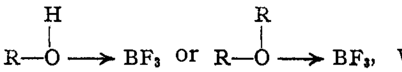
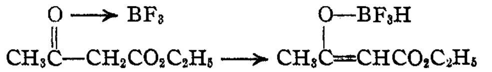
fluoride,  $R{-}\overset{H}{\overset{|}{O}}\longrightarrow BF_3$ or $R{-}\overset{R}{\overset{|}{O}}\longrightarrow BF_3$, which (with or without the intermediate formation of carbonium ions) alkylates the β-keto ester. Complexes are probably also formed between ethyl acetoacetate and boron trifluoride; the complex involving the ketone oxygen should facilitate the conversion of the β-keto ester into the "enol" form



$$CH_3\overset{O\longrightarrow BF_3}{\overset{\|}{C}}{-}CH_2CO_2C_2H_5 \longrightarrow CH_3\overset{O{-}BF_3H}{\overset{|}{C}}{=}CHCO_2C_2H_5$$

It is not known whether or not this is a prerequisite to the alkylation.[17]

As with the similar Friedel–Crafts type of reaction,[18] the alkylation of β-keto esters depends upon the reactivities of both components. Thus, the secondary and tertiary alcohols or ethers (and benzyl ether) are capable of alkylating ethyl acetoacetate, whereas the purely aliphatic primary alcohols or ethers, which are known to be less reactive,[18] fail to alkylate this β-keto ester under similar conditions. The failure of *s*-butyl alcohol to alkylate ethyl acetoacetate, and the low yields obtained with the tertiary alcohols, appear to be due to the predominance of side reactions. The relatively reactive compounds, ethyl acetoacetate and its methyl derivative are readily isopropylated whereas the less reactive compounds, ethyl α-isopropylacetoacetate and ethyl malonate, fail to be alkylated under similar conditions. It should be noted that not all relatively reactive compounds yielded alkyl derivatives. Ethyl benzoylacetate formed an insoluble boron trifluoride complex and failed to be alkylated. Nitromethane also failed to be alkylated.

Summary

A study has been made of the alkylations of β-keto esters and certain other active hydrogen compounds with alcohols and ethers in the presence of boron trifluoride. Certain of the reactions are of synthetic value. The results are considered in the light of the theory of condensations.

DURHAM, NORTH CAROLINA RECEIVED OCTOBER 16, 1942

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[17] Results, which will be published shortly, on the acylation of ketones with anhydrides indicate that the enol form of the ketone is acylated.

[18] See Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 309–310.

[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

The Configuration of Starch and the Starch–Iodine Complex. I. The Dichroism of Flow of Starch–Iodine Solutions[1]

BY R. E. RUNDLE AND R. R. BALDWIN

Introduction

The X-ray diffraction studies of Bear and French,[2] and the optical studies of Frey-Wyssling,[3] have established rather conclusively that native, granular starches and retrograded starches, both of which exhibit "A" or "B" X-ray diffraction patterns, have essentially linearly extended-chain configurations. Hanes[4] has, nevertheless, suggested a helical configuration for the starch chain, and this suggestion has been adopted and extended by Freudenberg and co-workers.[5] The reason for suggesting this configuration and almost the entire evidence for it, is that it will explain certain properties of starch which as yet are not well understood. These may be summarized as follows:

(1) Various enzyme actions suggest that glucose residues, six apart down the starch chain, are quite close to each other. For example, the enzyme from *B. macerans* converts starch into cycloamyloses of six or more glucose residues per molecule,[6] and α-amylase, according to Hanes,[4,7] degrades starch into a dextrin containing six glucose residues per molecule.

(2) Starch and its degradation products form highly colored addition products with iodine, the achroic point coming at about six glucose residues; that is, dextrins of less than six glucose residues show little or no intensification of the color of an iodine solution. Hanes[4] believes

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[1] Journal Paper No. J-1037 of the Iowa Agricultural Experiment Station, Ames. Project No. 660. Supported in part by a grant from the Corn Industries Research Foundation.

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

[3] A. Frey-Wyssling, *Naturw.*, **28**, 78 (1940); *Ber. Schweiz. Bot. Ges.*, **50**, 321 (1940).

[4] C. S. Hanes, *New Phytologist*, **36**, 101, 189 (1937).

[5] K. Freudenberg, E. Schaaf, G. Dumpert and T. Ploetz, *Naturw.*, **27**, 850 (1939).

[6] D. French and R. E. Rundle, THIS JOURNAL, **64**, 1651 (1942).

[7] This is probably incorrect; see K. Meyer, "Adv. in Colloid Science," Interscience Pub. Inc., New York, N. Y., 1942, p. 171.

that one turn in a helix having six glucose residues per turn is necessary for iodine color.

