atoms which causes a dispersion of charge through N(1)—C(11)—N(2). As a consequence the N(1)—C(2) and N(2)—C(3) bonds are longer at 1·400 (5) and 1·407 (4) Å respectively.

The naphthalene rings, imidazolium ring and the methyl C atom are all coplanar, with a maximum deviation from the mean plane of 0·054 (5) Å, indicating that the entire cation is a completely delocalized π system. The Cl^- anion is 2·314 (6) Å removed from the plane of the cation. The anion is the receptor of two strong hydrogen bonds, one from water, to form a complex bridge between pairs of cations of the form N—H···Cl^-···H—O···H—O···H—N. The remaining two water H atoms form weaker hydrogen bonds with the Cl^- anion. A stereo packing diagram of the molecules is shown in Fig. 2. The molecules form stacks along the **a** direction. The two independent interplanar separations between adjacent molecules are 3·57 (3) and 3·49 (3) Å. The bond lengths and angles of the hydrogen bonds are given in Table 3. Other bond lengths and angles fall in the normal ranges.

We thank the Natural Sciences and Engineering Research Council of Canada for operating grants to RJB and BER. We also thank the Canadian International Development Agency for support of YL and the University of Regina for computing time.

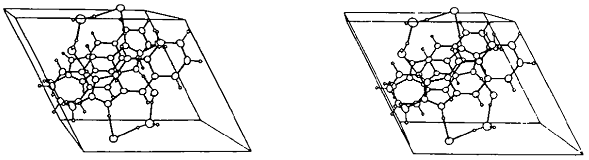


Fig. 2. Stereo packing diagram of the molecules along the *a* axis. The *a* axis is into the page, the *b* axis is vertical and the *c* axis is horizontal.

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

X—H···*Y*	*X*—H (Å)	H···*Y* (Å)	*X*···*Y* (Å)	*X*—H···*Y* (°)
N(2)—H(O2)···Cl	1·03 (4)	2·07 (4)	3·096 (3)	176 (3)
O(2)—H(O22)···Cl	1·05 (7)	2·18 (6)	3·179 (5)	150 (2)
O(1)—H(O12)···O(2)	0·95 (4)	1·77 (4)	2·712 (5)	169 (5)
N(1)—H(O1)···O(1)	0·94 (4)	1·78 (4)	2·698 (5)	167 (2)
O(1)—H(O11)···Cl	0·85 (4)	2·36 (4)	3·202 (4)	172 (4)
O(2)—H(O21)···Cl	0·82 (5)	2·36 (5)	3·226 (4)	176 (4)

References

Craven, B. M., McMullan, R. K., Bell, J. D. & Freeman, H. C. (1977). *Acta Cryst.* B**33**, 2585–2589.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Martínez-Carrera, S. (1966). *Acta Cryst.* **20**, 783–789.

Stewart, J. M. & Hall, S. R. (1984). *Tech. Rep.* TR-873.2. Computer Science Center, Univ. of Maryland, College Park, MD, USA.

Will, G. (1969). *Z. Kristallogr.* **129**, 211–221.

Acta Cryst. (1988). C**44**, 1051–1054

Structures of Two Isomeric Thiodisaccharides

By Gene B. Carpenter

Department of Chemistry, Brown University, Providence, Rhode Island 02912, *USA*

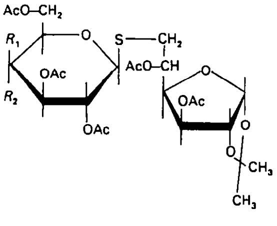
and Helmut Kristen

Sektion Chemie, Wilhelm-Pieck-Universität, Buchbinderstrasse 9, 2500 *Rostock, German Democratic Republic*

(*Received* 22 *October* 1987; *accepted* 15 *February* 1988)

