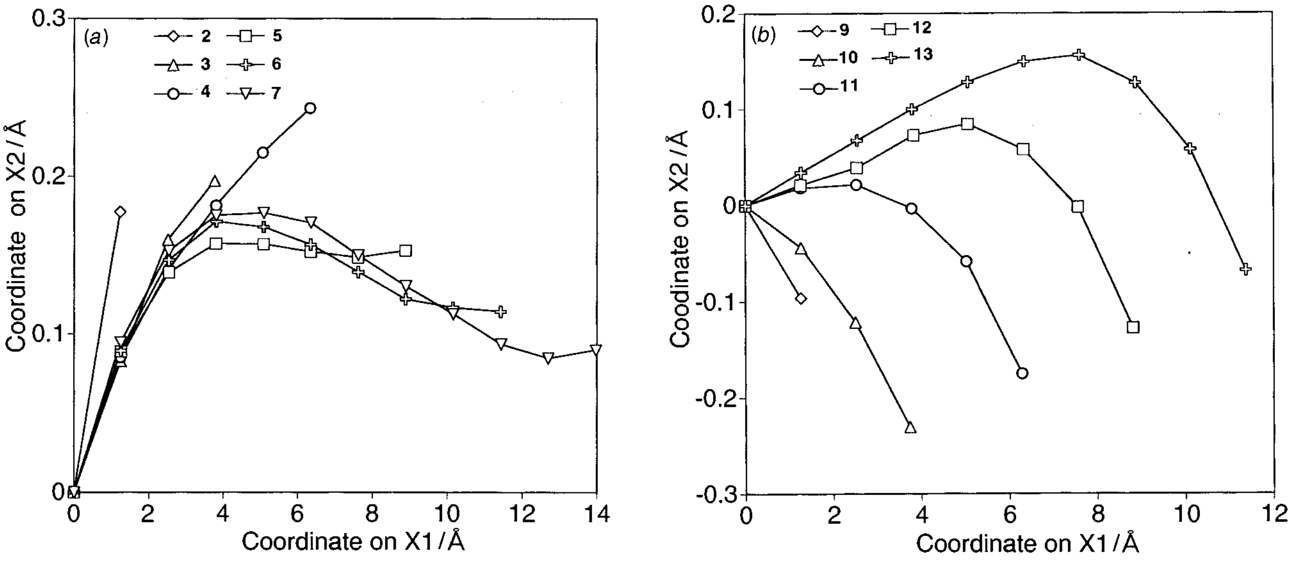
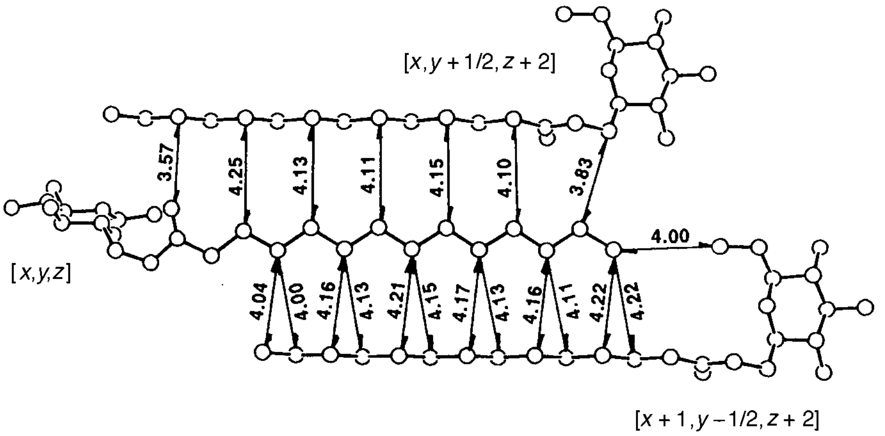


Fig. 4 Plot of the distance from the reference line to the mid-point of the C–C bond of the alkyl chain against the distance from the mid-point of the C(8)–C(9) bond



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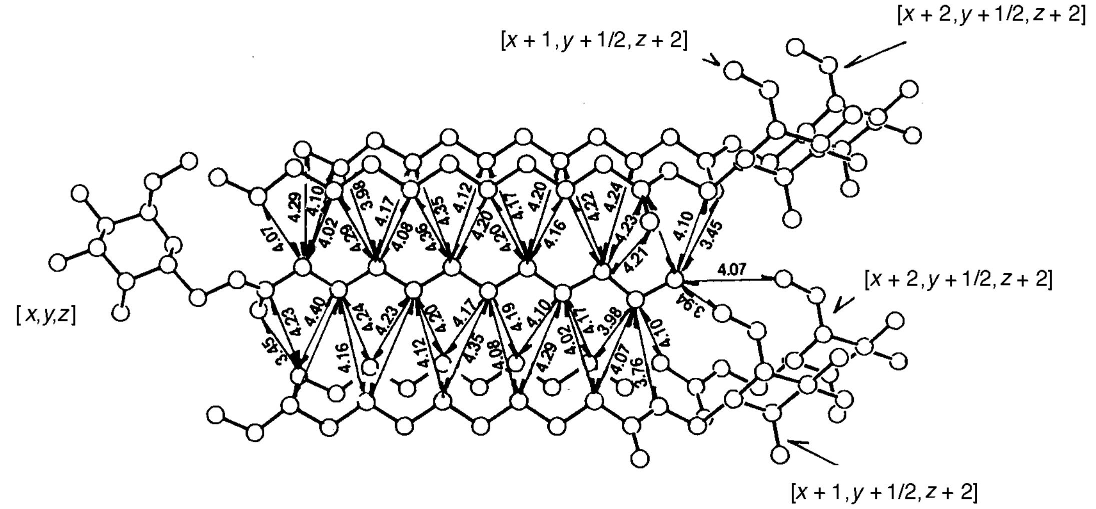

