[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Configuration of Starch in the Starch–Iodine Complex. V. Fourier Projections from X-Ray Diagrams[1]

BY R. E. RUNDLE

By consideration of optical properties[2] and lattice constants deduced from X-ray powder diagrams,[3] it has been possible to present a fairly detailed picture of the structure of the starch–iodine complex or, strictly, the amylose–iodine complex, where amylose is the unbranched component of starch. In the complex the amylose chains assume the configuration of a very tight helix about 13 Å. in diameter, 8 Å. in period,[4] containing six glucose residues per helix turn. From the dimensions of the helix it appears that the normals to the glucose rings are roughly normal to the helix axis, so that the helix period is approximately the van der Waals diameter of a glucose ring. The helices are nearly circular in cross-section, and pack together as in the closest packing of circular cylinders. The interior of the helix is a cavity which the iodine apparently occupies.

More recently it has been found that amylose forms molecular complexes with a number of types of linear organic molecules.[5] These compounds are structurally similar to the iodine complex, as shown by their X-ray diffraction patterns, and again the organic molecule appears to occupy the helix interior.[6]

In spite of the details of structure obtained, previous investigations of the amylose–iodine complex made no use of intensity data from X-ray diagrams, and on the surface it appears optimistic to attempt use of the data now available. In the first place, only powder data are available,[7] and in the second place these extend only to Bragg spacings of about 2 Å., not low enough to expect the resolution of atoms in the structure. Nevertheless, the structure of the amylose helix would be very much more satisfying if it were certain that the structure is consistent with all the X-ray data, including intensities.

Fortunately, resolution far too poor for the location of atoms might still be expected to resolve the gross features of helices, and at this stage of the structural determination even that would be worth attempting. Moreover, the powder data which are available are, except for the difficulties noted above, exceedingly well suited to Fourier projection work.

First, it is possible to obtain diagrams of the iodine complex, where all the important reflections are of the form (*hk*0), so their indices may be unambiguously assigned even though the unit cell is large. Second, the structure contains at least a two-fold screw-axis normal to the (001) plane, so that reflections (*hk*0) will have real structure factors.[3b] Third, the iodines are in special positions in the projection on the (001) plane, and the iodine scattering determines the signs of all the structure factors of reflections (*hk*0). Finally, a crystalline modification of amylose is available which appears to be structurally identical with the amylose–iodine complex, except that iodine is missing from the structure. Reflections (*hk*0) from this modification of amylose have real structure factors whose signs can be obtained by a study of the amylose–iodine diagram. Hence, it is possible to project the amylose structure onto (001) using intensity data which are essentially independent of iodine scattering.

"Anhydrous" V-Amylose and its Iodine Complex.—Previously V-amylose[8] patterns have been reported for wet and dry butanol-precipitated amylose, the latter with butanol removed.[3b] The lattice constants of the dried butanol precipitate previously reported were not identical with those of the iodine complex.[3] The difference was that the hexagonal lattice spacing of the dried butanol precipitate (equivalent to the diameter of the amylose helix) was 13.7 Å., while the spacing of the iodine complex was 13.0 Å.

More recently it has been found that the original dried butanol precipitate was poorly dried, and that further drying produces a material with lattice constants indistinguishable from those of the iodine complex. The situation is quite parallel with that reported for two forms of the fatty acid complex.[6] In both cases density measurements indicate that amylose with the 13.7 Å. spacing is a monohydrate (one water molecule per glucose residue) while amylose with the 13.0 Å. spacing is essentially anhydrous.

For our purposes the identity of the lattice constants of the "anhydrous" amylose and the amylose iodine complex is the essential point. Reflec-

---

[1] Journal Paper No. J-1429 of the Iowa Agricultural Experiment Station, Project 639. Supported in part by a grant from the Corn Industries Research Foundation.

[2] (a) R. Rundle and R. Baldwin, THIS JOURNAL, 65, 554 (1943); (b) R. Rundle and D. French, *ibid.*, 65, 558 (1943).

[3] (a) R. Rundle and D. French. *ibid.*, 65, 1707 (1943); (b) R. Rundle and F. Edwards, *ibid.*, 65, 2200 (1943).

[4] The helix period, the only doubtful deduction from the powder data, has recently been confirmed by fiber diagrams, F. Senti and L. Witnauer, *ibid.*, 68, 2407 (1946).

[5] R. Bear, *ibid.*, 66, 2122 (1944); R. Whistler and G. Hilbert, *ibid.*, 67, 1161 (1945).

[6] F. Mikus, R. Hixon and R. Rundle, *ibid.*, 68, 1115 (1946).