Abstract. Two isomeric thiodisaccharides of formula $C_{27}H_{38}O_{16}S$, $M_r = 650{\cdot}62$, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}5$–$1{\cdot}6\ \text{cm}^{-1}$, $T \sim 298$ K. (1) 3,5-Di-*O*-acetyl-6-*S*-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl]-6-deoxy-1,2-*O*-isopropylidene-6-thio-α-D-glucofuranose, triclinic, $P1$, $a = 8{\cdot}018$ (1), $b = 9{\cdot}834$ (2), $c = 11{\cdot}240$ (2) Å, $\alpha = 78{\cdot}51$ (1), $\beta = 80{\cdot}64$ (1), $\gamma = 85{\cdot}68$ (1)°, $V = 856{\cdot}04$ (25) Å^3, $Z = 1$, $D_x = 1{\cdot}26\ \text{g cm}^{-3}$, $F(000) = 344$, $R = 0{\cdot}050$ for 3126 unique observed reflections with $I > \sigma(I)$. (2) 3,5-Di-*O*-acetyl-6-*S*-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl]-6-deoxy-1,2-*O*-isopropylidene-6-thio-α-D-glucofuranose, monoclinic, $P2_1$, $a = 5{\cdot}589$ (1), $b = 20{\cdot}161$ (6), $c = 14{\cdot}983$ (3) Å, $\beta = 94{\cdot}52$ (2)°, $V = 1682{\cdot}95$ (64) Å^3, $Z = 2$, $D_x = 1{\cdot}28\ \text{g cm}^{-3}$, $F(000) = 688$, $R = 0{\cdot}053$ for 2909 unique observed reflections with $I > \sigma(I)$. The molecules have the same connectivity, and differ only in the gluco–galacto configurations; the consequence is that the galacto isomer is more extended than the gluco. The r.m.s. difference for 46 equivalent bonds in the two isomers is 0·016 Å, which is about three times the least-squares estimate.

Introduction. The structures of compounds (1) and (2) were determined to verify that a novel synthesis (Kristen, Boye, Schoknecht & Tesch, 1987) of thiodisaccharides yielded the expected products.



(1) $R_1 = H, R_2 = OAc$

(2) $R_1 = OAc, R_2 = H$

$Ac = COCH_3$

Experimental. Prepared by nucleophilic ring opening of 1,2-*O*-isopropylidene-5,6-anhydro-α-D-glucofuranose with 2,3,4,6-tetra-*O*-acetyl-1-deoxy-1-thio-*β*-D-glucopyranose and -galactopyranose, respectively. Details of the synthesis will be published elsewhere. Colorless single crystals mounted on glass fiber with quick-setting epoxy cement. Nicolet *R*3*m*/*E* diffractometer system, graphite monochromator, unit-cell parameters by least-squares refinement of 23–25 reflections ($23 \leq 2\theta \leq 35°$), θ–2θ scans at variable rates (4·9–29·3° min^{-1}), $2\theta_{max} = 50°$, three reflections monitored every 97 reflections, correction made for 2% decrease in intensity over the course of data collection, no absorption correction, observed reflections with $I > \sigma(I)$ used for refinement, maximum $(\sin\theta)/\lambda = 0{\cdot}59$ Å^{-1}. Structure by direct methods; H atoms inserted in ideal positions, all C—H bond lengths fixed at 0·96 Å; anisotropic thermal parameters for S, all O, and C(13) through C(27) atoms, isotropic parameters for atoms C(1) through C(12) and fixed isotropic parameters for H atoms (about 20% greater than that of carrying atom). C atoms in the more rigid parts of the molecule treated as isotropic in order to keep the total number of parameters less than one-eighth the number of measurements. Absolute structures (Jones, 1984) tested by η refinement (Rogers, 1981) although Friedel equivalents not measured. Refined by cascade block-diagonal least squares on *F*, about 100 parameters per block chosen automatically on the basis of type of parameter and the shift/e.s.d. ratio, atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations were performed on a Data General Eclipse S140 computer using the *SHELXTL* 5·1 (Sheldrick, 1985) program package.

(1) Irregular crystal, approximately 0·32 × 0·38 × 0·62 mm, index range $0 \leq h \leq 9$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$, 3231 measured unique intensities, $R_{int} = 0{\cdot}008$, 3126 unique observed data used for refinement, origin specified by fixing coordinates of S atom, refinement of 335 parameters converged to $R = 0{\cdot}050$, $wR = 0{\cdot}061$, $w = 1/[\sigma^2(F) + 0{\cdot}00020F^2]$ where $\sigma^2(F)$ is from counting statistics, goodness of fit = 2·62, $|\Delta/\sigma|_{max} = 0{\cdot}10$ in final cycle; highest peak in final difference map 0·26, lowest hole −0·25 e Å^{-3}. $\eta = 0{\cdot}98$ (22), suggesting that the structure is absolute.

