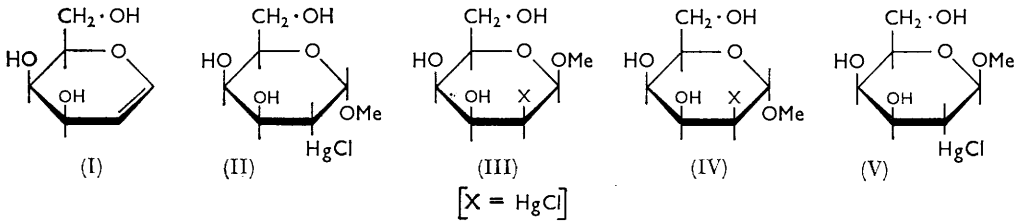
745. *Partial Determination of the Crystal Structure of Methyl 2-Chloromercuri-2-deoxy-α-D-talopyranoside*

By JESSIE BAIN and MARJORIE M. HARDING

This compound was prepared by the methoxymercuration of D-galactal followed by replacement of the acetoxy-group by chlorine. The crystals have space-group $P2_12_12_1$ with $a = 6{\cdot}68$, $b = 13{\cdot}6$, $c = 11{\cdot}9$ Å. *X*-Ray analysis of the (100) projection showed that the ClHg group and the CH_3O group both occupy axial positions in the six-membered ring, confirming that the compound is the one named above, and that *trans*-addition to the double bond of D-galactal took place.

THE compound was prepared by Riddell and Schwarz [1] by the methoxymercuration [2] (with mercuric acetate in methanol) of D-galactal (I), followed by replacement of the acetoxy-group by chlorine. The partial crystal structure determination was undertaken to establish whether this addition to a double bond is *cis* or *trans*; *cis* addition would give



the compound (II) or (III), while *trans* addition would give (IV) or (V). The observation [1] that reduction with borohydride converts it into methyl 2-deoxy-α-D-galactoside restricts the possibilities to (II) or (IV).

EXPERIMENTAL

Crystals were obtained from ethyl acetate–ethanol; $C_7H_{13}O_5HgCl$, $M = 413$, m. p. 137—139° (decomp.), $[\alpha]_D^{20}$ +52° (*c* 1 in CH_3OH), orthorhombic, $a = 6{\cdot}68 \pm 0{\cdot}1$, $b = 13{\cdot}6 \pm 0{\cdot}1$, $c = 11{\cdot}9 \pm 0{\cdot}1$ Å, $U = 1088$ Å^3, $Z = 4$, $D_{calc.} = 2{\cdot}53$ g. cm.$^{-3}$, $F(000) = 768$; space-group $P2_12_12_1$, Cu-K_α radiation, single crystal oscillation and Weissenberg photographs about the *a* axis.

Intensities of 166 0*kl* reflections were estimated visually and corrected for Lorentz and polarisation effects but not for absorption. The positions of the mercury and chlorine atoms found from a sharpened Patterson projection, and used to derive signs for electron density projections, and difference projections. Small amendments to the mercury and chlorine co-ordinates and temperature factors were made, and then the electron density projection shown in Figure 1 was calculated.

Individual carbon and oxygen atoms are not, with one fortunate exception, resolved. Our interpretation of the electron density map was made with the help of a Dreiding molecular model; it was somewhat simplified by the knowledge that the Cl–Hg bond must be nearly perpendicular to *a*, since the projected Hg–Cl distance is 2·38 ± 0·10 Å (cf. Hg–Cl = 2·282 Å in CH_3HgCl [3]). It was immediately clear that the mercury atom must be in an axial position of the six-membered ring. Figure 2 shows the compounds (II—(V) with chair conformations in which mercury is axial. The differences, as " seen " by *X*-rays, are small. The structure

[1] W. Riddell and J. C. P. Schwarz, unpublished work.
[2] G. R. Inglis, J. C. P. Schwarz, and L. McLaren, *J.*, 1962, 1014.
[3] W. Gordy and J. Sheridan, *J. Chem. Phys.*, 1954, **22**, 92.