(3) Space models of starch chains permit helical structures.[8] The helical models built by Freudenberg[5] have a hole through the helix large enough to admit iodine molecules with their long axes coincident with the helix axis (Fig. 1). In addition, the starch helix possesses a hydrocarbon lining. Freudenberg, *et al.*, account for the blue starch–iodine color on the basis of the hydrocarbon lining, for iodine in solution in nonpolar solvents, such as hydrocarbons, is generally blue to violet, while it is brown in polar solvents, such as water.

(4) The iodine addition products of the cycloamyloses can be accounted for by a mechanism very similar to that proposed for the starch–iodine complex.[5]

Several objections to the helical configuration of the starch chain have been set forth by Meyer.[9] One of the more important of these objections appears from the seemingly incontrovertible evidence for the extended chains in starch. Bear[10] has pointed out, however, that it need not be a question of an extended chain *or* a helical chain, but that both may be possible. So far only the "A" and "B" crystalline modifications of starch have been studied, and they only are known to possess extended chains. Another modification of starch, "V" starch, is known,[11] and X-ray diffraction patterns of this modification are at least not in disagreement with a helical configuration.[10]

Meyer[9] points out that the helical model is incapable of explaining the many other colored iodine addition products which are known.[12] Since no one model is likely to do so, this is not a serious shortcoming of any model proposed for a particular iodine complex.

In the opinion of the authors, the only real objection to the proposals of Hanes and of Freudenberg is that evidence concerning the validity of the proposals is almost entirely lacking. That the proposals deserve more serious study seems evident from their ability to explain many confusing starch problems.

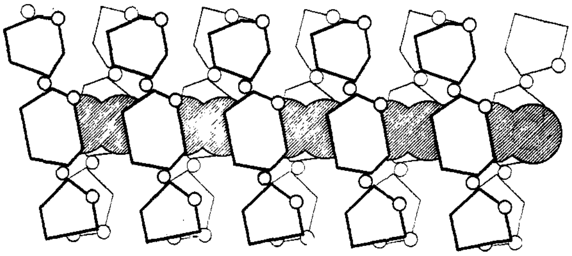

Fig. 1.—Model of helical starch chain with iodine molecules in the center of the helix.

Theory of the Dichroism of Flow of Starch–Iodine Solutions.—On the basis of the helical model of the starch–iodine complex (Fig. 1) dichroism of flow of starch–iodine solutions is to be expected. The iodine molecules associated with the starch are located in the center of the helix, and the long axes of the iodine molecules are coincident with the helix axis. A velocity gradient, such as that produced by a rotating concentric cylinder apparatus, would be expected to orient the long starch helices preferentially along the flow lines. This would result in the preferred orientation of the long axes of the iodine molecules parallel with the flow lines. The type of dichroism to be expected from such orientation can be understood from the pleochroism of iodine crystals.

According to an unpublished work of Dr. F. H. Spedding, the pleochroism of the crystals indicates that light with its electric vector parallel to the long axis of the iodine molecule is strongly absorbed, while light with its electric vector normal to the long axis of the molecule is but slightly absorbed (Fig. 2). This is in agreement with existing theories, and with observations of dichroism and pleochroism in other crystals.[13] From this it appears that light with its electric vector parallel to the long axis of the helical starch–iodine addition product should be absorbed strongly; light with its electric vector normal to the helix axis should be absorbed hardly at all (Fig. 1). In accordance with this, starch–iodine solutions, under the influence of a velocity gradient, should absorb light with its electric vector parallel to the flow lines more strongly than light with its electric vector normal

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(8) G. Caesar and M. Cushing, *J. Phys. Chem.*, **45**, 776 (1941), have built space models of starch chains and imply that helical chains are sterically necessary. Evidence from space models cannot be taken too seriously, however. This is particularly true in dealing with sugars where the true configuration of the pyranose ring and the glucosidic bond angles are still in doubt.

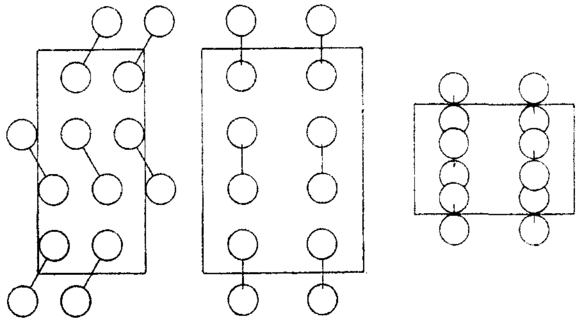
(9) K. Meyer and P. Bernfeld, *Helv. Chim. Acta*, **24**, 389 (1941).

(10) R. S. Bear, THIS JOURNAL, **64**, 1388 (1942).

(11) J. Katz, *et al.*, *Z. physik. Chem.*, **A150**, 60 (1930); **A158**, 337 (1932); **A167**, 129 (1933).

(12) G. Barger, "Some Applications of Organic Chemistry to Biology and Medicine," McGraw-Hill Book Co., New York, N. Y., 1930.

