

the size of the 1-alkyl substituents and is correlated with the size of the folding angle as in other phenothiazines. All the C–H bond lengths and C–C–H and H–C–H bond angles are within reasonable ranges of magnitudes. The packing of 1-ethylphenothiazine in the crystal is shown in Fig. 3. There are no intermolecular contacts less than van der Waals distances.

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Methyl 4,6-Bis(*O-p*-chlorobenzoyl)-2,3-dideoxy-3-*C*-(methoxycarbonylmethyl)- α -D-ribohexopyranoside

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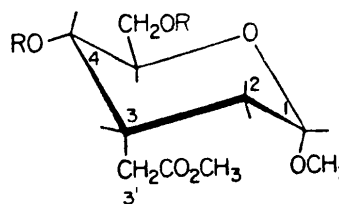
Abstract. Crystals of the title compound, $C_{24}H_{24}Cl_2O_8$, $M_r = 511.35$, are monoclinic, $P2_1$, $a = 5.752(3)$, $b = 15.436(3)$, $c = 13.698(3)$ Å, $\beta = 93.74(3)^\circ$, $D_m = 1.43$, $D_x = 1.40$ Mg m $^{-3}$, $Z = 2$. The structure was determined from Cu $K\alpha$ diffractometer data (with great difficulty), and refined to $R = 0.042$ for 898 reflexions. The six-membered pyranose ring is in the chair conformation, with the bulkier 4,6-*p*-chlorobenzoyl substituents equatorial, and the 1-OMe and 3-CH $_2$ CO $_2$ Me groups axial. Bond lengths and angles and intermolecular distances are normal. The extremities of the *p*-chlorobenzoyl groups exhibit large thermal librations [r.m.s. displacement as large as 0.56 (1) Å for one Cl].

Introduction. The title compound [(1), $R = ClC_6H_4CO-$] is a branched-chain sugar which was of interest because of possible antibiotic properties, and an X-ray crystal analysis was undertaken to verify structural assignments based on NMR data (Rosenthal & Catsoulacos, 1968). The X-ray study was begun in

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1967 (by DLH shortly after arrival in Vancouver from Antarctica, after a journey by Land Rover through South America).



The unit-cell dimensions were obtained by least-squares refinement based on 2θ values for 30 reflexions, and intensities were measured on a Datex automated GE XRD-6 diffractometer with nickel-filtered Cu $K\alpha$ radiation and a θ – 2θ scan technique. The scan speed was 1° min^{-1} , with 40 s background measurements before and after the scan. The intensities exhibited a rapid decrease with increasing θ , so that the data set was rather limited. Of 1028 reflexions in the range $0 < \theta \leq 45^\circ$, 898 had $I/\sigma(I) > 2.0$, where $\sigma(I) = S + B + (0.02S)^2$, S = scan and B = normalized background count. Crystal dimensions were $0.25 \times 0.05 \times 0.04$ mm, and no absorption corrections were considered necessary ($\mu = 28 \text{ cm}^{-1}$).

Early attempts to determine the structure involved Patterson methods and efforts to pack the *p*-chloro-

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benzoyl groups in the (103) plane, 103 being the most intense reflexion, and despite long periods of study of the sharpened three-dimensional Patterson function and the weighted reciprocal lattice (by DLH and JT), all efforts to solve the structure were unsuccessful. Direct methods with tangent refinement also failed to yield a solution, and at that stage (1970) the analysis was abandoned.

Several subsequent attempts to determine the structure also failed. More recently, various applications (by RAP) of *MULTAN* with as many as 500 *E*'s failed to produce any solution. The structure was finally solved (by ES) with the use of *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). It was noted that previous *MULTAN* runs always involved choice of a low-ranking *E* as one of the

origin-determining reflexions (usually 113, ranked number 86 in the list). Phase determination was therefore initiated with only the 170 highest *E*'s (*i.e.* only five *E*'s per atom), 50 of which were eliminated from the phase-determining process; the 43 lowest *E*'s were used for a $\Psi(0)$ test. The origin-determining reflexions were 103, 106, and 136 (rank 1, 6, and 5), four symbols were used, 023, 16 $\bar{4}$, 123, and 10 $\bar{3}$ (rank 2, 3, 7, and 125), and the 206 reflexion (rank 8) was assigned phase zero from \sum_1 relations. 18 sets of phases were generated; one set had the lowest *R* factor and the lowest $\Psi(0)$ value, and the *E* map calculated with these phases revealed 27 of the 34 non-hydrogen atoms in the molecule. After 14 years the structure was solved!