(2) Irregular crystal approximately 0·30 × 0·44 × 0·66 mm, index range $0 \leq h \leq 6$, $0 \leq k \leq 24$, $-17 \leq l \leq 17$, 3077 measured unique intensities (not including space-group absences), $R_{int} = 0{\cdot}016$, 2909 unique observed data used for refinement, origin specified by fixing *y* coordinate of S, refinement of 337 parameters converged to $R = 0{\cdot}053$, $wR = 0{\cdot}058$, $w = 1/[\sigma^2(F) + 0{\cdot}00060F^2]$ where $\sigma^2(F)$ is from counting statistics, goodness of fit = 1·50, $|\Delta/\sigma|_{max} = 0{\cdot}04$ in final cycle; highest peak in final difference map 0·24, lowest hole −0·25 e Å^{-3}. $\eta = 1{\cdot}40$ (25), suggesting that the structure is absolute.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.* In the tables the description 'gluco-thiodisaccharide' is used for (1) instead of the full name; similarly 'galacto-thiodisaccaride' is used for (2). Fig. 1 is a thermal-ellipsoid plot of molecule (1), showing the atom-numbering scheme; Fig. 2 similarly for molecule (2); the numbering scheme is the same. The primary difference between the two isomers is at atom C(10): (1) has the gluco configuration, (2) has the galacto configuration. The pyranose rings are in chair conformation and the substituent groups are attached equatorially at C(8), C(9) and C(11). At C(10) the acetyl group of the gluco molecule is also equatorial, whereas that of the galacto molecule is axial. This simple difference at one end of the molecule causes a large difference in overall shape: the two halves of the molecules differ in rotation about the C(5)—C(6) single bond in such a way that the galacto isomer is more extended. Although the packing possibilities for the two may be the cause of the differing shapes, no intermolecular contacts in either crystal are notably short.

The sample standard deviation for the lengths (uncorrected for the effect of thermal motion) of 46 equivalent bonds in the two molecules, $[\sum(\Delta D)^2/45]^{1/2}$, is 0·0157 Å, whereas the typical standard deviation estimated from least squares is 0·005. The larger differences tend to occur for bonds involving the atoms with larger thermal motion. A small component of this r.m.s. difference comes from the fact that the bonds in compound (2) are on average 0·0026 Å longer than for compound (1); this seems to be the consequence of the slightly lower typical thermal motion for the former. In spite of the large differences in lengths of individual bonds in the two isomers, the large number of

