

Fig. 2. Packing diagram of the molecules in the unit cell viewed down the *b* axis.

in Fig. 2. The phenyl ring attached to C5 is stacked along the *a* axis with a distance of 6.25 (2) Å. The molecule forms zigzag chains running along the *c* axis. The packing of the molecules in the unit cell is governed by van der Waals interactions.

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Structure of Methyl 4-*O*-Benzoyl-6-bromo-3-tosyl-2,6-dideoxy-β-*D*-arabino-hexopyranoside

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Abstract. C₂₁H₂₃BrO₇S, *M_r* = 499.37, monoclinic, *P*2₁, *a* = 8.897 (3), *b* = 8.213 (2), *c* = 15.334 (4) Å, β = 102.69 (3)°, *V* = 1093 (1) Å³, *Z* = 2, *D_m* = 1.51, *D_x* = 1.517 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 19.89 cm⁻¹, *F*(000) = 512, *T* = 295 K, final *R* = 0.044, *wR* = 0.048 for 1473 independent reflections with *I* > 2.0σ(*I*) and 271 variables. The compound contains a substituted pyranose ring in the normal chair conformation. The bromomethylene, benzoyl and tosyl substituents are equatorial and the methoxy is axial.

Introduction. As part of a synthesis of several naturally occurring oligosaccharides found in the anti-

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cancer agent mithramycin, a variety of partially protected monosaccharides have been prepared (Binkley, 1985). The title compound is a previously unisolated intermediate in the preparation of 2,6-dideoxy sugars to be used as oligosaccharide building blocks (Binkley & Sivik, 1986) and represents the first reported structural characterization of this class of compound by single-crystal X-ray diffraction.

Experimental. The title compound was formed in 30% yield by stirring an ethyl acetate solution of methyl 4-*O*-benzoyl-2,6-dibromo-2,6-dideoxy-β-*D*-arabino-hexopyranoside in the presence of Raney nickel powder for 24 h under an atmosphere of hydrogen. The Raney nickel was removed by filtration.

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Table 1. Positional parameters and equivalent isotropic thermal parameters (Å²)
$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B _{eq}
Br	0.33540 (8)	0.088	1.07091 (5)	5.48 (2)
S	0.9157 (2)	0.0281 (3)	0.7476 (1)	4.25 (4)
Ob1	0.5050 (5)	-0.0211 (6)	0.8042 (3)	3.9 (1)
Ob2	0.3762 (6)	0.1796 (7)	0.7196 (4)	6.3 (1)
Om	0.8423 (5)	-0.0086 (7)	1.0685 (3)	4.8 (1)
Op	0.6406 (5)	0.1754 (6)	1.0210 (3)	3.9 (1)
O(s1)	1.0422 (5)	-0.0110 (7)	0.8186 (3)	5.2 (1)
O(s2)	0.9335 (5)	0.1306 (7)	0.6767 (3)	5.8 (1)
Ot	0.7891 (4)	0.1192 (6)	0.7882 (3)	4.1 (1)
C1	0.8034 (7)	0.1439 (9)	1.0340 (5)	4.3 (2)
C2	0.8551 (7)	0.1666 (9)	0.9497 (5)	4.1 (2)
C3	0.7593 (7)	0.0660 (8)	0.8719 (4)	3.7 (2)
C4	0.5893 (6)	0.095 (1)	0.8672 (4)	3.7 (1)
C5	0.5524 (7)	0.0675 (8)	0.9570 (4)	3.3 (1)
C6	0.3810 (7)	0.104 (1)	0.9560 (5)	4.5 (2)
Cb	0.4001 (7)	0.036 (1)	0.7320 (4)	4.4 (2)
Cb1	0.3203 (7)	-0.099 (1)	0.6773 (5)	4.1 (2)
Cb2	0.3484 (9)	-0.259 (1)	0.6988 (5)	5.5 (2)
Cb3	0.269 (1)	-0.378 (1)	0.6456 (6)	6.9 (2)
Cb4	0.1660 (9)	-0.338 (1)	0.5692 (6)	8.0 (3)
Cb5	0.136 (1)	-0.180 (2)	0.5465 (7)	10.1 (3)
Cb6	0.213 (1)	-0.055 (1)	0.6012 (6)	7.1 (3)
C(m)	0.812 (1)	-0.031 (1)	1.1549 (5)	6.3 (2)
Cr1	0.8253 (8)	-0.1521 (9)	0.7038 (5)	4.3 (2)
Cr2	0.734 (1)	-0.153 (1)	0.6198 (6)	6.1 (2)
Cr3	0.665 (1)	-0.300 (1)	0.5885 (5)	7.3 (3)
Cr4	0.6879 (8)	-0.4400 (9)	0.6356 (5)	5.4 (2)
Cr5	0.7802 (8)	-0.438 (1)	0.7192 (5)	4.8 (2)
Cr6	0.8477 (8)	-0.295 (1)	0.7531 (5)	4.6 (2)
Cr7	0.610 (1)	-0.599 (1)	0.5991 (7)	7.5 (3)