A difference map revealed the remaining seven atoms, and refinement then proceeded by full-matrix least-squares methods. At *R* = 0.094, a further difference map revealed 18 of the 24 hydrogen atoms; all 24 H atoms were included at calculated positions, but their parameters were not refined. Each enantiomer was then refined separately, with inclusion of anisotropic thermal parameters and anomalous-dispersion corrections for all non-hydrogen atoms. Scattering factors were from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with final weighting scheme $\sqrt{w} = |F_o|/5$ for $|F_o| < 5$, 1 for $5 \leq |F_o| \leq 25$, and $25/|F_o|$ for $|F_o| > 25$. For the enantiomer with the chemically-known configuration, final *R* and *R_w* were 0.042 and 0.048, respectively, for the 898 reflexions with *I* > 2σ(*I*) (307 parameters), and 0.053 and 0.048, respectively, for all 1028 measured reflexions. [The opposite enantiomer had *R* and *R_w* of 0.044 and 0.050 for the 898 reflexions, and may be rejected at the 99.5% significance level (Hamilton, 1965).] Final positional parameters are listed in Table 1.*

Discussion. The molecule (Fig. 1, correct absolute configuration shown) contains a six-membered pyranose ring in the chair conformation, with the bulkier 4,6-*p*-chlorobenzoyl substituents equatorial, and the 1-OMe and 3-CH₂CO₂Me groups axial. The ring is slightly flattened, the magnitudes of the internal torsion angles ranging from 49 to 61°. Within the rather limited accuracy of the analysis, bond lengths ($\sigma = 0.011$ – 0.02 Å) and angles ($\sigma = 0.7$ – 2°) are normal. Mean values for the lengths of the various types of bond are: C(*sp*³)–C(*sp*³) = 1.51, C(*sp*³)–C(*sp*²) = 1.51, C(*sp*²)–C(ar) = 1.47, C(*sp*³)–O = 1.42,

Table 1. Positional (fractional, $\times 10^4$) and equivalent isotropic thermal ($\text{\AA}^2, \times 10^3$) parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> *
Cl(1)	408 (11)	–2322†	6160 (3)	185‡
Cl(2)	5271 (7)	6067 (4)	4487 (3)	126‡
O(1)	–2207 (11)	3526 (5)	8974 (5)	67
O(2)	1147 (14)	3580 (6)	9998 (5)	68
O(3)	100 (11)	1122 (7)	11837 (5)	90
O(4)	3668 (13)	1133 (7)	11349 (5)	97
O(5)	–2011 (12)	1215 (6)	8498 (5)	69
O(6)	–5397 (15)	571 (6)	8705 (6)	95
O(7)	–1419 (13)	3467 (6)	6936 (6)	74
O(8)	1313 (15)	2517 (8)	6618 (6)	95
C(1)	–1282 (22)	3566 (8)	9950 (9)	68
C(2)	–2107 (18)	2811 (10)	10556 (8)	69
C(3)	–1724 (15)	1941 (8)	10085 (7)	53
C(4)	–2643 (17)	1989 (8)	9029 (8)	61
C(5)	–1641 (14)	2745 (8)	8487 (7)	56
C(6)	2094 (23)	4285 (8)	9489 (10)	88
C(7)	818 (17)	1635 (7)	10214 (8)	59
C(8)	1396 (19)	1276 (7)	11226 (8)	58
C(9)	4443 (20)	751 (11)	12262 (10)	108
C(10)	–3509 (22)	565 (9)	8375 (8)	64
C(11)	–2518 (23)	–135 (8)	7832 (8)	62
C(12)	–3657 (22)	–926 (11)	7777 (9)	81
C(13)	–2745 (37)	–1600 (9)	7235 (11)	104
C(14)	–731 (38)	–1477 (13)	6801 (10)	109
C(15)	374 (29)	–711 (14)	6861 (10)	106
C(16)	–472 (24)	–36 (9)	7375 (9)	81
C(17)	–2635 (18)	2821 (10)	7454 (8)	75
C(18)	529 (24)	3234 (11)	6550 (8)	70
C(19)	1624 (20)	3960 (10)	6037 (8)	62
C(20)	3640 (22)	3794 (8)	5558 (9)	74
C(21)	4721 (24)	4450 (12)	5095 (10)	91
C(22)	3818 (24)	5255 (10)	5100 (9)	79
C(23)	1851 (25)	5443 (9)	5558 (12)	99
C(24)	782 (21)	4780 (11)	6024 (10)	85

* *U_{eq}* is one-third the trace of the diagonalized anisotropic temperature factor matrix.

