mendous difference between the ease with which dichroism of flow is produced in the different experiments would seem to be significant in spite of the qualitative character of the present experiments.

Further Application of Dichroism of Flow.—The study of the dichroism of flow of starch-iodine solutions is not limited to qualitative observation. Quantitative observation of the degree of orientation during flow can be made. This observation, together with measurements of the velocity gradient, viscosity, and temperature of the solution should permit calculation of the axial ratios of the starch helices in straight-chain fractions. These studies require better apparatus than is now available. Such equipment is now under construction and results will be reported in a subsequent paper.

The authors wish to acknowledge their indebtedness to Dr. T. J. Schoch of Corn Products, Inc., for generous samples of his starch fractions, and to Dr. R. M. Hixon of Iowa State College for the waxy maize and other waxy starches used in these experiments.

Summary

1. Starch–iodine solutions exhibit dichroism of flow; light with its electric vector parallel to the flow lines is more strongly absorbed than light with its electric vector normal to the flow lines.

2. The dichroism of flow is shown to require that the long axes of the iodine molecules in the complex be parallel to the long axis of the starch–iodine complex. Two structures of the complex fulfil this requirement, including the helical model of Fig. 1.

3. The dichroism of flow exhibited by various starches and starch fractions is in agreement with the straight-chain, branched-chain model for the two components of starch.

4. Dichroism of flow is proposed as a method for the determination of the axial ratios of the starch–iodine complex.

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[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

The Configuration of Starch and the Starch–Iodine Complex. II. Optical Properties of Crystalline Starch Fractions[1]

BY R. E. RUNDLE AND DEXTER FRENCH

In a previous paper[2] the discovery of the dichroism of flow of starch–iodine solutions was reported, and it was shown that this dichroism requires that the long axes of the iodine molecules in the complex be oriented preferentially parallel to the long axis of the starch molecule. This orientation can be interpreted in terms of a structure similar to Fig. 1 of (2). Here the starch chain forms a helix enclosing the iodine molecules; the helix axis and the long axes of the iodine molecules are coincident. The orientation can also be explained in terms of an extended, essentially linear, starch chain with the iodine molecules arranged parallel to the chain. To decide between these two possibilities, single crystals, or even spherocrystals, of the starch–iodine complex should be invaluable. Of equal value would be single crystals or spherocrystals of starch in the helical configuration. As Frey-Wyssling has pointed out,[3] the optical properties of helical-chain starch should be quite different from starch in the "A" or "B" modification where the chains are known to be extended.[3,4]

Very fortunately all of these materials can now be examined. Schoch has discovered that starch may be fractionated with butanol.[5] The butanol-precipitated fraction, corresponding to the unbranched component of starch, is obtained as flattened spherocrystals, usually having the appearance of rosets (Fig. 1). Kerr and Severson[6] have applied Schoch's butanol precipitation to a hot water extract of starch, and have obtained what appear to be single crystals,

(1) Journal Paper No. J-1038 of the Iowa Agricultural Experiment Station, Ames. Project No. 660. Supported in part by a grant from the Corn Industries Research Foundation. A portion of this paper was presented before the American Chemical Society at Memphis, 1942.

(2) R. E. Rundle and R. R. Baldwin, THIS JOURNAL, **65**, 554 (1943).

(3) A. Frey-Wyssling, *Naturwissenschaften*, **28**, 78 (1940); *Ber. Schweig. Bot. Ges.*, **59**, 321 (1940).

(4) R. S. Bear and D. French, THIS JOURNAL, **63**, 2298 (1941).

(5) T. J. Schoch, *Cereal Chem.*, **18**, 121 (1941).

(6) R. W. Kerr and G. M. Severson, THIS JOURNAL, **65**, 193 (1943).

Fig. 1.—Schoch's amylose (butanol precipitated fraction of starch, stained with iodine to make it more easily visible; magnification about 400 times).

very minute, yet large enough to permit examination of their optical properties (Fig. 2). Both materials can be stained with iodine with no apparent loss of their crystalline properties and presumably, therefore, with no appreciable change in the configuration of the starch chains. It is then to be expected that if the starch–iodine complex involves helical starch chains, the new crystalline products of Schoch and of Kerr and Severson will have the desired helical configuration.[7] The birefringence of these materials and their dichroism after staining with iodine have accordingly been examined.

(7) Upon dispersing in solution and subsequent retrogradation the above materials show the normal "A" and "B" diffraction patterns, and in this form the starch chains must be extended. Chain configuration is then a function of treatment and not of the starch component.