Table 2. Bond distances (Å), bond angles (°) and selected torsion angles (°)

Br—C6	1.897 (7)	C4—C5	1.501 (9)
S—O(s1)	1.420 (5)	C5—C6	1.551 (9)
S—O(s2)	1.411 (6)	Cb—Cb1	1.476 (11)
S—Or	1.589 (5)	Cb1—Cb2	1.365 (13)
S—Cr1	1.746 (8)	Cb1—Cb6	1.384 (10)
Ob1—C4	1.446 (8)	Cb2—Cb3	1.366 (11)
Ob1—Cb	1.365 (7)	Cb3—Cb4	1.360 (11)
Ob2—Cb	1.204 (10)	Cb4—Cb5	1.36 (2)
Om—C1	1.374 (9)	Cb5—Cb6	1.403 (15)
Om—C(m)	1.419 (10)	Cr1—Cr2	1.362 (10)
Op—C1	1.441 (7)	Cr1—Cr6	1.387 (11)
Op—C5	1.423 (7)	Cr2—Cr3	1.396 (14)
Or—C3	1.435 (8)	Cr3—Cr4	1.348 (13)
C1—C2	1.476 (11)	Cr4—Cr5	1.361 (10)
C2—C3	1.545 (9)	Cr4—Cr7	1.527 (13)
C3—C4	1.517 (9)	Cr5—Cr6	1.367 (11)
O(s1)—S—O(s2)	121.4 (3)	Br—C6—C5	112.9 (4)
O(s1)—S—Or	108.4 (3)	Ob1—Cb—Ob2	122.1 (6)
O(s1)—S—Cr1	108.9 (3)	Ob1—Cb—Cb1	111.1 (6)
O(s2)—S—Or	103.3 (3)	Ob2—Cb—Cb1	126.8 (6)
O(s2)—S—Cr1	109.3 (3)	Cb—Cb1—Cb2	123.1 (6)
Or—S—Cr1	104.1 (3)	Cb—Cb1—Cb6	116.2 (8)
C4—Ob1—Cb	118.4 (6)	Cb2—Cb1—Cb6	120.7 (8)
C1—Om—C(m)	113.2 (6)	Cb1—Cb2—Cb3	120.2 (7)
C1—Op—C5	111.6 (5)	Cb2—Cb3—Cb4	119.9 (9)
S—Or—C3	119.6 (4)	Cb3—Cb4—Cb5	120.9 (9)
Om—C1—Op	112.2 (6)	Cb4—Cb5—Cb6	120.1 (8)
Om—C1—C2	110.6 (6)	Cb1—Cb6—Cb5	118 (1)
Op—C1—C2	110.7 (5)	S—Cr1—Cr2	119.7 (7)
C1—C2—C3	112.6 (6)	S—Cr1—Cr6	120.6 (6)
Or—C3—C2	110.4 (5)	Cr2—Cr1—Cr6	119.6 (7)
Or—C3—C4	106.7 (5)	Cr1—Cr2—Cr3	117.2 (8)
C2—C3—C4	109.1 (6)	Cr2—Cr3—Cr4	123.3 (7)
Ob1—C4—C3	107.0 (6)	Cr3—Cr4—Cr5	118.9 (7)
Ob1—C4—C5	109.1 (6)	Cr3—Cr4—Cr7	121.8 (7)
C3—C4—C5	110.4 (5)	Cr5—Cr4—Cr7	119.2 (7)
Op—C5—C4	109.9 (5)	Cr4—Cr5—Cr6	119.5 (7)
Op—C5—C6	106.2 (5)	Cr1—Cr6—Cr5	121.4 (7)
C4—C5—C6	112.0 (5)		
Op—C1—Om—C(m)	-63.1	Ob1—Cb—Cb1—Cb2	1.1
Op—C5—C6—Br	-54.9	C2—C3—Or—S	94.5
C3—C4—Ob1—Cb	-122.4	C3—Or—S—Cr1	-6.2
C4—Ob1—Cb—Ob2	0.0	Or—S—Cr1—Cr2	-140.5

The reaction mixture was then treated with tosyl chloride in pyridine solution, and the product was purified by chromatography on silica gel using hexane–ethyl acetate (3:1) as the eluent. Crystals were obtained by slow evaporation from CHCl₃. A single prismatic crystal of dimensions 0.35 × 0.32 × 0.22 mm was chosen for analysis. Geometric and intensity data were collected using an Enraf–Nonius CAD-4 automated diffractometer with graphite-monochromated Mo Kα radiation at room temperature. Measured density was determined by flotation. Unit-cell constants were calculated on the basis of 25 intense reflections in the range 10.90 < 2θ < 22.32°. Observed systematic absences (0k0, k = 2n + 1) and the chirality of the molecule indicates that the space group is P2₁. A total of 2164 unique reflections were obtained by the ω–2θ scan method within the range 2 < θ < 25° (-10 < h < 10, 0 < k < 9, 0 < l < 18). Of these, 1473 had I > 2σ(I) and were deemed suitable for refinement. An empirical correction for absorption, ranging from 0.82 to 1.0, was applied. The Br atom was readily located by heavy-atom Patterson methods and the remaining structure deduced by subsequent iterative difference Fourier synthesis and least-squares analyses. Positional parameters for all non-methyl H atoms were determined by examination of difference electron density maps. Coordinates of methyl H atoms were calculated assuming reasonable bond distances and angles. All non-H atoms were refined anisotropically. Positional and isotropic

