

96. *The X-Ray Analysis of Methyl 3,4,6-Tri-O-acetyl-2-chloromercuri-2-deoxy- β -D-glucopyranoside.*

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The configurations of the substituents of the pyranose ring in this substance were determined by a two-dimensional X-ray analysis of this compound: they were found all to be attached equatorially.

THE X-ray analysis of methyl 3,4,6-tri-O-acetyl-2-chloromercuri-2-deoxy- β -D-glucopyranoside, obtained by methoxymercuration of tri-O-acetyl-D-glucal¹ with subsequent conversion into the mercurichloride, was undertaken to establish the stereochemistry of this molecule at positions 1 and 2. The molecule is dissymmetric and must therefore crystallise in a non-centrosymmetric space group. In such a case heavy-atom methods, with one heavy atom per asymmetric unit, yield double solutions which may be difficult to resolve. Fortunately, a projection down one of the axes of this compound's crystals is centrosymmetric, and the positions of the other atoms of the molecule can be determined unequivocally in this projection. The stereochemistry of the pyranose ring is well enough established to determine completely the configuration of the attached groups from a simple two-dimensional analysis.

Experimental.—The crystals, which were prepared by Inglis, Schwarz, and McLaren,¹ were elongated prisms with their long axis parallel to the crystallographic *b*-axis. The crystal data

¹ Inglis, Schwarz, and McLaren, unpublished work.

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for $C_{13}H_{18}ClHgO_8$ are: $M = 538.4$; monoclinic; $a = 12.12 \pm 0.01$; $b = 8.19 \pm 0.01$; $c = 9.02 \pm 0.01$ Å; $\beta = 93^\circ 11' \pm 3'$; $U = 894$ Å³; $D_m = 2.01$ g./c.c. (by flotation); $Z = 2$, $D_c = 2.00$ g./c.c.; $F(000) = 514$. Space group $P2_1(C_2^2)$. Weissenberg photographs were taken with Cu- K_α radiation ($\mu = 188$ cm.⁻¹). An approximately cylindrical crystal, with diameter 0.4 mm., was used. The intensities were measured by the multiple film technique, by visual comparison against a calibrated scale. Absorption and Lorentz polarisation corrections were then applied.

Structure determination. The position of the mercury atom was found by studying the weighted reciprocal lattice of the $h0l$ reflections. The Fourier transform of two points is a series of parallel bands of intense regions separated by straight lines of zero intensity. These lines are at right angles to the line joining the two points, and their spacing is inversely

TABLE 1.
Atomic co-ordinates.

	x	z		x	z		x	z		x	z
Hg	0.046	0.172	C ₄	0.258	0.567	C ₁₁	0.537	0.678	O ₄	0.362	0.627
Cl	0.992	0.939	C ₅	0.167	0.700	C ₁₂	0.267	0.883	O ₅	0.195	0.822
			C ₆	0.216	0.802	C ₁₃	0.280	0.879	O ₆	0.420	0.130
			C ₇	0.833	0.567				O ₇	0.460	0.617
C ₁	0.022	0.500	C ₈	0.315	0.200	O ₁	0.921	0.440	O ₈	0.321	0.986
C ₂	0.088	0.383	C ₉	0.267	0.182	O ₂	0.064	0.619			
C ₃	0.224	0.425	C ₁₀	0.441	0.642	O ₃	0.300	0.320			

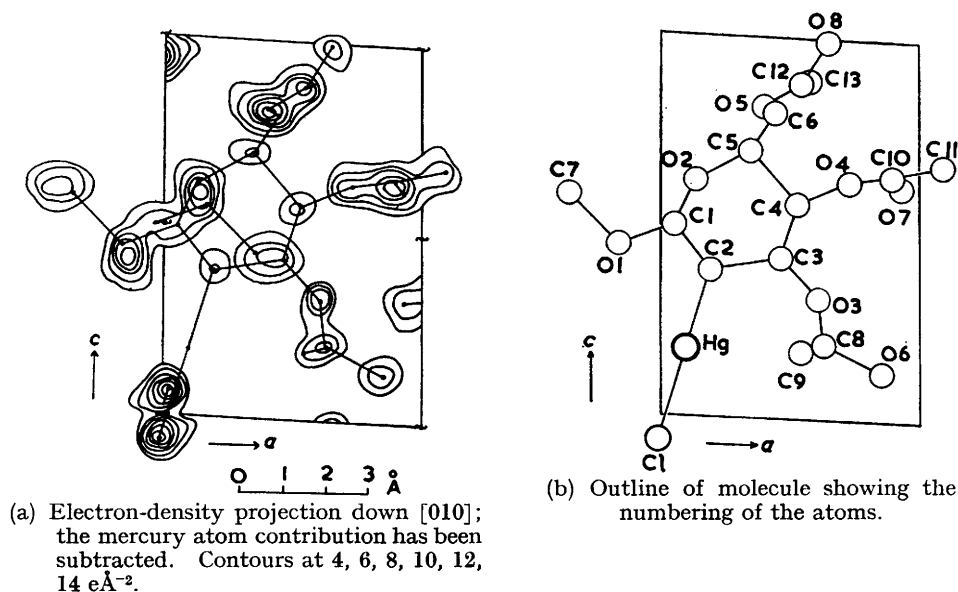
TABLE 2.
Calculated and observed structure factors.