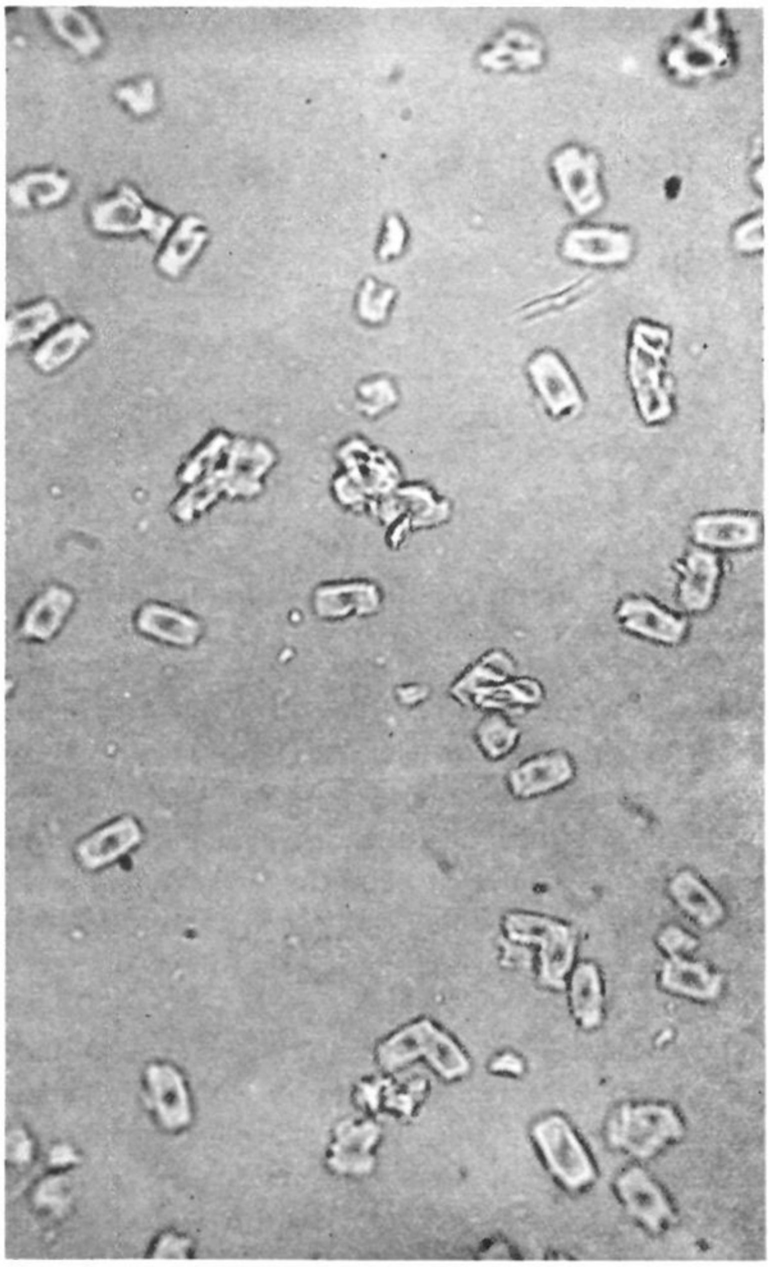
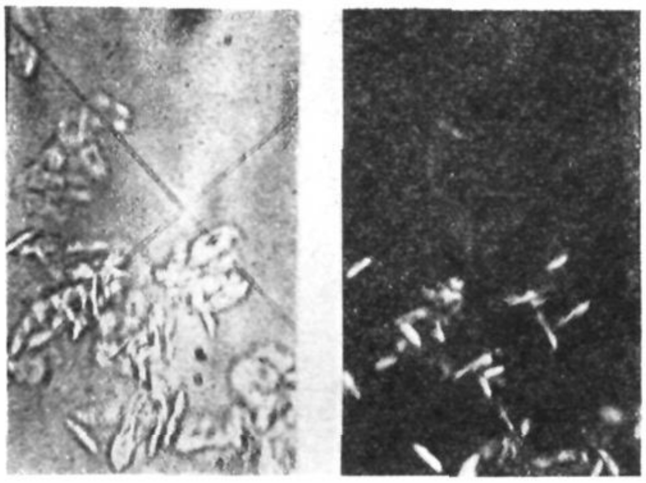


Fig. 2.—Crystalline amylose (Kerr 1942), magnification about 400 times.

Birefringence.—The "crystalline amylose" of Kerr and Severson consists of small rectangular platelets (Fig. 2). The platelets appear uniaxial, or very nearly so, when examined using crossed nicols. On edge they are quite birefringent (Fig. 3), and using a red-plate it is found that the retardation of light with its electric vector parallel to the surface of the platelet is greater than the retardation of light with its electric vector normal to the platelet. The platelets are then optically negative.