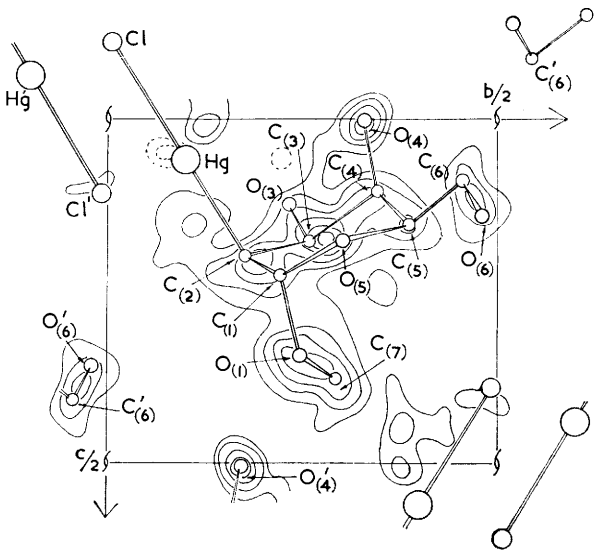


FIGURE 1. (100) Electron density projection, with signs determined by Hg and Cl, and with the Hg and Cl contributions subtracted. The contours are at 3, 5, 7, 9 . . . eÅ^{-2} (full lines), and −3, −5 eÅ^{-2} (dotted lines).

(IV) can be satisfactorily fitted to the observed electron density as shown in Figure 1. Structure (II) cannot be fitted satisfactorily; there is no electron density in the region required for the axial CH_2OH, and the peak which represents $O_{(4)}$ in structure (IV) cannot be accounted for. Similarly unsuccessful attempts were made to fit the models (III) and (V), and some distorted boat forms were also investigated.

Structure factors were calculated including all the C and O atoms of model (IV). The R

Observed and calculated structure factors

	F_c	F_o
00*l*		
2	153	184
4	87	−95
6	97	−89
8	93	−111
10	70	−77
01*l*		
2	154	−185
3	76	97
4	88	−108
5	73	−76
6	104	−108
7	122	−132
8	16	−8
9	68	−80
10	31	34
11	30	−45
12	32	36
14	22	26
02*l*		
0	20	28
1	64	−61
2	123	122
3	145	−178
4	25	−28
5	196	−224
6	93	−81
7	82	−88
8	41	−32
9	20	22
11	56	64
13	64	60
15	13	25
03*l*		
1	31	−28
2	213	−181
3	41	−24
03*l*		
4	203	−232
5	11	8
6	115	−125
7	63	56
8	27	−38
9	46	52
10	46	53
11	31	31
12	70	71
14	32	36
04*l*		
0	115	−84
1	49	−37
2	175	−177
3	138	−123
4	94	−92
5	90	−104
6	77	81
7	58	−61
8	108	125
9	10	13
10	78	69
11	40	38
12	9	10
14	29	−22
15	8	18
05*l*		
1	237	−199
2	11	2
3	133	−123
5	12	8
7	99	117
8	10	2
9	118	130
10	10	1
11	43	40
06*l*		
0	125	−136
1	71	58
2	99	−96
3	136	123
4	17	−22
5	86	80
6	53	62
7	50	42
8	131	109
10	85	81
11	24	−30
13	20	−25
14	14	−17
07*l*		
1	40	−57
2	123	110
3	23	−32
4	152	162
6	89	93
7	25	25
8	19	17
9	20	28
10	35	−31
11	15	23
12	39	−48
14	17	−33
08*l*		
0	95	86
1	67	74
2	40	29
3	136	154
4	36	−39
5	114	125
6	21	−23
7	28	34
8	19	−12
10	26	−22
08*l*		
11	35	−41
13	25	−38
09*l*		
1	154	141
2	62	56
3	64	55
4	64	68
5	48	−51
6	48	59
7	61	−62
9	43	−33
10	17	−22
11	23	−24
12	20	−23
010*l*		
0	137	141
1	18	13
2	90	88
4	10	0
5	21	−9
6	50	−60
8	76	−67
10	36	−44
011*l*		
1	93	92
2	42	−40
3	17	30
4	51	−42
5	35	−32
6	55	−44
7	59	−57
8	19	−19
9	42	−42
10	15	20
11	6	−16
012*l*		
0	31	49
1	35	8
2	24	27
3	68	−66
5	84	−79
6	18	−11
7	47	−38
9	13	15
013*l*		
1	16	−11
2	49	−48
3	17	−19
4	71	−64
6	49	24
7	19	14
9	17	16
10	8	17
014*l*		
0	59	−53
2	54	−37
3	39	−28
4	9	−10
5	30	−34
6	16	14
7	14	−19
8	32	38
015*l*		
1	16	−43
7	22	35
016*l*		
0	29	−33
1	13	17
2	23	−28
3	24	26
5	15	16