h	F_c	$ F_o $	h	F_c	$ F_o $	h	F_c	$ F_o $	h	F_c	$ F_o $	h	F_c	$ F_o $	h	F_c	$ F_o $
$h00$			$h02$			$h03$			$h05$			$h07$			$h09$		
0	478	—	—15	—6	8	3	—54	43	—9	—30	24	—13	—10	8	—10	9	9
1	171	—	—14	—4	0	4	—17	17	—8	—56	48	—12	—6	8	—9	6	9
2	117	121	—13	2	0	5	—4	0	—7	—69	71	—11	—7	0	—8	5	0
3	128	128	—12	16	13	6	23	19	—6	—55	58	—10	—6	0	—7	1	0
4	101	120	—11	16	27	7	39	42	—5	—61	69	—9	6	0	—6	—4	0
5	19	16	—10	40	33	8	40	37	—4	—56	63	—8	15	15	—5	—17	16
6	—15	15	—9	70	62	9	54	58	—3	—24	23	—7	28	27	—4	—24	27
7	—30	31	—8	87	85	10	29	27	—2	3	0	—6	24	22	—3	—26	29
8	—67	74	—7	96	91	11	31	27	—1	41	41	—5	47	45	—2	—33	36
9	—50	44	—6	106	88	12	21	19	0	82	90	—4	53	66	—1	—41	41
10	—47	48	—5	110	108	13	16	13	1	77	76	—3	41	44	0	—31	35
11	—30	24	—4	83	86	14	5	0	2	76	81	—2	21	23	1	—28	31
12	—25	22	—3	131	122				3	84	87	—1	31	34	2	—30	35
13	—14	13	—2	8	17	$h04$			4	80	77	0	14	13	3	—13	15
14	—8	8	—1	—11	16	—14	11	10	5	57	57	1	—8	13	4	—1	0
15	—3	0	0	—64	85	—13	16	15	6	29	27	2	—22	17	5	—1	0
			1	—66	59	—12	19	15	7	0	0	3	—37	37	6	3	0
			2	—72	76	—11	13	13	8	—1	0	4	—48	45	7	13	14
			3	—160	167	—10	10	0	9	—8	0	5	—50	45	8	9	13
			4	—117	122	—9	—4	8	10	—15	14	6	—36	34	9	10	15
			5	—109	108	—8	—27	24	11	—18	15	7	—34	28			
—15	—9	8	6	—73	77	—7	—44	41	12	—17	17	8	—29	28	$h010$		
—14	—14	12	7	—42	46	—6	—46	43	13	—10	14	9	—25	26	—8	—10	14
—13	—20	19	8	—9	0	—5	—72	77				10	—8	12	—7	—9	13
—12	—22	19	9	2	0	—4	—98	94	$h06$			11	—6	7	—6	—13	17
—11	—20	12	10	16	17	—3	—92	98	—13	—10	9				—5	—20	23
—10	8	9	11	30	31	—2	—98	102	—12	—18	21				—4	—23	22
—9	8	0	12	26	23	—1	—55	63	—11	—23	19				—3	—15	19
—8	43	43	13	21	17	0	—88	91	—10	—27	22	$h08$			—2	—19	23
—7	79	83	14	15	13	1	3	0	—9	—24	23	—11	7	7	—1	—10	12
—6	90	85	15	12	9	2	7	15	—8	—22	23	—10	11	9	0	—3	6
—5	132	124				3	51	55	—7	—17	15	—9	18	17	1	—1	0
—4	175	144	$h03$			4	64	65	—6	2	0	—8	21	19	2	4	0
—3	179	160	—15	7	3	5	65	62	—5	16	13	—7	20	20	3	8	10
—2	90	95	—14	13	9	6	88	86	—4	51	48	—6	21	20	4	17	19
—1	85	86	—13	27	21	7	63	57	—3	47	43	—5	19	20	5	12	17
0	45	48	—12	27	22	8	57	55	—2	74	83	—4	4	0	6	12	19
1	45	57	—11	42	40	9	39	36	—1	62	76	—3	5	0	7	7	12
2	—10	0	—10	50	44	10	25	27	0	82	88	—2	—4	0			
3	—14	13	—9	49	43	11	—1	0	1	58	62	—1	—32	34			
4	—81	88	—8	44	38	12	1	0	2	34	40	0	—37	41			
5	—81	88	—7	31	33	13	—2	0	3	43	36	1	—46	45	$h011$		
6	—66	59	—6	38	40	14	—8	8	4	—2	0	2	—37	35	—5	—7	9
7	—67	77	—5	—54	58				5	—8	0	3	—37	35	—4	—4	7
8	—74	70	—4	—101	95				6	—12	0	4	—37	35	—3	0	0
9	—44	45	—3	—82	85	$h05$			7	—20	16	5	—31	30	—2	2	0
10	—30	27	—2	—61	56	—14	3	5	8	—40	37	6	—22	20	—1	5	7
11	—22	20	—1	—166	164	—13	—1	0	9	—28	27	7	—6	0	0	10	10
12	1	0	0	—126	130	—12	—5	0	10	—20	22	8	—3	0	1	13	17
13	—3	0	1	—125	145	—11	—15	14	11	—19	26	9	2	0	2	11	16
14	6	0	2	—95	92	—12	—29	27	12	—16	22	10	3	7	3	9	15
15	10	8															

