Studies on the Schardinger Dextrins. IX. Structure of the Cyclohexaamylose-Iodine Complex*

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Iodine reacts with cyclohexaamylose (Schardinger's alpha-dextrin) in aqueous solution to form an iodide-free crystalline complex, $(C_6H_{10}O_5)_6 \cdot I_2 \cdot 14 H_2O$. From optical studies and two- and three-dimensional Patterson plots, it is concluded that the iodine molecule axes are parallel to the (100) plane and inclined about 45 degrees to the y axis. The only reasonable structure consistent with the data is a cylindrical or torus-like cyclic carbohydrate molecule coaxial with and enclosing each iodine molecule. Consideration of the possible packing arrangements of the cyclic molecules in the unit cell, as well as measurements of scale models, lead to a diameter of the torus of approximately 13 Å and a thickness of 6·7 Å. Attempts to determine more exactly the arrangement of carbon and oxygen atoms by the isomorphic replacement technique were not successful.

Introduction

Action of *Bacillus macerans* upon starch gives crystalline Schardinger dextrins (Schardinger, 1908) (Cyclo-amyloses) containing six to eight glucose units per molecule. (French, 1949, 1950). They are chemically homogeneous and react readily with iodine to form a variety of brown and blue crystalline inclusion compounds analogous to starch–iodine complexes. That the short-chain amylodextrins do not react to form colored complexes with iodine is considered strong evidence that a ring or helical structure is essential to this type of complex formation (Freudenberg, 1939).

Following a preliminary survey (French, 1958) of the various Schardinger dextrin complexes with iodine, iodides and alcohols, the authors selected the iodide-free iodine complex of cyclohexaamylose for the more detailed study reported herein. The absence of iodide ions and cations makes the structure interpretation simpler, though perhaps less interesting or significant with respect to the starch–iodine complexes. Furthermore, the fact that various alcohol complexes are nearly isomorphous with the iodine complex invited application of the isomorphic replacement technique.

A study of the cyclohexaamylose–iodine complex was therefore undertaken to determine the location of the iodine atoms in the complex with the further hope of obtaining information on the arrangement of the glucose units in the dextrin.

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Structure determination

Preparation of the crystals

Finely powdered iodine was heated with an equimolar amount of cyclohexaamylose in aqueous solution. The red brown complex which crystallized on slow cooling was filtered off and washed with water.
Other cyclohexaamylose crystals were prepared using as solvents water, and fifty percent solutions of aqueous *n*-propanol, ethanol and methanol.

Physical data

Crystals of the iodine complex possess orthorhombic symmetry; on Weissenberg and precession patterns all odd orders of $(h00)$, $(0k0)$, and $(00l)$ are missing. The space group is $P2_12_12_1-D_2^4$ requiring four (or a multiple of four) molecules per unit cell. The lattice constants are:

$a_0 = 14 \cdot 38 \pm 0 \cdot 05$, $b_0 = 36 \cdot 07 \pm 0 \cdot 05$, $c_0 = 9 \cdot 43 \pm 0 \cdot 03$ Å (calculated density 1·99 g.cm.$^{-3}$).

Analysis: Calculated for $(C_6H_{10}O_5)_6 \cdot I_2 \cdot 14 H_2O$:

$\quad$ I = 17·2%, $(C_6H_{10}O_5)$ = 65·7%, H_2O = 17·1%.

Observed: I = 17·5%, $(C_6H_{10}O_5)_6$ (by optical rotation) = 64·9%, H_2O (by difference) = 17·6%.

Table 1. *Lattice constants of the pseudoisomorphs*

Complexing agent	a_0	b_0	c_0
Iodine	14·38 Å	36·07 Å	9·43 Å
n-Propanol	14·24	37·30	9·43
Ethanol	14·31	37·46	9·43
Methanol	13·94	36·83	9·47
Water	15·1	33·8	9·6
Water (crystal from another batch)	14·78	33·96	9·51

The iodine complex is more nearly isomorphous with

dextrins from n-propanol, ethanol, and methanol than with the crystals from water (Table 1). With the lower lacohols and water, the rate and extent of loss of solvent appeared to vary with the crystals studied, so that the cell dimensions are somewhat variable.

Optical study

Examination of the iodine complex under the polarizing microscope indicated little or no pleochroism when the crystals were viewed along the x axis. When examined along the y or z axes, the crystals were pleochroic changing in color from light amber to orange red; light was absorbed at a minimum when the electric vector was parallel to the x axis. From these results it can be concluded that the iodine molecule axes are parallel to (100) and inclined at approximately 45 degrees to the y and z axes.