Schoch's "rosets" are found to be optically positive; that is, light with its electric vector along the radius of the nearly circular "roset" is retarded more than light with its electric vector tangential to the "roset." Thus, when viewed between crossed nicols using a first-order red-plate, the "rosets" appear yellow and green in alternate quadrants—green along the direc-



Ordinary light Crossed nicols

Fig. 3.—Kerr's crystalline amylose: platelets showing birefringence are on edge.

tion of the greatest retardation of the red-plate.

Close examination of "crystalline amylose" and Schoch's butanol-precipitate reveals a great deal of similarity. Indeed, Schoch's material has the appearance of being formed from several crystals of "crystalline amylose" growing from a common center with the normals to the platelets all in one plane.

Dichroism.—Upon staining with iodine, "crystalline amylose" platelets are light blue when viewed with light normal to the platelet surface, and again they appear to be uniaxial. On edge they are extremely dichroic; light with its electric vector normal to the plate is very strongly absorbed, while light with its electric vector in the plane of the platelet is very weakly absorbed (Fig. 4).

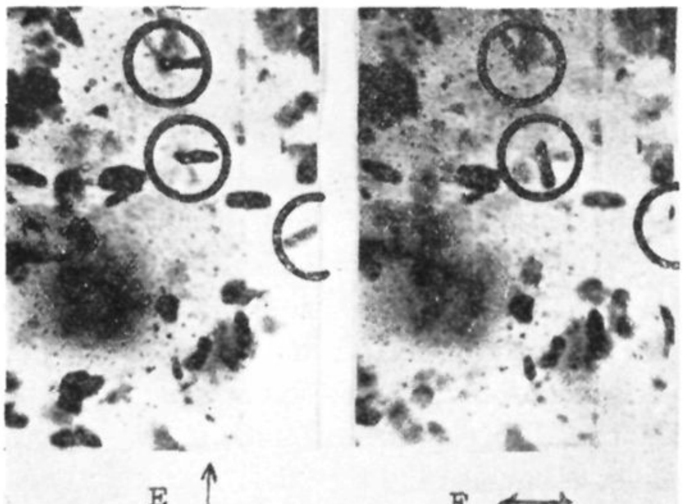


Fig. 4.—Kerr's crystalline amylose stained with iodine. Pictures taken with equal exposures in plane polarized light. Arrow is in the direction of the electric vector. Note that absorption is greatest when **E** is normal to the platelet surface. Platelets circled are on edge.

Schoch's material is also very dichroic when stained with iodine; polarized light is absorbed strongly in the portion of the "roset" where the electric vector is tangential to the circular "roset," very weakly where the electric vector is radial to the "roset," causing the "roset" to appear light and dark in alternate quadrants in polarized light.

Interpretation of the Optical Properties.—Any attempt to interpret the optical properties of these materials in terms of a starch–iodine complex consisting of an extended starch chain fails. If an extended, essentially linear starch chain were adopted as a model it would be expected that the polarizability along the chain would be greater than normal to the chain,[8] and light with its electric vector parallel to the chain would be retarded more than light with its electric vector normal to the chain.[9] The birefringence of "crystalline amylose" would then indicate that the starch chains lie in the plane of the platelet. The dichroism after staining with iodine would require that the iodine molecules be normal to the platelet, and therefore normal to the extended starch chain.[10] But according to the dichroism of flow of starch–iodine solutions, the iodine molecules must be parallel to the extended chain if the extended chain model for the complex is adopted.[2] This discrepancy is such that it would appear that no extended chain model for the starch–iodine complex can be made satisfactory.

On the other hand the optical properties appear quite in harmony with a helical structure. On the basis of Silberstein's theory[8] it would seem possible, if not probable, that a starch helix would have its greatest polarizability normal to the helix axis. On this basis the dichroism and birefringence of "crystalline amylose" would be quite understandable. The birefringence would indicate that the axes of the helices were normal to the plane of the platelet (Fig. 5), and the

(8) Silberstein, *Phil. Mag.*, **33**, 92, 521 (1917).

(9) This has now been verified experimentally for starch. Films and fibers of starch, showing "B" X-ray diffraction patterns, have been prepared. The method of production leaves little doubt of the orientation of the chains in the fiber. These fibers are optically positive, just as are cellulose fibers. A further report on starch films and fibers will be made soon by Daasch, French and Rundle.