---

* Tables of bond lengths and bond angles for non-H atoms, anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44772 (49 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U/U_{eq}		x	y	z	U/U_{eq}
Gluco-thiodisaccharide					Galacto-thiodisaccharide				
S	3683	8250	3707	69 (1)*	S	2887 (2)	6635	1296 (1)	53 (1)*
C(1)	7438 (6)	6213 (4)	6786 (4)	67 (1)	C(1)	5290 (7)	8011 (2)	4745 (3)	50 (1)
C(2)	6169 (5)	5805 (4)	7947 (4)	68 (1)	C(2)	7379 (7)	7594 (2)	5156 (3)	47 (1)
C(3)	4750 (5)	6900 (4)	7798 (3)	62 (1)	C(3)	7587 (6)	7023 (2)	4509 (2)	41 (1)
C(4)	4938 (5)	7376 (3)	6431 (3)	54 (1)	C(4)	6544 (6)	7326 (2)	3637 (2)	43 (1)
C(5)	4201 (5)	8815 (4)	5966 (3)	61 (1)	C(5)	5399 (7)	6839 (2)	2954 (2)	44 (1)
C(6)	4539 (5)	9309 (4)	4600 (4)	65 (1)	C(6)	4485 (7)	7180 (2)	2096 (3)	53 (1)
C(7)	5518 (4)	7153 (3)	3347 (3)	55 (1)	C(7)	5208 (7)	6430 (2)	573 (2)	44 (1)
C(8)	5004 (5)	5939 (3)	2843 (3)	52 (1)	C(8)	4388 (7)	5832 (2)	3 (3)	45 (1)
C(9)	6559 (4)	5116 (4)	2366 (3)	53 (1)	C(9)	5972 (7)	5715 (2)	−758 (3)	50 (1)
C(10)	7853 (5)	6038 (3)	1533 (3)	53 (1)	C(10)	6494 (7)	6349 (2)	−1252 (3)	48 (1)
C(11)	8253 (5)	7153 (4)	2195 (3)	58 (1)	C(11)	7370 (7)	6875 (2)	−580 (3)	50 (1)
C(12)	9525 (6)	8163 (5)	1470 (4)	80 (1)	C(12)	7946 (8)	7525 (2)	−996 (3)	63 (1)
C(13)	6864 (7)	3893 (4)	7085 (4)	79 (2)*	C(13)	8518 (9)	8685 (3)	5134 (4)	86 (2)*
C(14)	6099 (10)	3005 (5)	6395 (5)	112 (3)*	C(14)	10020 (13)	9101 (3)	4619 (9)	201 (6)*
C(15)	8185 (8)	3117 (5)	7806 (5)	103 (2)*	C(15)	8308 (18)	8891 (4)	6112 (5)	193 (5)*
C(16)	4304 (6)	8136 (4)	9442 (3)	69 (1)*	C(16)	7030 (8)	5958 (2)	5139 (3)	57 (1)*
C(17)	4649 (9)	9426 (5)	9833 (4)	104 (2)*	C(17)	5224 (10)	5487 (3)	5408 (4)	79 (2)*
C(18)	1543 (8)	9757 (4)	6865 (5)	105 (2)*	C(18)	6859 (7)	5724 (2)	2869 (2)	49 (1)*
C(19)	−231 (9)	9402 (6)	7351 (7)	141 (3)*	C(19)	8924 (9)	5329 (3)	2604 (4)	75 (2)*
C(20)	2450 (7)	4823 (7)	3794 (5)	104 (2)*	C(20)	2619 (8)	4942 (2)	775 (3)	54 (1)*
C(21)	1596 (9)	3929 (8)	4892 (7)	146 (3)*	C(21)	3236 (9)	4398 (2)	1425 (3)	66 (2)*
C(22)	6034 (6)	2813 (4)	2190 (4)	72 (2)*	C(22)	5928 (11)	4876 (3)	−1884 (3)	85 (2)*
C(23)	5544 (9)	1967 (5)	1350 (6)	110 (3)*	C(23)	4333 (16)	4395 (4)	−2380 (4)	124 (3)*
C(24)	10097 (6)	5288 (4)	90 (4)	68 (1)*	C(24)	4432 (7)	6755 (3)	−2593 (3)	64 (2)*
C(25)	11529 (7)	4264 (5)	−2 (5)	92 (2)*	C(25)	2094 (9)	6945 (4)	−3047 (3)	93 (2)*
C(26)	10092 (8)	10362 (5)	1894 (7)	105 (2)*	C(26)	11250 (8)	8224 (2)	−511 (3)	66 (2)*
C(27)	10371 (9)	11068 (6)	2864 (7)	127 (3)*	C(27)	12376 (11)	8572 (3)	280 (4)	91 (2)*
O(1)	6720 (4)	7360 (3)	6044 (2)	65 (1)*	O(1)	4721 (5)	7766 (1)	3868 (2)	60 (1)*
O(2)	6705 (4)	7947 (2)	2450 (2)	62 (1)*	O(2)	5566 (5)	6996 (1)	21 (2)	49 (1)*
O(3)	7601 (4)	5040 (3)	6217 (3)	81 (1)*	O(3)	6168 (5)	8664 (2)	4727 (2)	65 (1)*
O(4)	5584 (4)	4508 (3)	7850 (2)	74 (1)*	O(4)	9392 (5)	8022 (2)	5116 (2)	64 (1)*
O(5)	5050 (4)	8074 (3)	8316 (2)	77 (1)*	O(5)	6034 (4)	6512 (1)	4774 (2)	47 (1)*
O(6)	3546 (6)	7197 (4)	10068 (3)	116 (2)*	O(6)	9132 (6)	5871 (2)	5202 (4)	111 (2)*
O(7)	2404 (4)	8700 (3)	6401 (3)	77 (1)*	O(7)	7250 (5)	6380 (1)	2750 (2)	49 (1)*
O(8)	2185 (7)	10798 (4)	6841 (6)	174 (3)*	O(8)	5085 (6)	5506 (2)	3145 (2)	66 (1)*
O(9)	4036 (3)	5046 (3)	3850 (2)	65 (1)*	O(9)	4619 (5)	5263 (1)	576 (2)	52 (1)*
O(10)	1828 (7)	5289 (10)	2933 (6)	252 (4)*	O(10)	673 (6)	5084 (2)	475 (2)	86 (1)*
O(11)	6076 (3)	4164 (2)	1679 (2)	63 (1)*	O(11)	4687 (6)	5237 (2)	−1326 (2)	66 (1)*
O(12)	6367 (7)	2357 (3)	3202 (3)	113 (2)*	O(12)	8052 (9)	4949 (3)	−1929 (3)	123 (2)*
O(13)	9323 (3)	5160 (3)	1267 (2)	64 (1)*	O(13)	4307 (4)	6568 (2)	−1748 (1)	53 (1)*
O(14)	9664 (5)	6118 (4)	−716 (3)	97 (1)*	O(14)	6278 (6)	6781 (4)	−2932 (2)	134 (3)*
O(15)	9861 (5)	9024 (3)	2286 (3)	96 (1)*	O(15)	9199 (6)	7928 (2)	−309 (2)	71 (1)*
O(16)	9997 (12)	10874 (5)	847 (6)	203 (4)*	O(16)	11962 (7)	8213 (2)	−1238 (3)	90 (1)*

*Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

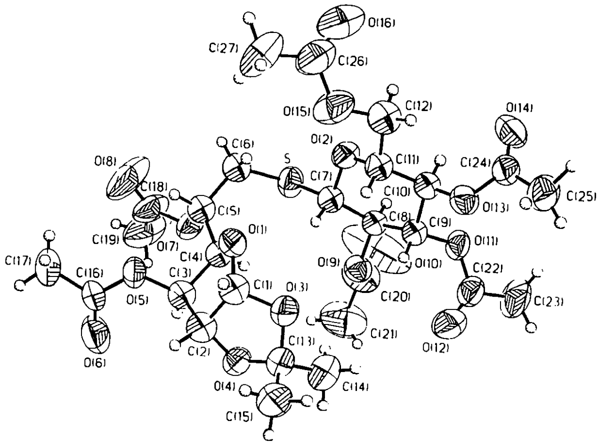


Fig. 1. Thermal-ellipsoid (50% probability) plot of (1). H atoms are shown as small spheres of arbitrary radius.

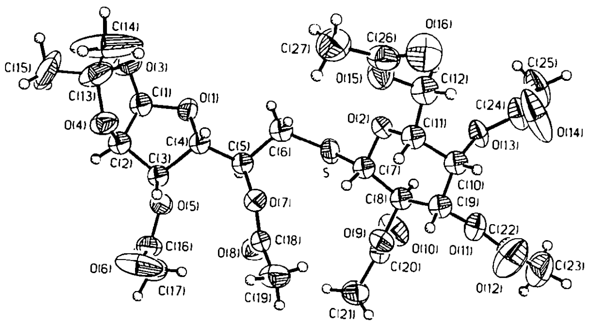


Fig. 2. Thermal-ellipsoid plot (50% probability) of (2). H atoms are shown as small spheres of arbitrary radius.

chemically equivalent bonds makes the averages meaningful. Table 2 shows the (unweighted) average lengths for chemically equivalent bonds, together with the sample standard deviation. The O–C (ester) bond is typified by C(3)–O(5), the O–C (acetate) bond by O(5)–C(16). The standard deviations are significantly larger than are expected from the usual optimistic least-squares estimates.

The Nicolet *R*3*m*/*E* crystallographic system was purchased with an instrument grant to Brown University from the National Science Foundation (CHE-8206423).

Table 2. *Average bond lengths* (Å) *for chemically equivalent bonds in compounds* (1) *and* (2)

Bond type	Number	Average length	Range
S—C	4	1·808 (10)	1·798–1·820
O—C in pyranose ring	4	1·428 (6)	1·421–1·435
O—C in 5-rings	12	1·416 (8)	1·405–1·430
C—C in pyranose ring	8	1·518 (7)	1·504–1·528
C—C in 5-rings	6	1·516 (10)	1·500–1·528
O—C (ester)	12	1·439 (8)	1·425–1·449
O—C (acetate)	12	1·338 (14)	1·318–1·356
C=O in acetyl groups	12	1·184 (15)	1·150–1·203
$C—CH_3$	16	1·482 (20)	1·452–1·536
C—C (other)	6	1·508 (11)	1·496–1·523

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JONES, P. G. (1984). *Acta Cryst.* **A40**, 660–662.