Parameter determination

Complete three-dimensional data for the iodine complex were obtained using a Weissenberg camera and Ni-filtered Cu $K\alpha$ radiation. Weissenberg films of $(hk0)$ data, timed to give a film factor of two, were prepared for the methanol pseudoisomorph. Precession films of $(0kl)$ data were obtained similarly using Zr-filtered Mo $K\alpha$ radiation. All intensities were estimated by visual comparison and corrected for Lorentz and polarization factors. The relative values of F^2 for $(hk0)$ and $(0kl)$ were then placed on an absolute scale (Wilson, 1942). Correction for absorption was considered to be unnecessary.

The Patterson function for the iodine complex was then projected onto the (001), (100), and (010) planes. The Patterson function involving approximately 800
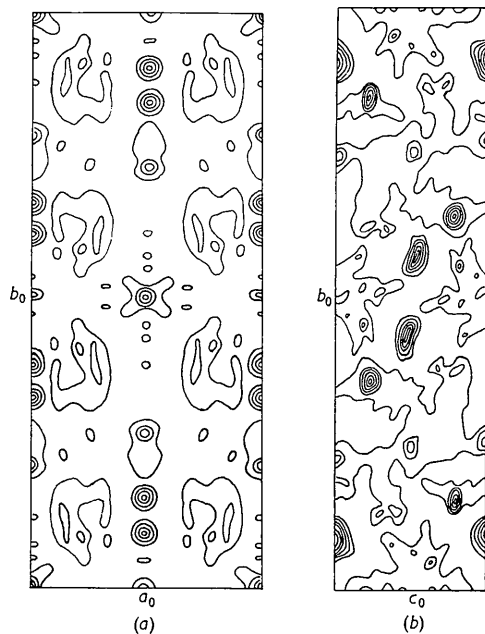

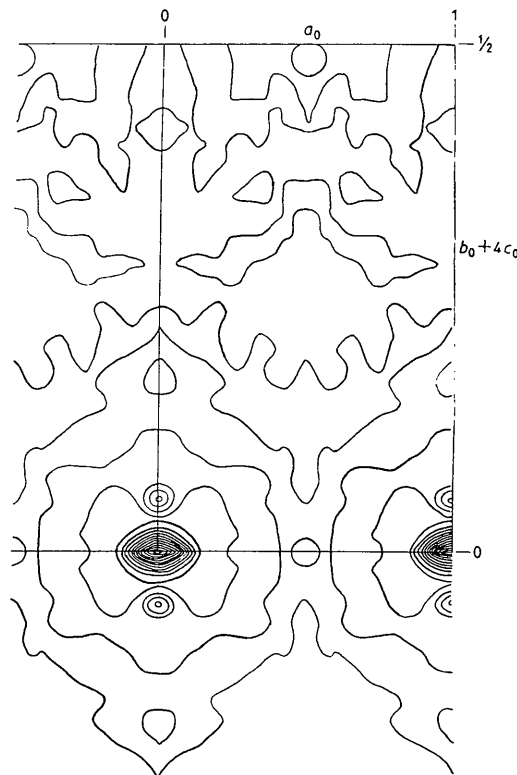Fig. 2. Patterson section $(X, Y, 4Y)$.

independent terms, was calculated for sixteen sections parallel to (100) at intervals of $2/60$ along the x axis. The iodine parameters resulting from inspection of these sections were as follows: $x_1 = 0.250$, $y_1 = 0.153$, $z_1 = 0.500$, $x_2 = 0.250$, $y_2 = 0.095$, and $z_2 = 0.292$ expressed as fractions of the corresponding unit-cell dimensions.

From these parameters, structure factors were calculated and Fourier projections were made upon the (001) and (100) planes (Fig. 1(a) and (b)). Application of Booth's back correction method (1948) changed the y_1 parameter to 0.150. The observed iodine–iodine bond distance was 2·81 Å.

In an attempt to see more clearly the arrangement of carbohydrate about the iodine, a plot was made for the Patterson section $(X, Y, 4Y)$ through the origin (Fig. 2). This plane is essentially perpendicular to molecular axes for half the iodine and carbohydrate molecules but nearly parallel to the molecular axes for the other half (Fig. 3).