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Fig. 5 The distances between the alkyl chains of adjacent molecules

the alkyl chain moiety of the α-galactoside derivatives are greater than those of the β-glucoside derivatives. Two carbon atoms at the end of the alkyl chain in the β-glucosides have thermal parameters greater than those of other carbon atoms in the alkyl chain. The second carbon atom from the end of the alkyl chain in the α-galactoside has the greatest thermal parameter of the carbon atoms in the alkyl chain. The carbonyl oxygen atoms in the α-glucosides have the greatest thermal parameters, regardless of the very similar values of those in the alkyl chain of the β-glucosides. These values of the thermal

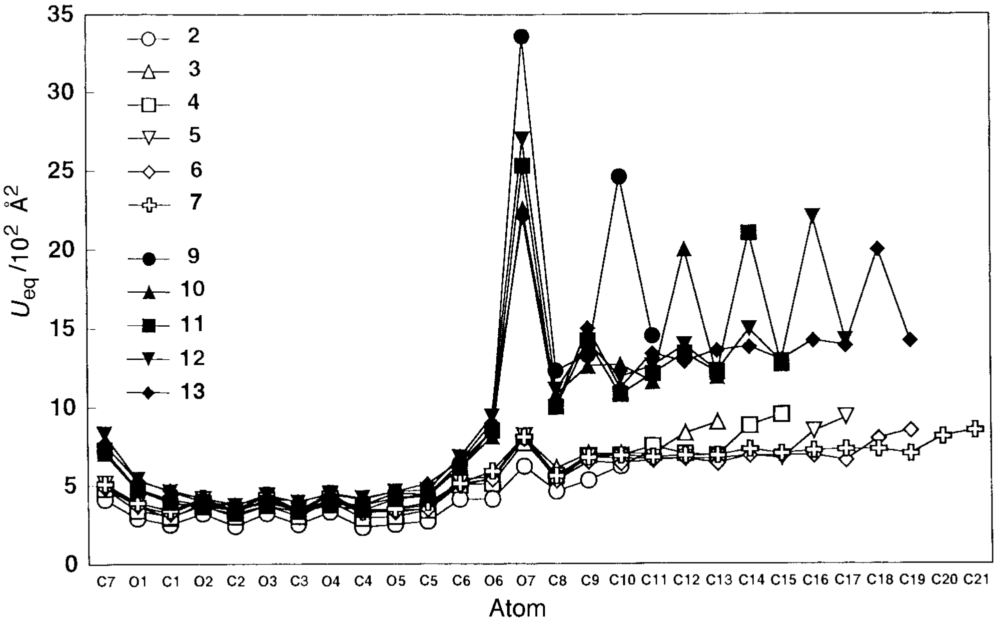

Fig. 6 Plot of isotropic thermal parameters of β-glucosides **2**–**7** and α-galactosides **9**–**13**

