Crystal Structure and Absolute Configuration of Methyl 3,4-Di-*O*-acetyl-6-deoxy-6-iodo-2-*O*-*p*-tolylsulphonyl-α-D-mannopyranoside

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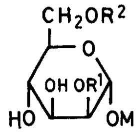
The title compound (7) was isolated as a minor product of successive tosylation, acetylation and iodide displacement of methyl α-D-mannopyranoside (1). Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, a = 9.293(2), b = 14.220(6), c = 16.969(6) Å, Z = 4. The structure was solved from diffractometer data by heavy-atom techniques, and refined by block-diagonal least-squares methods to R 0.052 for 1 802 independent reflections. The results supply the constitution and absolute configuration (8). The conformation of the pyranoside ring is $^4C_1$ ($\equiv C1$) in the solid state and ^1H n.m.r. studies showed this to be the predominant conformation in solution also.

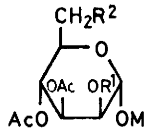
METHYL 3,4-di-*O*-acetyl-6-deoxy-6-iodo-2-*O*-*p*-tolylsulphonyl-α-D-mannopyranoside (7) was isolated as a minor product in the preparation of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-mannopyranoside [1] (6) according to standard procedures. Selective esterification of methyl α-D-mannopyranoside (1) with 1.1 mol of toluene-*p*-sulphonyl chloride in pyridine gave mainly the 6-*O*-tosyl derivative (2) but a small quantity of the 2,6-ditosylate (3) was also formed. This is in accord with the known relative reactivities of the hydroxy-groups in methyl α-D-hexopyranosides which have been found generally to follow the order: C-6 > C-2 > C-3 > C-4 for sulphonation of methyl α-D-glucopyranoside, methyl α-D-galactopyranoside, and methyl α-D-mannopyranoside.[2,3] The reaction mixture containing the 6-tosylate (2) and the 2,6-ditosylate (3) was acetylated *in situ* to give the respective acetates (4) and (5) which were also not isolated but treated directly with sodium iodide heated under reflux in butanone. Under these conditions, displacement of primary 6-*O*-tosyl groups occurs readily but secondary *O*-tosyl groups, particularly at C-2,[4] are inert. The product therefore consisted of the known 6-iodide (6) [1] and the 6-iodo-2-tosylate (7) as a minor component, readily separated because of its insolubility in ether.

The ^1H n.m.r. spectrum of (7) in deuteriopyridine was susceptible to first-order analysis. The first-order coupling constants suggest that the molecule exists predominantly in the $^4C_1$ conformation (8) in solution. Thus, the doublet at τ 5.03 was assigned to H-1 and the small value of $J_{1,2}$ (2.0 Hz) is characteristic of equatorial–equatorial coupling as found in conformation (8). The quartet at τ 4.84 was assigned to H-2 on the basis of the coupling constants ($J_{1,2}$ 2.0 and $J_{2,3}$ 3.0 Hz). The latter is rather small for an equatorial–axial coupling which suggests some distortion of the pyranose ring at C-2 from the ideal $^4C_1$ conformation (8) in solution. This does not appear to be the case in the crystal. The resonances centred on τ 4.5 and 4.62 were assigned to H-3 and H-4 respectively but are not able to be analysed on a first-order basis since they overlap. The fact that the H-3 and H-4 resonances occurred at lower field than the H-2 resonance suggested that the compound was the 3,4-di-*O*-acetyl-2-*O*-tosyl isomer (7), since acetyl groups have a greater deshielding effect than tosyl groups.

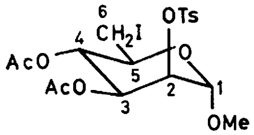
An *X*-ray analysis of the minor component was undertaken in order to determine the structure and absolute configuration independently. These results confirmed that (8) is correct.



	R1	R2
(1)	H	H
(2)	H	Ts
(3)	Ts	Ts



	R1	R2
(4)	Ac	OTs
(5)	Ts	OTs
(6)	Ac	I
(7)	Ts	I



(8)

EXPERIMENTAL

Evaporations were carried out under reduced pressure. M.p.s were determined on a Reichert hot-stage. Optical rotations were determined with a Perkin-Elmer 141 automatic polarimeter (1 dm tube). ^1H N.m.r. spectra were determined at 100 MHz on a Varian HA 100 spectrometer † with tetramethylsilane as internal standard. First-order chemical shifts and coupling constants are quoted.