† Fixed to define origin.

‡ Anisotropic parameters ($\text{\AA}^2, \times 10^3$);

	<i>U₁₁</i>	<i>U₂₂</i>	<i>U₃₃</i>	<i>U₁₂</i>	<i>U₁₃</i>	<i>U₂₃</i>
Cl(1)	311 (7)	117 (3)	123 (3)	107 (4)	–7 (4)	–33 (3)
Cl(2)	124 (3)	117 (3)	135 (3)	–39 (3)	–4 (2)	35 (3).

* Anisotropic thermal parameters, hydrogen atom parameters, ring torsion angles, bond lengths, bond angles, packing diagram, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36814 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

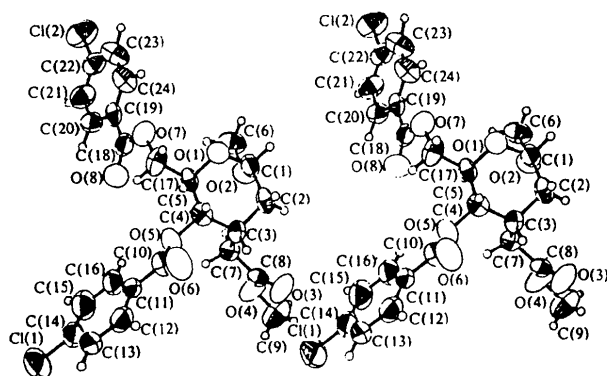


Fig. 1. Stereoview of the molecule; 50% probability ellipsoids for non-hydrogen atoms.

$C(sp^2)-O = 1.32$, $C(sp^2)=O = 1.19$, $C(ar)-C(ar) = 1.37$, $C-Cl = 1.74$ Å [where $C(ar)$ is in an aromatic ring]; the ranges of the values of bond angles (and means) are: angles at $C(sp^3) = 106-113$ (111), at $C(ar) = 118-123$ (120), at $O = 113-120$ (116), and for carboxyl groups, $C-C=O = 125-128$ (126), $C-C-O = 110-112$ (111), $O-C=O = 123^\circ$.

The molecules are held together in the crystal by van der Waals forces, with no very strong intermolecular attractions. The extremities of the molecule exhibit considerable thermal motion, particularly the *p*-chlorobenzoyl groups. The largest thermal parameter is $U_{11} = 0.311$ Å² for Cl(1), corresponding to a large root-

mean-square displacement of 0.56 (1) Å; this might indicate some disorder in the position of that *p*-chlorobenzoyl group, although a description in terms of large thermal vibration seems not unreasonable. The high thermal parameters for Cl might be the reason for the difficulties encountered in interpretation of the Patterson function. The planes of the *p*-chlorobenzoyl groups lie close to (103), but otherwise none of the early models show any correspondence to the true structure.

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4-(2-Amino-4-oxo-2-imidazolin-5-ylidene)-2-bromo-4,5,6,7-tetrahydropyrrolo-[2,3-*c*]azepin-8-one Methanol Solvate: a New Bromo Compound from the Sponge *Acanthella Aurantiaca*

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Abstract. C₁₁H₁₀BrN₅O₂·CH₄O, $M_r = 356.07$, monoclinic, $P2_1/n$, $a = 11.943$ (1), $b = 16.252$ (2), $c = 7.253$ (2) Å, $\beta = 93.43$ (2)°, $U = 1405.2$ (6) Å³, $Z = 4$, $D_x = 1.69$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu(Cu K\alpha) = 46.1$ cm⁻¹. The structure was solved by the heavy-atom method and refined to an R value of 0.042 for 1997 independent observed reflexions. The molecule contains a seven-membered ring in an

approximate boat conformation. The packing is governed by a network of intermolecular hydrogen bonds, involving also the methanol O atom.

Introduction. The title compound (I) is a new metabolite containing Br; it was separated by chromatography from the butanolic extract of the Red Sea sponge *Acanthella Aurantiaca* (Cimino, De Rosa, De Stefano,