KRISTEN, H., BOYE, H., SCHOKNECHT, A. & TESCH, T. (1987). 4th Eur. Carbohydr. Symp., Darmstadt, Federal Republic of Germany, July 12–17, 1987. Abstr. A115.

ROGERS, D. (1981). *Acta Cryst.* **A37**, 734–741.

SHELDRICK, G. M. (1985). *SHELXTL*. Release 5.1. Nicolet Analytical Instruments, Madison, Wisconsin, USA.

Acta Cryst. (1988). C**44**, 1054–1057

Structure of Anhydrous Octyl α-D-Glucopyranoside. A Comparison with its Hemi- and Monohydrate

BY H. VAN KONINGSVELD

Laboratory of Applied Physics, Delft University of Technology, Lorentzweg 1, 2628 *CJ Delft, The Netherlands*

AND J. C. JANSEN AND A. J. J. STRAATHOF

Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, 2628 *BL Delft, The Netherlands*

(*Received* 4 *December* 1987; *accepted* 10 *February* 1988)

Abstract. $C_{14}H_{28}O_6$, $M_r = 292{\cdot}37$, monoclinic, $P2_1$, $a = 5{\cdot}140\,(2)$, $b = 7{\cdot}604\,(2)$, $c = 19{\cdot}939\,(4)$ Å, $\beta = 92{\cdot}18\,(2)°$, $V = 778{\cdot}7\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}25$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}05$ cm^{-1}, $F(000) = 320$, $T = 293$ K, $R = 0{\cdot}049$ for 1682 observed reflections $[I > \sigma(I)]$. The conformation of octyl α-D-glucopyranoside in the anhydrous crystal is similar to the conformation in the hemihydrate and monohydrate crystals of the same compound. The structure consists of alternating regions of polar and nonpolar groups, resulting from the close packing of fully extended hydrocarbon chains between hydrogen-bonded layers of glucopyranoside rings. The packing is strictly analogous to that in the anhydrous decyl homologue. The hydrogen-bonding scheme between the polar groups in anhydrous octyl α-D-glucopyranoside greatly resembles the hydrogen bonding in the hemihydrate crystal, but differs from that in the monohydrate crystal. The octyl chain packing is different from the chain packing in both the hemihydrate and monohydrate crystals.

Introduction. A new method for the preparation of alkyl α-D-glucopyranosides (alkyl = octyl, decyl, dodecyl) by selective crystallization from a mixture with the β-anomer has recently been developed (Straathof, Romein, van Rantwijk, Kieboom & van Bekkum, 1987). In order to achieve crystallization in the presence of traces of water, further improvement of this method is under study (Straathof, van Bekkum & Kieboom, 1988). Elucidation of the crystal structures of alkyl D-glucopyranosides might result in an optimization of the crystallization step, thus making octyl α-D-glucopyranoside much better available. Knowledge of the crystal structure will also be of importance to the study of alkyl α-D-glucopyranosides as liquid crystals (Jeffrey, 1986, and references cited therein) and membrane protein solubilizing detergents (Dorset & Rosenbusch, 1983, and references cited therein).

Recently, we solved the crystal structure of octyl α-D-glucopyranoside monohydrate (van Koningsveld, Jansen & Straathof, 1986). Simultaneously, Jeffrey, Yeon & Abola (1987) submitted a paper describing the identical structure. They also described a hemihydrate, which, like the monohydrate, consisted of alternating regions of polar and nonpolar groups, resulting from the close packing of fully extended hydrocarbon chains between hydrogen-bonded layers of glucopyranoside rings. In this paper the crystal structure of anhydrous octyl α-D-glucopyranoside is reported and compared with the hemihydrate and monohydrate crystals of the same compound and with the anhydrous decyl homologue (Moews & Knox, 1976).

Experimental. Octyl α-D-glucopyranoside monohydrate (Straathof *et al.*, 1987) was recrystallized from

0108-2701/88/061054-04$03.00