Methyl 2,3,4-*Tri*-O-*acetyl*-6-*deoxy*-6-*iodo*-α-D-*mannopyranoside* [1] (6) *and Methyl* 3,4-*Di*-O-*acetyl*-6-*deoxy*-6-*iodo*-2-O-p-*tolylsulphonyl*-α-D-*mannopyranoside* (7).—A suspension of methyl α-D-mannopyranoside (1) (100 g) in anhydrous pyridine (1 l) was cooled to −20 °C and stirred while a solution of toluene-*p*-sulphonyl chloride (108 g, 1.10 mol) in pyridine (250 ml) was added dropwise over 15 min. After being set aside for 16 h at 0°, acetic anhydride (200 ml, 4 mol) was added and the reaction mixture

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† The n.m.r. spectrum was determined by the Physicochemical Measurements Unit, Harwell.

[1] J. Lehmann and A. A. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 4469; A. L. Raymond and E. F. Schroeder, *ibid.* 1968, **70**, 2785.

[2] R. C. Chalk, D. H. Ball, and L. Long, jun., *J. Org. Chem.*, 1966, **31**, 1509.

[3] D. H. Ball and F. W. Parrish, *Adv. Carbohydrate Chem.*, 1968, **23**, 233.

[4] A. C. Richardson, *Carbohydrate Res.*, 1969, **10**, 395.

was stored for 16 h at −10 °C. The reaction mixture was poured into ice–water (*ca.* 7 l) and the resulting syrup separated and washed by decantation. The syrup was dissolved in dichloromethane (*ca.* 800 ml) and the solution shaken with 2M-hydrochloric acid (3 × 400 ml) and water (2 × 400 ml). The solution was dried ($MgSO_4$) and evaporated to a golden-yellow syrup (*ca.* 210 g).

The syrup was dissolved in butanone (1.25 l), dry sodium iodide (150 g, *ca.* 2 mol) was added and the mixture heated under reflux for 16 h. It was cooled, filtered, and the filtrate evaporated. The residual syrup was dissolved in dichloromethane (*ca.* 800 ml) and the solution shaken with aqueous sodium thiosulphate (× 2), water, and then dried ($MgSO_4$). The solution was evaporated and the resulting syrup dissolved in diethyl ether (*ca.* 200 ml). The small, insoluble residue which remained was washed with ether and recrystallized from ethanol to give long needles of *methyl* 3,4-*di*-O-*acetyl*-6-*deoxy*-6-*iodo*-2-O-p-*tolylsulphonyl*-α-D-*mannopyranoside* (7) (2.3 g, 1.3%), m.p. 199—201 °C, $[\alpha]_D^{23}$ +14° (*c* 1.1 in $CHCl_3$); τ (C_5D_5N, 60°) 2.10 (2 H, d) and 2.78 (2 H, d) (tosyl *meta*- and *ortho*-protons, respectively), *ca.* 4.5 (1 H, overlapped q, H-3), 4.62 (1 H, overlapped t, $J_{3,4} \sim J_{4,5} \sim$ 10 Hz, H-4), 4.84 (1 H, q, $J_{1,2}$ 2.0 Hz, $J_{2,3}$ 3.0 Hz, H-2), 5.03 (1 H, d, $J_{1,2}$ 2.0 Hz, H-1), 6.12 (1 H, complex m, H-5), 6.50 (1 H, q, $J_{5,6a}$ 2.5 Hz, $J_{6a,6b}$ 11.0 Hz, H-6a), 6.68 (3 H, overlapped s, methoxy), 6.75 (1 H, overlapped q, $J_{5,6b}$ 8.0 Hz, $J_{6a,6b}$, 11.0 Hz, H-6b), 7.79 (3 H, s, tosyl Me protons), 8.00 (3 H, s), and 8.18 (3 H, s) (Ac protons) (Found: C, 39.8; H, 4.3. $C_{18}H_{23}IO_9S$ requires C, 39.8; H, 4.3%).