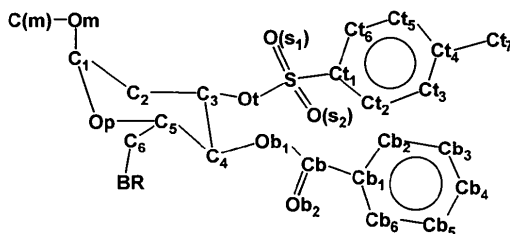


Fig. 1. Atom-numbering scheme.

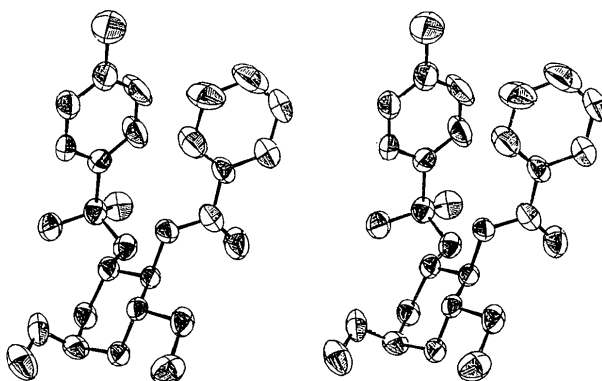


Fig. 2. Stereo representation of the molecule.

thermal parameters for the H atoms were fixed throughout all subsequent refinements. Least-squares refinement converged to final $R = 0.044$, $wR = 0.048$, $S = 1.416$. At this point all subsequent shifts were found to be $< 0.001\sigma$. A single prominent peak is evident on the difference electron density map measuring $0.67 \text{ e } \text{\AA}^{-3}$ in the immediate vicinity of Br. Otherwise, all remaining difference peaks were found to be $< 0.39 \text{ e } \text{\AA}^{-3}$. Anomalous scattering of Br and S atoms was employed for verification of the proper choice of enantiomeric configuration, following the statistical criterion proposed by Hamilton (1965). The opposite enantiomorph refined to final reliability indices of $R = 0.051$, $wR = 0.057$. Scattering factors for neutral atoms and anomalous-scattering parameters for Br and S atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a PDP 11/60 utilizing the *SDP-Plus* package (Frenz, 1978).

Discussion. Refined positional parameters for all atoms and equivalent isotropic B values are supplied in Table 1. Atom numbering follows the scheme indicated in Fig. 1. Fig. 2 shows a stereo *ORTEP* (Johnson, 1976) representation of the molecule. Interatomic bonding distances and angles are supplied in Table 2.* Bond distances and angles are, generally, as expected. The one exception to this is

* Lists of structure factors, complete bond distances and angles, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55634 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1012]

the exocyclic C—O bond at C1 in the pyranose ring. At 1.37 \AA , this bond is significantly shorter than anticipated, but is consistent with previously reported structures with pyranose substituents (Birnbaum, Roy, Brisson & Jennings, 1987; Kim & Jeffrey, 1967; Berman, Chu & Jeffrey, 1967) in which an O atom is attached at one of the anomeric positions. As is often the case, e.s.d.'s in atomic positions generally worsen in direct proportion to distance from the heavy atoms (Br and S) in the structure. The pyranose ring exists in the chair conformation with all substituents, except for the methoxy group at C1 (one of the anomeric C atoms), in equatorial positions. The phenyl C atoms of the tosyl and benzoyl substituents are approximately planar within the limitations of the data exhibiting minimal overlap (closest contact being that between atoms Cb2 and C13, with a non-bonded distance of 3.62 \AA). The planes described by these two rings intersect at an angle of 13.5° .

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A Chloride of a Substituted Heterocyclic Analogue of Chrysene: $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}^+\cdot\text{Cl}^-$

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Abstract. 12-Amino-6-hydroxyethylbenzo[*i*]phenanthridinium chloride, $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}^+\cdot\text{Cl}^-$, $M_r = 324.83$, monoclinic, $P2_1/n$, $a = 18.554$ (3), $b = 10.466$ (2), $c = 7.959$ (4) \AA , $\beta = 91.78$ (3) $^\circ$, $V = 1545$ (1) \AA^3 , $Z = 4$,

$D_x = 1.40 \text{ g cm}^{-3}$, $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$, $\mu = 22.43 \text{ cm}^{-1}$, $F(000) = 680$, $T = 298 \text{ K}$, $R = 0.034$, $wR = 0.037$, for 1115 reflections with $I > 3\sigma(I)$. The polynuclear framework is remarkably planar with the largest inter-ring-plane angle, $A/C = 4^\circ$. Bay-region dimensions, with beach bond C—C = 1.450 (6) \AA and beach C—C—C bond angles close to

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