[7] The fiber data now available[4] would still not resolve coincident reflections of the powder diagrams.

[8] Starch and amylose precipitated by alcohols have a distinctive type X-ray pattern, called the "V" pattern by J. Katz, *Z. physik. Chem.*, A150, 60 (1930). These patterns are quite different from the granular starch patterns. Apparently granular starch and starch precipitating spontaneously from water solution have a different (linearly extended) chain configuration. See R. Rundle, L. Daasch and D. French, THIS JOURNAL, 66, 130 (1944).

TABLE I

POWDER REFLECTIONS FROM AMYLOSE–IODINE COMPLEX AND "ANHYDROUS" V-AMYLOSE

Iodine complex		V-Amylose		Indices	
$\sin^2\theta/\lambda^2$	I(obs.)	$\sin^2\theta/\lambda 2$	I(obs.)	Hexagonal	Orthorhombic
0.00197	40	0.00197	20	(100)	(110) (020)
.00591	20	.00592	40	(110)	(200) (130)
.00792	12	.00787	8	(200)	(220) (040)
.00996	vvw	.00982	15	(111)	(201) (131)
.01158	vvw	.01180	12	(201)	(221) (041)
.01384	64	.01382	62	(210)	(240) (310) (150)
.01781	16	.01794	12	(300)	(330) (060)
.02189	vvw	.02161	10	(301) (112)	(331) (061) (202) (132)
.02375	4	....	nil	(220)	(400) (260)
.02573	8	....	nil	(310)	(420) (350) (170)
.02976	vw	.0293	6	(212) (311)	(242) (152) (312) (351) (421) (171)
.03178	3	....	nil	(400)	(440) (080)
.03775	8	....	nil	(320)	(370) (280) (510)
.04155	12	.04133	3	(410)	(460) (190) (530)
.04551	vvw	.04557		(411)	(461) (191) (531)
.04763	vvw			(402)	(442) (082)
.05360	1			(330)	(600) (390)
.05549	3			(420)	(480) (2.10.0) (620)
.06165	1			(510)	(570) (1.11.0) (640)
.07114	2			(600)	(660) (0.12.0)
.07310	2			(430)	(4.10.0) (3.11.0) (710)

tions from the two materials obtained using CuK radiation, Ni filtered, and a powder camera of 10-cm. radius are compared in Table I. The iodine complex was prepared by treatment of the "anhydrous" amylose with iodine vapor.[3a]

Iodine Positions in the Iodine Complex.—The structure of the iodine complex is based on a lattice which is at least pseudohexagonal with a = 13.0 Å., c = 8.0 Å.[2] Since all reflections (hkl) with $l \neq 0$ are absent or extremely weak, the iodines must have general z parameters. (It seems possible that the iodine spacing is incommensurate with c.)[3a]

Reflections $(hk0)$, by contrast, are all present except (500) which has a low multiplicity factor and is near the limit of the observable reflections on the powder diagram. The intensities of the $(hk0)$ reflections are approximately proportional to the multiplicity factors after correction for Lorentz and polarization factors. The iodines must, consequently, be located on a simple, two-dimensional, hexagonal net. These positions for the iodines are verified by the observation that marked deviations in the expected intensities of reflections from the iodine complex (based on iodine scattering from the above positions) are accompanied by considerable intensity of the same reflections on the "anhydrous" amylose diagrams (Table II). The deviations must, then, be the result of relatively large amylose contributions to these reflections.

TABLE II

AMYLOSE–IODINE COMPLEX

Indices (hexagonal)	$F(hk0)$ obs.	F calcd. Simple hexagonal	F calcd. Interstitial positions	Amylose contribution
(100)	14	20	−15	−
(110)	17	20	30	−
(200)	15	20	−15	−
(210)	33	20	−15	+
(300)	27	20	30	+
(220)	16	20	30	−
(310)	16	20	−15	−
(400)	16	20	−15	−
(320)	20	20	−15	
(410)	26	20	30	+
(500)	0	20	−15	−
(330)	12	20	30	−
(420)	15	20	−15	−
(510)	9	20	−15	−
(600)	21	20	30	
(430)	15	20	−15	−

It is noteworthy that the iodine positions, as revealed by X-ray diffraction, are helpful in deciding whether the iodines must be within the helix or in interstices between helices. If the iodines are within the helix the iodine positions are consistent with those found above. On the other hand, there are two interstices per helix (Fig. 1) at ± ($^1/_3$ $^2/_3$) in the (001) plane. Structure factors calculated for iodines at this set of positions are compared in Table I with structure factors obtained from observed intensities and with those calculated for iodines at (000). Placing the iodines in all the interstitial positions is incompatible with the observed X-ray intensities. If iodines enter the interstices they must enter only half the interstices in a regular fashion, such as entering only the set of interstices labelled + in Fig. 1. Since the hexagonal character of the structure suggests that the helices are essentially circularly symmetrical, it seems unlikely that the two sets of interstitial positions, + and − of Fig. 1, can differ enough that only one is available to iodine. Of course this argument depends on correctness of the helical structure.