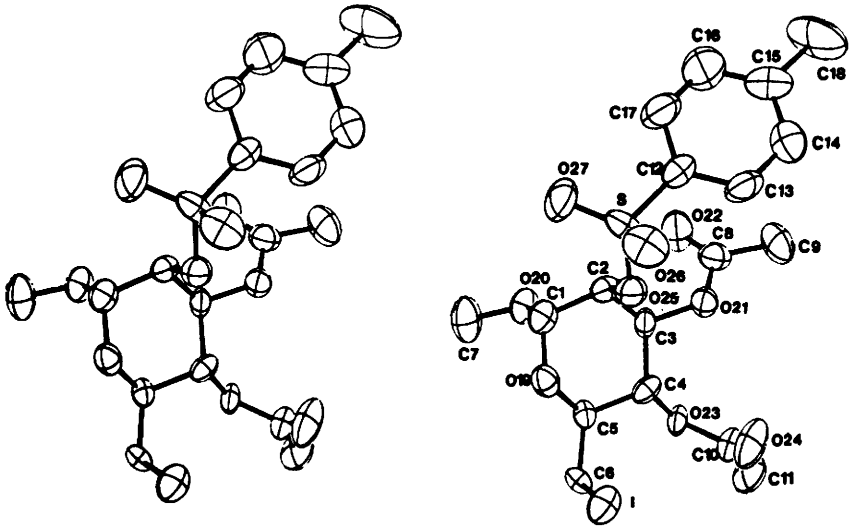

FIGURE 1 Stereopair for the molecule of methyl 3,4-di-*O*-acetyl-6-deoxy-6-iodo-2-*O*-*p*-tolylsulphonyl-α-D-mannopyranoside, showing the atom numbering system used in the analysis

The ethereal solution from the preceding part was treated with light petroleum (b.p. 40—60 °C) until it became slightly turbid, seeded with an authentic sample of compound (6) and set aside at room temperature to give compound (6) (117 g, 53%). Recrystallization from di-isopropyl ether gave pure methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-mannopyranoside (6) (78 g, 35%), m.p. 95—97 °C after transition 80—82 °C, $[\alpha]_D^{23}$ +43° (*c* 1.0 in $CHCl_3$) {lit.,[1] m.p. 91—92 °C (from 95% EtOH), $[\alpha]_D^{25}$ +37.0° (*c* 0.6 in $CHCl_3$)}.

Crystal Data.—$C_{18}H_{23}O_9SI$, $M = 542.35$, Orthorhombic, $a = 9.293(2)$, $b = 14.220(6)$, $c = 16.969(6)$ Å, $U = 2\,242(1)$ Å^3, $D_m = 1.60$ g cm^{-3}, $Z = 4$, $D_c = 1.606$ g cm^{-3}, $F(000) = 1\,088$. Space group $P2_12_12_1$ uniquely from systematic absences. Mo-K_α radiation, $\lambda = 0.710\,73$ Å; μ(Mo-K_α) = 15.83 cm^{-1}.

A crystal *ca.* 0.3 × 0.5 × 0.7 mm³ was used for intensity measurements. Accurate cell dimensions were obtained by least-squares refinement of 15 high-angle θ values measured on a diffractometer.

The intensities of reflections were measured by Mo-K_α radiation filtered by a graphite-crystal incident-beam monochromator on a Syntex $P\bar{1}$ diffractometer * at a take-off angle of 3°. The intensities of 2 284 independent reflections were measured [to 2θ(Mo-K_α) < 50°] by the θ—2θ scan technique with a variable scan rate of 4—24° min^{-1}, background counts being taken at each end of the scan range. 1 802 reflections were considered observed, having $I > 3\sigma(I)$. Standard reflections, measured periodically, showed no significant change in intensity during data collection. Lorentz and polarization corrections were applied. Atomic scattering factors were taken from ref. 5, except those for hydrogen which were taken from ref. 6.

Structure Determination and Refinement.—N.R.C. crystallographic programs [7] were used for the solution and refinement of the structure. Calculations were carried out on the University of Petroleum and Minerals IBM 370/145 and 158 Computers.

The positions of iodine and sulphur atoms were deduced from a three-dimensional Patterson function, and the complete structure emerged from two three-dimensional Fourier maps.

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* Intensity data were collected by the Molecular Structure Corporation, P.O. Box DF, College Station, Texas 77840, U.S.A.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[7] F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, 1966, N.R.C. Crystallographic Programs for the IBM 360 System, World List of Crystallographic Computer Programs, 2nd edn., Appendix, Oesthock, Utrecht, p. 52. These programs were used on IBM 370/145 and 158 Computers.