proportional to the distance between the points. In this structure the diffraction pattern will be dominated by the mercury atom contributions. The absent and very weak $h0l$ reflexions were plotted on a reciprocal net and were found to lie on straight lines. Hence the mercury-mercury vector was determined and, as these atoms are related by the screw axis of the space group, their co-ordinates were immediately obtained with respect to an origin located on a screw-axis.

Structure factors for this one-atom structure were then calculated, and a difference map was obtained. The latter is shown in Fig. 1. The positions of the remaining atoms were then assigned as shown by the skeleton diagram superimposed on the map in Fig. 1. Some refinement of the atomic co-ordinates by difference maps was necessary. The reliability index, R , for the one-atom structure is 23.5%, and for the 23-atom structure (hydrogen omitted from the calculations) is 10.4%. (For these figures all unobserved reflexions were given a value of 4 electrons.)

The co-ordinates of the atoms are given in Table 1. It is not possible in this analysis to distinguish between oxygen and carbon atoms by crystallographic means. Chemical knowledge of the molecule was used as much as possible for this purpose, but the methyl group and the carbonyl-oxygen atom in an acetyl group are not necessarily correctly labelled.



Calculated and observed values of the structure factors are shown in Table 2.

Accuracy. The accuracy was estimated by Cruickshank's method.² The results are $\sigma(\rho) = 1.1 \text{ e}/\text{\AA}^3$, $\sigma(x) = \sigma(y) = \sigma(z) = 0.0026 \text{ \AA}$ for the mercury atom, 0.017 \AA for the chlorine atom, and about 0.06 \AA for the light atoms. Although the analysis is not accurate enough for discussions of bond lengths, the precision is high enough to be certain of the approximate positions of all the atoms except hydrogen. None of the projected bond lengths is significantly abnormal.

Conclusions.—The uncertainty of the configuration at positions 1 and 2 gives rise to four possible stereoisomers. Only one of these, namely, that with all the groups equatorially attached, has a projection which satisfies the electron-density map in Fig. 1, and this is the β -glucopyranoside structure. Brook and Wright³ have carried out an X-ray analysis on a product obtained by methoxymercuration of cyclohexene, intending to determine its stereochemistry, but the positions of the carbon atoms are not accurate

² Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

³ Brook and Wright, *Acta Cryst.*, 1951, **4**, 50.

enough to distinguish between a "chair-type" and an "extended" ring,^{4,5} and the configuration remained uncertain. In the present work, the positions of the substituent groups are determined, and these are sufficient to show that the ring, in this case, is in the Sachse-Mohr chair form. There is thus no doubt about the configuration of the molecule, and this is the first analysis that determines unequivocally the stereochemistry of a product of methoxymercuration.

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⁴ Berg, Lay, Rodgman, and Wright, *Canad. J. Chem.*, 1958, **36**, 358.

⁵ Abercrombie, Rodgman, Barucha, and Wright, *Canad. J. Chem.*, 1959, **37**, 1328.