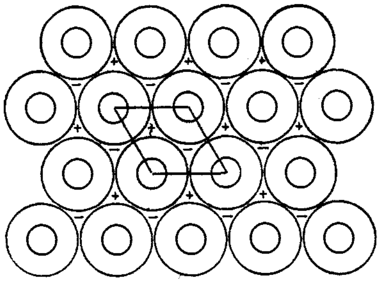

Fig. 1.—Interstitial positions for closest packing of helices. There are two interstices per hexagonal cell outlined above. If the iodines are in the interstices they can occupy only the + interstices or the − interstices, not both.

Fourier Projection of the Iodine Complex.—A visual estimate of the intensities of the X-ray reflections ($hk0$) from the amylose–iodine complex has been made by comparing the reflections with powder reflections of known relative intensities. Structure factor values, $F_{(hk0)}$, have been calculated from the intensities corrected for Lorentz, polarization and multiplicity factors. These values are listed in Table II.

Evidence has been cited previously[3b] indicating that alternate amylose chains run in opposite directions, so that the hexagonal lattice chosen for the amylose–iodine complex is almost certainly a pseudo-lattice. The true lattice is probably orthorhombic with twice the volume of the pseudo lattice. Consequently, orthorhombic indices should be assigned, and in Table I these are listed as well as the hexagonal indices. Because of the pseudo-hexagonal character of the structure there are a large number of coincidences in the set of orthorhombic indices which can be removed by neither powder nor fiber data.

The projection made from the data of Table II of necessity assumes full hexagonal symmetry of the projection, though it is believed that the structure is really only orthorhombic. This is unfortunate, but, in the author's opinion, it is probably not exceedingly serious in view of the low resolution which can be expected in the projection. There are no powder data from the iodine complex which demand the orthorhombic unit. It seems likely that only minor details in the structure require such a unit, and these cannot be expected to show up in a projection obtained from data as limited as those from the amylose–iodine diagram. In any case, there appears to be no way of eliminating the assumption.

The structure will have at least a two-fold screw-axis parallel to (001) (see the space group discussion of 3b), and the iodines must lie on this two-fold axis. Consequently, the structure factors, $F_{(hk0)}$, must be real, and, in view of the scattering power of iodine, positive.

Using the data of Table II a Fourier projection has been made using Lipson and Beevers strips and method.[9] The resulting projection is shown in Fig. 2.

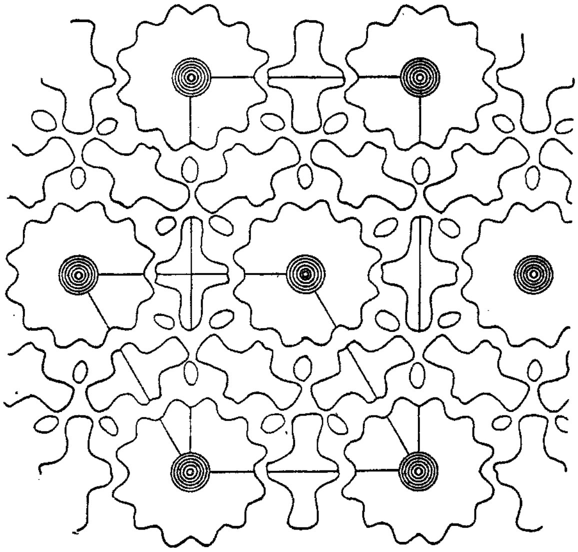

Fig. 2.—Fourier projection of the amylose–iodine complex onto (001). On the basis of deductions from lattice constants and optical properties,[2,3] the helix axis should be normal to the plane of projection. Hexagonal and orthorhombic unit cells are outlined on the projection.

Amylose Contributions to the F-Values.—The observed F-values of the iodine complex differ somewhat from those calculated for the iodine scattering alone (Table II). From the nature of the deviation one can determine the sign of the amylose contribution to the F-values. This determination is unambiguous for the reflections which can be seen on the "anhydrous" amylose diagram. The signs of amylose contributions, as given in Table II, were used in carrying out a Fourier projection of the "anhydrous" amylose structure.