Five cycles of isotropic refinement by block-diagonal least-squares gave R 0.155. A Hughes-type weighting scheme[8] of the form $w = 1$ for $|F_o| < 20$ and $\sqrt{w} = 20/|F_o|$ for $|F_o| > 20$ was used. Four more cycles of anisotropic refinement of all these atoms reduced R to 0.082. A difference-Fourier synthesis at this stage revealed all the 11 non-methyl hydrogen-atom positions. It was not possible to locate methyl hydrogens. In the next five cycles of refinement hydrogen atoms were allowed for as fixed-atom contribution with isotropic temperature factors 0.5 Å^2 higher than those of their parent atoms, and the remaining atoms were refined anisotropically, which reduced R to 0.052. At the end of refinement all shift-to-error ratios were <0.01. A final difference map showed no significant peaks except near methyl carbons, and these gave unacceptable C–H bond lengths and angles.

Allowance for anomalous dispersion for the iodine and sulphur atoms was applied to all these reflections for both possible molecular chiralities. $R(+)$, corresponding to configuration (8) was 0.052 4, while $R(-)$ from its enantiomorph, was 0.057 2. Application of Hamilton's significance test[9] shows that these values are strongly in favour of configuration (8) (at a confidence level $\gg 99\%$).

Figure 1 shows the stereopair for the molecule and the atom numbering system used and Figure 2 the [100] projection of the structure. Table 1 lists final fractional coordinates for non-hydrogen atoms and Table 2 the coordinates of the hydrogen atoms as derived from the difference map. Bond lengths and valence angles are listed in Table 3. Torsion angles are listed in Table 4, and the intermolecular contacts $\leqslant 3.6$ Å in Table 5. Anisotropic thermal parameters, observed and calculated structure factors are listed in Supplementary Publication No. SUP 22025 (7 pp., 1 microfiche).*