The least degree of overlap of atoms may be expected when the structure is projected onto the (100) plane. Therefore this projection was prepared on X-RAC using data from the methanol complex (Fig. 4). The phases and amplitudes were determined from the iodine positions using the isomorphic replacement technique. This necessitated an absolute scale for the structure factors. The agreement between the structure factors $(0kl)$ for the methanol complex and

Fig. 1. (a) Fourier projection on to the (001) plane.
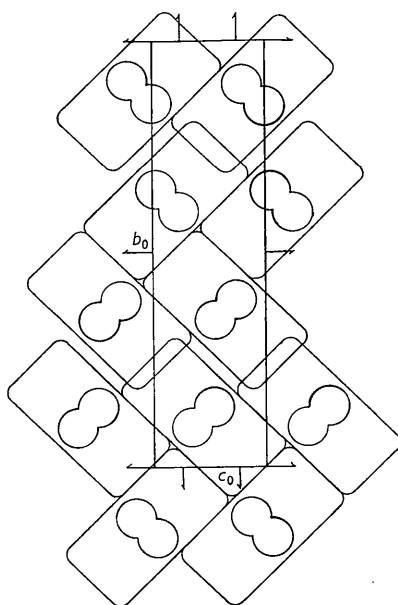(b) Fourier projection on to the (100) plane.

Fig. 3. Schematic drawing of the projection of the iodine complex on to the (100) plane. The iodine positions are taken from the Fourier projection.
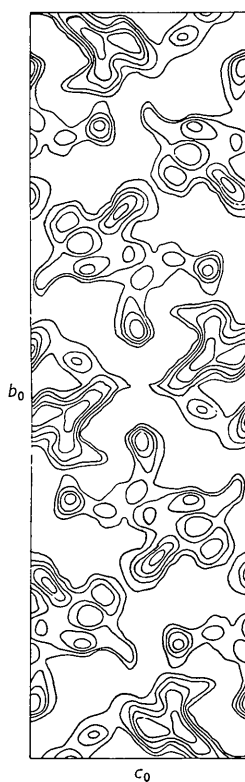

Fig. 4. Fourier projection of oxygen and carbon atoms on to the (100) plane.

the non-iodine contribution of the iodine complex is shown in Table 2. Inasmuch as the crystals are not strictly isomorphous, the agreement is sufficiently

Table 2. *Comparison of the observed structure factors for the methanol complex with the calculated non-iodine contribution of the iodine complex*

Indices	(Methanol complex) F_o	(Non-I_2 part of I_2 complex) F_c
(00)		
2	30	-24
4	36	-12
6	34	$+100$
(01)		
1	102	$+143$
2	94	-106
3	104	$+127$
4	64	-53
5	0	-28
6	0	-35
(02)		
0	0	$+2$
1	30	$+31$
2	96	-119
3	77	-77
4	126	$+151$
5	95	-30
6	0	-31
(03)		
1	202	-196
2	146	$+211$
3	55	-72
4	96	$+85$
5	0	$+26$
6	0	-19
(04)		
0	70	$+46$
1	160	$+191$
2	30	-48
3	30	-75
4	0	$+14$
5	0	$+19$
6	0	$+66$
(05)		
1	0	$+11$
2	118	-160
3	90	-108
4	122	-114
5	0	-68
6	0	$+25$
(06)		
0	46	$+67$
1	94	-121
2	208	-198
3	32	$+122$
4	70	-109
5	101	$+87$
6	0	-95
(07)		
1	62	$+82$
2	62	-65
3	104	-107
4	0	$+56$
5	0	$+38$
6	98	-43
(08)		
0	138	-94
1	52	$+22$
2	0	$+64$
3	36	$+4$

Table 2 (*cont.*)

| Indices	(Methanol complex) F_o	(Non-I$_2$ part of I$_2$ complex) F_c
4	0	+48
5	0	−25
6	60	−10
(09)		
1	142	+172
2	0	+19
3	90	−129
4	36	−160
5	0	−11
6	0	+68
(0,10)		
0	142	−127
1	172	−215
2	36	−35
3	92	−29
4	58	−59
5	0	+8
6	0	−35
(0,11)		
1	148	+138
2	0	−80
3	40	+105
4	62	−97
5	89	+94
6	0	+74
(0,12)		
0	164	+138
1	114	+114
2	56	−56
3	42	−16
4	0	−28
5	0	+18
6	0	+62
(0,13)		
1	94	+94
2	72	−78
3	30	+3
4	155	−198
5	0	−38
6	0	+95
(0,14)		
0	76	+67
1	99	−25
2	0	−44
3	0	−29
4	74	−54
5	0	−19
6	0	+39
(0,15)		
1	32	+51
2	0	+63
3	40	−132
4	87	−65
5	0	+66
6	148	+169
(0,16)		
0	185	+82
1	32	+105
2	208	+141
3	72	+9
4	0	+34
5	0	−2
6	0	+16

good to indicate that the absolute scale factor is of a reasonable magnitude.