Fourier Projection of the V-Amylose Structure.—Visual estimates of the intensities of the ($hk0$) reflections from the "anhydrous" V-pattern have been corrected to F values as described for the amylose–iodine complex. The $F_{(hk0)}$ values are listed in Table III. The signs given the F values are those obtained from the sign of the amylose contributions to the F values of the amylose–iodine complex. This is equivalent to assuming that the amylose structure is not materially altered by introducing iodine vapor into the "anhydrous" V-amylose. Since this is a reaction of iodine with the crystalline substance, and since the lattice is unchanged by the reaction, this assumption seems justifiable.

A Fourier map prepared again by the method of Beevers and Lipson using Beevers–Lipson strips and the data of Table III is shown in Fig. 3.

---

[9] H. Lipson and C. Beevers, *Proc. Phys. Soc., London*, **48**, 772 (1936).

TABLE III

"ANHYDROUS" V-AMYLOSE

Indices (hexagonal)	F_{hk0}	Sign from Table II
(100)	7	−
(110)	17	−
(200)	9	−
(210)	33	+
(300)	16	+
(220)	0	(−)
(310)	0	(−)
(400)	0	(−)
(320)	0	(−)
(410)	13	+

Discussion of the Projections.—The projection of the amylose-iodine structure (Fig. 2) has very predominant peaks in the positions expected for the iodines. The only other regions of high electron density lie about the iodine peak at a considerable distance and separated by a deep minimum. The maxima making up the region surrounding iodine are six in number, and are quite a satisfactory representation of a helix with its axis normal to the plan of projection.

Because of the necessary assumptions made in making the projection, the fact that there are six peaks in a circle about iodine is not a valid confirmation of the deduction from lattice and density data that there are six glucose residues per helix turn. The only important point in the projection seems to be that the distribution of other scattering matter about iodine is quite consistent with the previous concept of the structure as a helix with iodine in the interior of the helix.

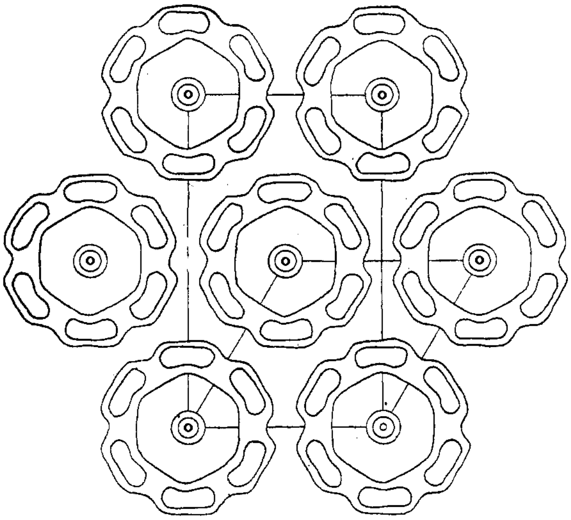

Fig. 3.—Fourier projection of "anhydrous" V-amylose onto (001). The helix axis should be normal to the plane of projection. Hexagonal and orthorhombic unit cells are outlined.

Because of the very sparse data from the "anhydrous" V-amylose, little is added by the projection of this structure except to confirm that the general region of high electron density due to amylose corresponds well with a helix of nearly circular cross section.

It is somewhat embarrassing to find that in this projection, too, there is a considerable peak at the center of the helix. An examination of Tables II and III will reveal, however, that this peak is probably accidental. It happens that a large number of (*hk*0) reflections from V-amylose are too weak to be seen. Judging from Table II, these reflections probably have negative structure factors. Also, the first reflections beyond those visible on the "V" diagram probably have negative structure factors. If these terms could be included, they would decrease the peak at the origin where they are all in phase. Inclusion of these weak terms would probably not alter seriously the rest of the projection, since they would not be in phase with each other at other points.

To conclude, the positions of the iodines in the (001) plane seem more consistent with a structure in which the iodines are within the helices rather than within interstices between helices. While projections of the amylose–iodine and V-amylose structure on (001) add no new details to the structures as previously presented, these projections do show that X-ray intensity data are fully consistent with the previous structure.

Summary

X-Ray intensities have been examined and have been found to be not inconsistent with the helical configuration of the amylose chain previously suggested for the amylose (starch)–iodine complex. Accepting the helical structure, the X-ray intensities are seen to define the iodine positions in the (001) plane.

AMES, IOWA RECEIVED JANUARY 24. 1947