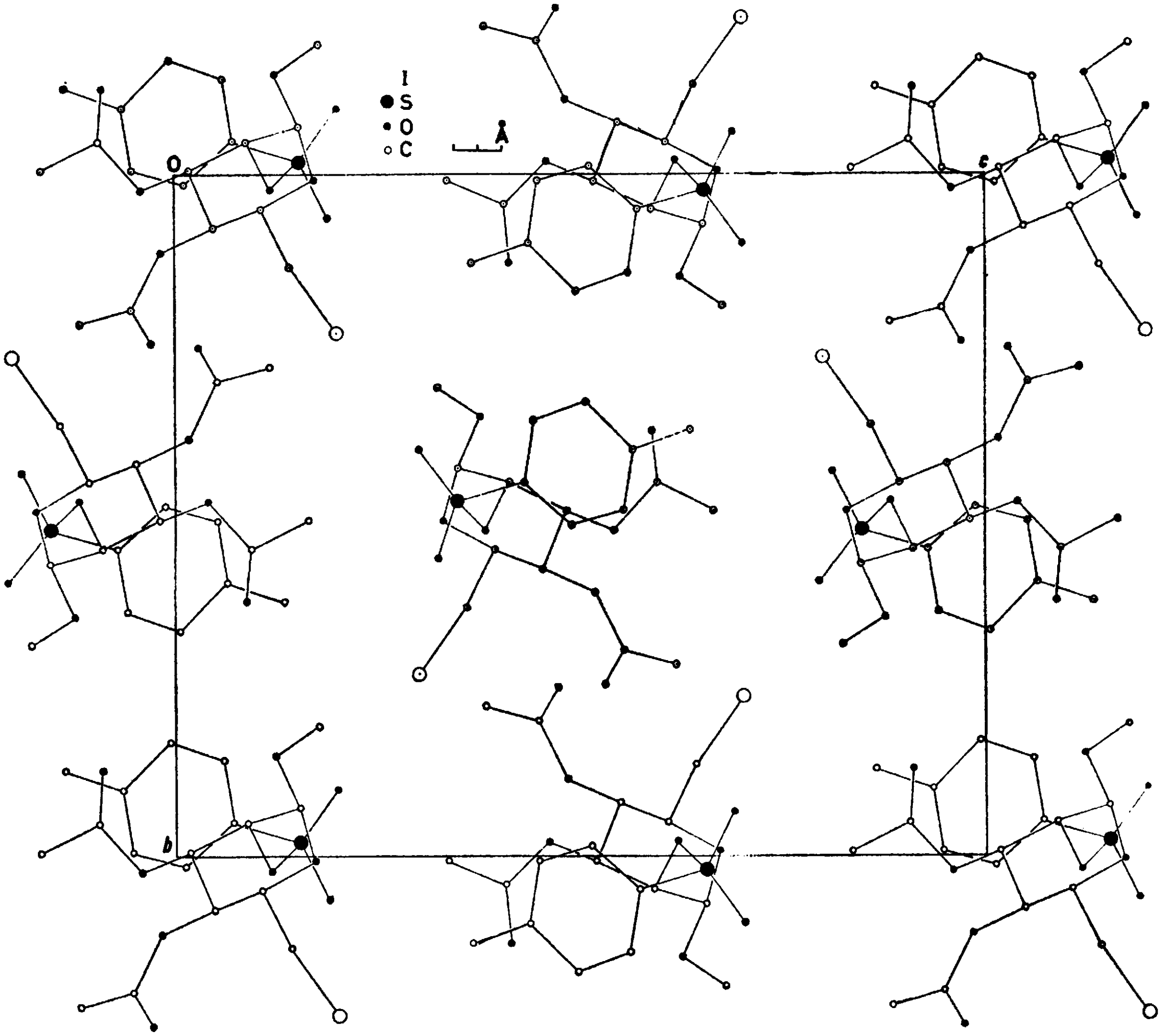

FIGURE 2 [100] Projection showing the packing of molecules

DISCUSSION

The pyranose ring in (8) is in the conventional $^4C_1$ (= $C1$) chair conformation with torsion angles ranging from 56.3 to 59.3°, as compared to 60° for an ideal chair conformation, 55.8—61.7° for an ideal

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[8] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

[9] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

TABLE 1

Fractional co-ordinates (× 10^5 for I, others × 10^4), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
I	80 068(9)	23 533(6)	20 177(5)
S	3 387(3)	−193(2)	1 527(2)
C(1)	6 976(12)	−735(7)	1 536(6)
C(2)	5 921(10)	−505(7)	890(6)
C(3)	6 647(10)	−96(7)	186(5)
C(4)	7 451(11)	780(7)	453(6)
C(5)	8 520(11)	508(8)	1 008(5)
C(6)	9 366(12)	1 309(8)	1 426(7)
C(7)	8 738(19)	−1 873(11)	1 779(9)
C(8)	5 325(13)	−475(10)	−944(8)
C(9)	4 537(17)	−95(12)	−1 638(7)
C(10)	7 924(14)	1 976(8)	−528(8)
C(11)	8 969(17)	2 210(12)	−1 152(9)
C(12)	2 444(12)	−526(8)	697(6)
C(13)	2 076(14)	152(8)	188(8)
C(14)	1 270(15)	−99(11)	−529(9)
C(15)	820(15)	−1 005(11)	−636(8)
C(16)	1 193(21)	−1 682(10)	−69(10)
C(17)	1 965(16)	−1 422(9)	592(10)
C(18)	−53(23)	−1 251(20)	−1 375(10)
O(19)	7 758(8)	77(5)	1 736(4)
O(20)	7 806(9)	−1 454(5)	1 225(5)
O(21)	5 694(8)	203(5)	−419(4)
O(22)	5 637(14)	−1 289(7)	−862(6)
O(23)	8 294(7)	1 121(5)	−203(4)
O(24)	6 968(13)	2 427(7)	−269(7)
O(25)	4 881(7)	185(5)	1 175(4)
O(26)	2 758(8)	598(7)	1 866(5)
O(27)	3 649(9)	−996(7)	1 994(6)

TABLE 2

Hydrogen fractional co-ordinates (× 10^3) derived from a ΔF map and unrefined

Atom	Attached to	*x*	*y*	*z*
H(11)	C(1)	653	−83	202
H(21)	C(2)	520	−88	88
H(31)	C(3)	749	−51	−4
H(41)	C(4)	683	125	60
H(51)	C(5)	927	5	80
H(61)	C(6)	12	110	176
H(62)	C(6)	953	170	108
H(131)	C(13)	220	70	20
H(141)	C(14)	93	40	−91
H(161)	C(16)	67	−240	−12
H(171)	C(17)	248	−193	93

pyranose ring,†,[10] and 54.8—56.0, 51.3—62.2, 56.2—60.5, 55.4—60.0, and 54.2—60.2° for sucrose,[11] α-D-glucose,[12] β-methyl maltoside,[13] β-DL-arabinose,[10] and methyl α-D-glucopyranoside.[14]