(10) Such a structure would be expected to lead to a hexagonal lattice. Bear, THIS JOURNAL, **64**, 1388 (1942), examined the first three or four X-ray diffraction lines from the "V" modification of starch. These, though not sufficient to give a sure indication of the type of lattice, were at least suggestive of a hexagonal lattice. "Crystalline amylose" and Schoch's butanol precipitate show excellent diffraction patterns both before and after staining with iodine. Results of an X-ray investigation of these materials will be reported in a subsequent paper in THIS JOURNAL.

dichroism would indicate that the iodine molecules have their long axes normal to the plane of the platelet. The iodine molecules would then have their long axes parallel to the long axis of the starch molecule, in this case the helix axis, in agreement with the requirements of the dichroism of flow experiment.[2] The helical model would also account for the uniaxial, optically negative character of the "crystalline amylose" platelets. The optically negative character of the platelets is hard to understand on the basis of an extended chain model.

Doubtless the elimination of all conceivable models but the helical model for the starch–iodine complex could not be accomplished by arguments as simple as those above, nor with optical data alone. All extended chain models do appear to be unsatisfactory, however, and aside from the helical model, no other structures for the starch–iodine complex have been proposed. At present it seems hard to think of any other structures which will so readily account for the optical properties of the crystalline materials reported here, and at the same time be in accord with the dichroism of flow of starch–iodine solutions. On the basis of optical properties the most satisfactory structure for "crystalline amylose" appears to be that of Fig. 5. Here a closest packing of helices was rather arbitrarily chosen as most likely.[10] All the properties of Schoch's butanol precipitate are in agreement with a structure composed of "crystalline amylose" platelets growing from a common center, the normal to the platelets in the plane of the "roset."

Acknowledgment.—The authors wish to acknowledge their indebtedness to Drs. T. J. Schoch, R. W. Kerr and G. M. Severson of Corn Products Refining Co. All the materials examined in this investigation were furnished by them, and the possibility of carrying out the research depended on the very important discoveries of methods of preparing crystalline starch fractions, discoveries due to Drs. Schoch, Kerr and Severson.

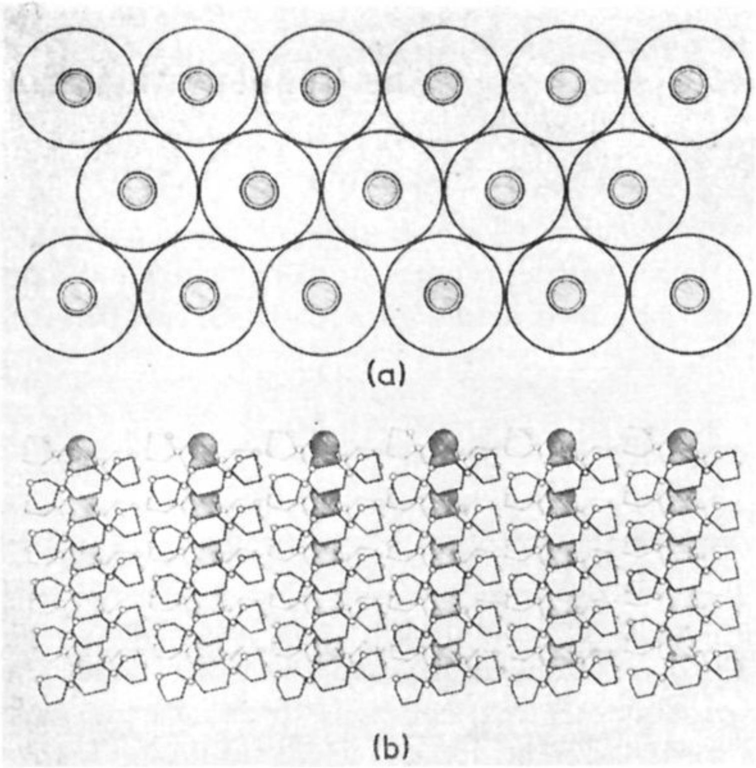


Fig. 5.—Structure of crystalline amylose-iodine complex: (a) face of platelet; (b) edge of platelet.

Summary

1. The "crystalline amylose" platelets of Kerr and Severson are optically negative, probably uniaxial. After staining with iodine they are highly dichroic; light with its electric vector in the plane of the platelet is weakly absorbed, light with its electric vector normal to the plane of the platelet is strongly absorbed.

2. The birefringence of the crystalline material from Schoch's butanol-fractionation of starch has been examined, together with its dichroism after staining with iodine. The material appears to be a multiple of "crystalline amylose" platelets with the normals to the platelets all in one plane.

3. The optical properties of the above materials are interpreted in terms of a helical starch chain. The starch–iodine complex probably has the structure of Fig. 1 of (2), and the structure shown in Fig. 5 is proposed for "crystalline amylose."

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