factor (observed reflections only) is 0·14, compared with 0·24 for mercury and chlorine alone. A difference electron density projection showed no evidence of large shifts or misplaced atoms. The positional parameters used are given in the Table below. The thermal parameters $B = 3·8$

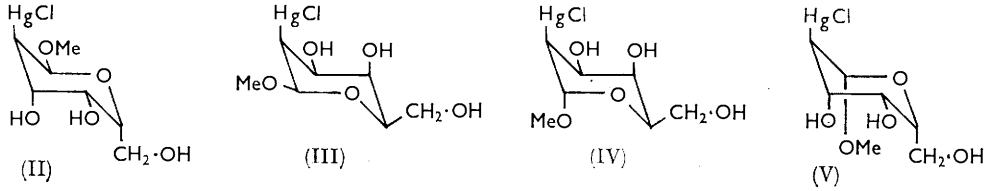


FIGURE 2. The compounds (II)—(V) are shown, with chair conformations, and with the ClHg-groups axial

Å² for Hg and Cl, and $B = 4$ Å² for C and O, were used. x Co-ordinates have not been determined, but a reasonable hydrogen-bonded scheme can be postulated for the packing of molecules in the lattice.

Atomic co-ordinates, referred to an origin on the 2-fold screw axis, parallel to *a*

	y	*z*
Hg ...	0·0997 ± 0·0008	0·0586 ± 0·0008
Cl ...	0·0075 ± 0·002	−0·1110 ± 0·002

	y	*z*
$C_{(1)}$	0·222	0·232
$C_{(2)}$	0·178	0·200
$C_{(3)}$	0·258	0·178
$C_{(4)}$	0·345	0·105
$C_{(5)}$	0·387	0·153
$C_{(6)}$	0·458	0·087

	y	*z*
$C_{(7)}$	0·292	0·378
$O_{(1)}$	0·248	0·344
$O_{(3)}$	0·234	0·125
$O_{(4)}$	0·330	0·002
$O_{(5)}$	0·300	0·178
$O_{(6)}$	0·482	0·142

DISCUSSION

If the molecule is assumed to be in a chair conformation, and the chemical evidence that the methoxyl group is α is accepted, structure (IV), with ClHg axial, is the only satisfactory interpretation of the electron density projection. This is the structure resulting from *trans* addition. Moreover, on its own, the crystallographic evidence is strongly against a β-glycoside structure or a boat conformation, but is not conclusive. *trans* Addition was similarly shown to occur in the methoxymercuration of tri-*O*-acetyl-glucal.[4]

$O_{(4)}$, the oxygen atom of an axial hydroxyl group, on the same side of the pyranose ring as the ClHg group, is well resolved. It is 3·0 Å (in projection) from the mercury atom; with undistorted bond angles of 109½° this projected distance should be ⩽2·6 Å. This hydroxyl group, or the ClHg group, or both, are therefore bent outwards from the ideal axial positions.

We thank Dr. Schwarz and Mr. Riddell for suggesting this problem and for providing the crystals.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF EDINBURGH. [*Received, November 20th*, 1964.]

[4] H. W. W. Ehrlich, *J.*, 1962, 509.