The C–C bond lengths in the pyranose ring are in the range 1.49(1)—1.52(1) Å, mean 1.51(1) Å, and the range of C–O distances is 1.41(1)—1.44(1) Å, mean 1.425(10) Å. The C(1)–O(20) bond of 1.39(1) Å is the shortest. Other C–O bond lengths are in the range 1.41(2)—1.46(2) Å, mean 1.44(2) Å. The foregoing bond length values agree very well with those commonly found in other

TABLE 3

Bond lengths (Å) and valence angles (°), with standard deviations in parentheses

(*a*) Distances

C(1)–C(2)	1.51(1)	C(8)–O(22)	1.20(2)
C(1)–O(19)	1.41(1)	C(10)–C(11)	1.48(2)
C(1)–O(20)	1.39(1)	C(10)–O(23)	1.38(1)
C(2)–C(3)	1.49(1)	C(10)–O(24)	1.18(2)
C(2)–O(25)	1.46(1)	C(12)–C(13)	1.39(2)
C(3)–C(4)	1.52(1)	C(12)–C(17)	1.36(2)
C(3)–O(21)	1.42(1)	C(12)–S	1.72(1)
C(4)–C(5)	1.52(1)	C(13)–C(14)	1.40(2)
C(4)–O(23)	1.45(1)	C(14)–C(15)	1.37(2)
C(5)–C(6)	1.50(2)	C(15)–C(16)	1.40(2)
C(5)–O(19)	1.44(1)	C(15)–C(18)	1.53(2)
C(6)–I	2.19(1)	C(16)–C(17)	1.38(2)
C(7)–O(20)	1.41(2)	O(25)–S	1.60(1)
C(8)–C(9)	1.49(2)	O(26)–S	1.39(1)
C(8)–O(21)	1.36(1)	O(27)–S	1.41(1)

(*b*) Angles

C(12)–S–O(25)	103.2(5)	C(9)–C(8)–O(21)	112.7(11)
C(12)–S–O(26)	110.2(5)	C(9)–C(8)–O(22)	124.0(13)
C(12)–S–O(27)	109.0(6)	O(21)–C(8)–O(22)	123.3(12)
O(25)–S–O(26)	104.3(5)	C(11)–C(10)–O(23)	108.8(11)
O(25)–S–O(27)	109.3(5)	C(11)–C(10)–O(24)	129.8(13)
O(26)–S–O(27)	119.6(6)	O(23)–C(10)–O(24)	121.3(12)
C(2)–C(1)–O(19)	109.5(8)	C(13)–C(12)–C(17)	118.5(11)
C(2)–C(1)–O(20)	104.2(8)	C(13)–C(12)–S	119.4(9)
O(19)–C(1)–O(20)	114.3(8)	C(17)–C(12)–S	122.0(10)
C(1)–C(2)–C(3)	111.9(8)	C(12)–C(13)–C(4)	120.2(11)
C(1)–C(2)–O(25)	109.6(8)	C(13)–C(14)–C(15)	120.7(14)
C(3)–C(2)–O(25)	107.7(8)	C(14)–C(15)–C(16)	118.6(14)
C(2)–C(3)–C(4)	107.6(8)	C(14)–C(15)–C(18)	119.1(14)
C(2)–C(3)–O(21)	114.4(8)	C(16)–C(15)–C(18)	122.3(15)
C(4)–C(3)–O(21)	106.0(7)	C(15)–C(16)–C(17)	120.0(15)
C(3)–C(4)–C(5)	108.9(8)	C(12)–C(17)–C(16)	121.8(14)
C(3)–C(4)–O(23)	108.2(8)	C(1)–O(19)–C(5)	114.7(7)
C(5)–C(4)–O(23)	106.1(8)	C(1)–O(20)–C(7)	113.6(10)
C(4)–C(5)–C(6)	114.9(9)	C(3)–O(21)–C(8)	114.7(8)
C(4)–C(5)–O(19)	109.2(8)	C(4)–O(23)–C(10)	118.0(8)
C(6)–C(5)–O(19)	106.8(8)	C(2)–O(25)–S	118.1(6)
C(5)–C(6)–I	112.9(7)		