Discussion

From the preliminary optical examination and the unit cell and space group, it was possible to arrive at a packing arrangement prior to the more detailed X-ray study. A space-filling model of cyclohexaamylose

(*a*)
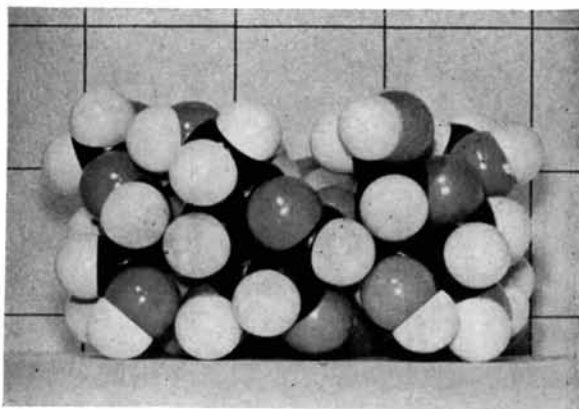
(*b*)

Fig. 5. Space-filling model of cyclohexaamylose (*a*) looking along molecular axis, (*b*) looking perpendicular to molecular axis. The model is photographed against a grid background with lines ruled at 5 cm. intervals, corresponding to 4·6 Å in the model.

(Fig. 5) is rather rigid if the glucose units have the $C1$ conformation (Reeves, 1950) and approximates a torus with an exterior diameter of 13 Å and a thickness of 7·5 Å. If the iodine molecules are enclosed by the torus and coaxial with it, the only packing arrangement consistent with the optical properties is that in Fig. 3, the exact location of the iodine atoms along the torus axis being uncertain. The location of

the iodine atoms as ascertained from the X-ray data confirms the general character of the packing of the carbohydrate part of the complex. The packing thickness of the torus, 6·7 Å, is substantially less than the 7·5 Å indicated by space-filling models. This economy of packing indicates that there is interpenetration such that neighboring molecules tend to fill each other's voids.

The central hole in the torus with a diameter of about 4·5 Å and a length of 6·7 Å is somewhat larger than necessary to accommodate the iodine molecule with diameter 4·3 Å and length 7·0 Å. The observed I–I bond distance, 2·81 Å, is essentially the distance in the normal I_2 molecule. In this case it is apparent that iodide ions are not necessary for complex formation, though the blue starch–iodine complex does not form in starch–iodine solutions devoid of iodide ions. Here, however, the crystalline α-I_2 complex is only a light tan-orange color in contrast to the metallic blue-orange complexes formed in the presence of iodides.

Attempts to locate carbohydrate in the Fourier projection onto the (100) plane (Fig. 4) were a failure. The factor that might well obscure the finer detailing of the cycloamylose structure is the high degree of hydration. Alternatively, the accuracy of the iodine parameters might be questioned, but the Patterson sections leave no doubt concerning the parameters since no major peaks occur other than those at $x = 0/60$ and $x = 30/60$ (Fig. 2).

The Patterson section $(X, Y, 4Y)$ is normal to one-half of the iodine molecule axes and parallel to the remainder. The peak at $b+4c = 3\cdot2/60$ and $a = 0/60$ results in an iodine–iodine vector distance of approximately 2·8 Å and occurs at the position expected for the iodine molecules whose axes lie parallel to the plane of section. If the iodine molecules are indeed surrounded by torus-like or cylindrical dextrin molecules, then the iodine–carbon and the iodine–oxygen vectors should occur at peaks providing an approximate representation of a cylinder with its axis normal to the plane of projection as observed in the section. The agreement between the Patterson map and that expected on the basis of a torus enclosing an iodine molecule is fair, but it appears that the structure is too complex to reveal any detail in the carbohydrate part.

It is interesting to compare the results of this study with those on amylose–iodine (Rundle & French, 1943). The amylose–iodine complex was indexed on a pseudo-hexagonal lattice. The high symmetry for so complicated a substance was explained on the grounds that the amylose chains approximated cylinders with closest packing. Space-filling models of an amylose helix using a 'chair' or 'boat' conformation for the pyranose rings gave an exterior diameter of the helix of approximately 13 Å. This was in good agreement with the observed lattice translation, $a_0 = 12\cdot97$ Å. From the amylose model the length of a turn in the helix was equal to the width of a glucose residue, about 7·5 to 7·8 Å, again in good agreement with the observed translation, $c_0 = 7\cdot91$ Å.

The results of Fourier projections of amylose and its iodine complex (Rundle, 1947) and this investigation make unnecessary any mechanism for the starch–iodine reaction in which iodine is adsorbed at the interstices or surfaces of crystallites (Meyer, 1941). Rather, it appears that specific iodine complex formation by starch and the Schardinger dextrins involves inclusion by helical or cyclic molecules.

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