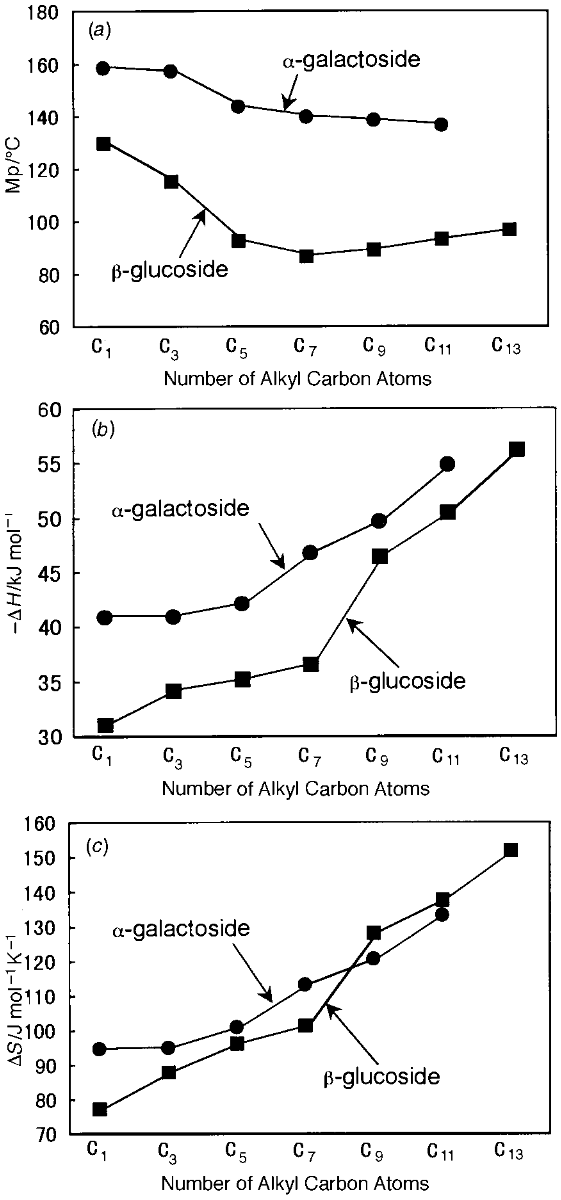

Fig. 7 Plot of melting point (*a*), melting enthalpy (*b*), and melting entropy (*c*) of each glycoside against the number of alkyl carbon atoms

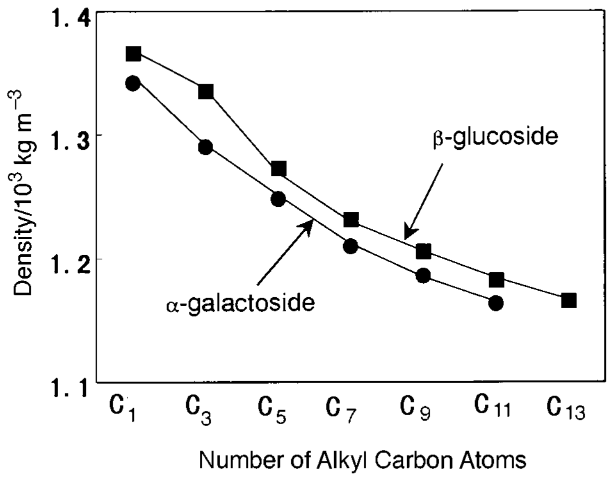

Fig. 8 Plot of density of the crystals against the number of alkyl carbon atoms

parameters in the alkyl chain are only slightly affected by the length of the alkyl chain, but are different between the β-glucosides and α-galactosides which differ in the alkyl chain packing.

Calorimetry

Melting temperatures, enthalpy and entropy of melting transitions are shown in Fig. 7. At melting temperature, the direct transition from crystal to isotropic liquid is observed by polarized microscopy, in contrast with the formation of the mesophase for alkyl glucosides.[24] The α-galactosides which have shorter hydrogen bonding distances than the β-glucosides show higher melting temperatures than the β-glucosides for a given alkyl chain length. The melting temperatures of the glucosides are at a minimum with a heptyl-length chain, while the melting temperatures of the galactosides continue to decrease as the alkyl chain length increases, up to a tridecyl-length chain; the rate of decrease changes at a pentyl-length chain. The same tendency is also observed for the enthalpy and entropy. The packing structure of the alkyl chains changes at heptyl and pentyl length for glucosides and the galactosides, respectively, gleaned from the angle measured between a pair of interdigitated alkyl chains (Table 6). The alkyl chain moiety contributes to the thermal stability of the crystal for chains longer than nonyl for the β-glucosides and heptyl for the α-galactosides, respectively. Densities of the crystals are shown in Fig. 8. A slight change in the difference of the density at C_7 for the β-glucosides, which is caused by a change in the packing of the alkyl chains is observed. This means that β-glucosides with alkyl chains C_1–C_7 cause a greater decrease in density with increasing chain length than is the case for C_7–C_{13}, due to less rigid packing of the alkyl chains. The alkyl chain packing in the β-glucosides is more stable than in α-galactosides with alkyl chains longer than nonyl, because the ΔH of melting of the α-galactosides decreases much more with increasing alkyl chain length than the ΔH of the β-glucosides with the corresponding

Conclusions

The arrangement of sugar moieties in the crystal are not significantly affected by the change in alkyl chain length. In spite of the variety of chain lengths, the same arrangement of alkyl chains is observed for the derivatives of β-glucoside or for the α-galactoside, except for the acetyl derivative of α-galactoside. The thermal stabilities of the crystals are affected by the types of sugar moiety and the packing structure of the alkyl chain moiety. Crystals of α-galactosides have higher thermal stability than those of β-glucosides. The elongation of the alkyl chain moiety decreases the thermal stability of the crystal, except for a slight increase in β-glucosides which have a longer alkyl chain than the nonyl group. This increase in thermal stabilities of the β-glucosides is caused by the ordered packing of the alkyl chain moieties. In contrast, the monotonic decrease in the thermal stabilities, *n*, of the α-galactosides is ascribed to the less-ordered packing of the alkyl chain moieties with greater thermal parameters than those in the β-glucosides.

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