TABLE 4

Torsion angles (°) in the pyranoside ring

C(1)–C(2)–C(3)–C(4)	−57.8
C(2)–C(3)–C(4)–C(5)	58.5
C(3)–C(4)–C(5)–O(19)	−58.4
C(4)–C(5)–O(19)–C(1)	59.3
C(5)–O(19)–C(1)–C(2)	−57.0
O(19)–C(1)–C(2)–C(3)	56.3
Mean	57.9

TABLE 5

Intermolecular contacts ⩽ 3.6 Å involving non-hydrogen atoms

Atoms	
I ··· O(27$^{\mathrm{I}}$)	3.27(1)
C(6) ··· O(24$^{\mathrm{II}}$)	3.60(2)
C(6) ··· O(26$^{\mathrm{III}}$)	3.39(1)
C(7) ··· O(22$^{\mathrm{IV}}$)	3.52(2)
C(9) ··· O(26$^{\mathrm{V}}$)	3.39(2)
C(11) ··· O(26$^{\mathrm{II}}$)	3.53(2)
C(13) ··· O(24$^{\mathrm{VI}}$)	3.45(2)
C(14) ···· O(23$^{\mathrm{VII}}$)	3.31(2)
C(16) ··· O(22$^{\mathrm{VIII}}$)	3.30(2)
C(17) ···· O(22$^{\mathrm{VIII}}$)	3.51(2)

* Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at *x*, *y*, *z*:

I $-x-1, \frac{1}{2}+y, \frac{1}{2}-z$
II $\frac{1}{2}+x, \frac{1}{2}-y, -z$
III $1+x, y, z$
IV $\frac{1}{2}+x, -y-\frac{1}{2}, -z$
VIII $-x-1\frac{1}{2}, -y, z-\frac{1}{2}$
VI $x-\frac{1}{2}, \frac{1}{2}-y, -z$
VII $x-1, y, z$
VIII $x-\frac{1}{2}, -y-\frac{1}{2}, -z$

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† Hypothetical pyranose ring with C–C 1.525, C–O 1.430 Å, valence angle at carbon atoms 109.5°, and that at ring oxygen atom 113.3°.

[10] S. H. Kim and G. A. Jeffrey, *Acta Cryst.*, 1967, **22**, 537.
[11] G. M. Brown and H. A. Levy, *Science*, 1963, **141**, 921.
[12] G. M. Brown and H. A. Levy, *Science*, 1965, **147**, 1038.
[13] S. S. C. Chu and G. A. Jeffrey, *Acta Cryst.*, 1967, **23**, 1038.
[14] H. M. Berman and S. H. Kim, *Acta Cryst.*, 1968, **B24**, 897.

carbohydrates.[15] In previous structure determinations of monosaccharides,[10,12,16-18] the C(1)–O(20) bond length has been found to be much shorter than others (1.376—1.404 Å). However, no such shortening has been observed in the α-methyl D-galactoside 6-bromohydrin,[19] β-methyl maltoside,[13] methyl α-D-glucopyranoside,[14] and methyl 4,6-dichloro-4,6-dideoxy-α-D-glucopyranoside.[20] In all these cases O(20) carries a methyl group and not a hydrogen atom, and the C(1)–O(20) distances range from 1.411 to 1.430 Å, almost equal to the mean (1.43 Å). It was suggested that the short bond in the α-position is an effect which is eliminated completely when the hydrogen atom is replaced by any substituent. In our case O(20) carries a methyl group but the C(1)–O(20) bond is still the shortest (1.39 Å).

The carbon valence angles within the pyranose ring vary from 107.6 to 111.9(8) [mean 109.4(8)°]; the angle at O(19) is 114.7(7), which is larger than the tetrahedral angle, which is commonly found in other pyranose rings.[10-12,14,19]

The mean C–C length in the phenyl ring [1.38(2) Å] is close to the accepted value [1.395(3)].[21] The mean C–C–C angle in the phenyl ring is 119.97(1.3)°, which is not significantly different from the expected 120°. All other bond distances and angles are as expected and do not deviate significantly from their standard values.

Intermolecular contacts ⩽3.6 Å are given in Table 5. None of them are especially short and are normal van der Waals contacts. The shortest contact between iodine and O(27) is 3.27 Å.

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