(13) K. S. Krishnan and A. Dasgupta, *Nature*, **126**, 12 (1930); K. S. Krishnan and B. Mukhopadyag, *ibid.*, **132**, 411 (1933); C. Raman and S. Bhagarantam, *Ind. J. Phys.*, **4**, 57 (1929).



E ↑ more strongly absorbed
E → less strongly absorbed

E ↑ very strong absorption
E → very weak absorption

E ↑ rather strong absorption
E → very weak absorption

Fig. 2.—Projections on (010), (100) and (001) faces of the orthorhombic iodine unit cell. Light is considered to be traveling normal to the plane of the projection. Direction of electric vector is given by arrow following E.

to the flow lines. Examination of starch–iodine solutions during flow reveals that this is the case.

It is possible, of course, to explain the observed dichroism of flow by any structure in which the long axes of the iodine molecules and the long axis of the starch–iodine complex are parallel. In place of the helical structure of Fig. 1 it is possible that the starch–iodine complex consists of an extended, essentially linear, starch chain with the long axes of the associated iodine molecules parallel to the starch chain. Though the dichroism of flow of a starch solution is not in itself sufficient to decide between these two alternative structures, any acceptable structure for the complex must be in accord with the observed dichroism. This has not been true of most starch–iodine structures heretofore proposed.[9,12]

The authors wish to point out again that the proposed helical configuration of the starch chain in the starch–iodine complex does not imply a helical configuration for the chain in granular or retrograded starch, and that criticism of the helical model, based on the chain configuration in these forms, is not valid. Neither would the helical configuration of the starch chains in the iodine complex require that starch in solution have the helical configuration. In spite of the fact that a blue color appears at once on adding iodine to a starch solution, the reaction to form the starch–iodine complex is fairly slow. Potentiometric methods indicate that the activity of iodine added to a starch solution continues to decrease for a period of several minutes.[14] Whether this reaction involves a slow association of iodine with starch in the same configuration which it possesses in solution, or whether a change in the configuration of the starch chains is also involved is as yet unknown.

Starch Components During Flow

Recently evidence has been advanced in the literature supporting the presence of branched-chain and unbranched-chain components in starch,[14,15] and methods of fractionating starch into two components of quite different properties have been developed.[7,16,17] Quantitative methylation studies have been the chief support for the branched and unbranched structures for the two components. Methylation procedures are confronted by so many serious difficulties, however, that acceptance of the structures has not been universal. Since unbranched, more nearly linear, starch chains should orient more readily during flow than branched molecules, dichroism of flow should provide an important check on the proposed structures for the two starch components. With this in mind several starches and starch components were examined. The results are summarized below.

(1) The butanol precipitated fraction from Schoch's fractionation of both corn and potato starches showed a noticeable dichroism of flow even in very dilute solution.

(2) For ordinary blue-staining starches, dichroism of flow of iodine-stained starch pastes was easily observed.

(3) The component from Schoch's fractionation which is not precipitated by butanol showed a doubtful dichroism of flow. If the last traces of blue-staining starch were removed from this fraction by absorption on cellulose according to the method of Tanret and of Pacsu,[17] no detectable dichroism was observed.

(4) Glycogen stained with iodine showed no dichroism of flow.

(5) Iodine-stained pastes of waxy maize, glutinous rice, or red-staining starches in general showed little, if any, dichroism of flow.

Of the starches and starch fractions examined in the above experiments, Schoch's butanol precipitate corresponds in its physical properties to Meyer's "amylose" or unbranched component.

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[14] F. L. Bates, D. French and R. Rundle, This Journal, **65**, 142 (1943).

[15] For a review, see (7).

[16] T. J. Schoch, *Cereal Chem.*, **18**, 121 (1941).

[17] (a) C. Tanret, *Compt. rend.*, **158**, 1355 (1914); (b) E. Pacsu This Journal, **63**, 1168 (1941).

while Schoch's non-precipitated fraction corresponds to Meyer's "amylopectin" or branched component.[18] The blue-staining starches contain appreciable quantities of the unbranched components, while the red-staining, waxy starches consist almost wholly of the branched component.[14,19] Glycogen, according to methylation data,[20] is more highly branched than the branched component of any known starches.

These experiments indicate quite clearly that the component of starch which has been assigned an unbranched structure is more easily oriented by flow than that component assigned a branched chain structure. The results of these experiments are equally valid for the extended chain or helical chain models for the starch–iodine complex. They provide entirely independent, physical support for the proposed branched and unbranched structures for the two components of starch, structures which have heretofore been based almost entirely on chemical evidence.

Experimental Study of Dichroism of Flow

Qualitative observation of the dichroism of flow of viscous starch pastes can be made with crude apparatus. In our work concentric cylinder apparatus with rotating inner cylinders were used (Fig. 3). similar to those described for the observation of birefringence of flow.[21] The optical system is simpler, however, and since starch–iodine solutions absorb light strongly the length of the cylinders should be less than is usually employed in birefringence of flow experiments.

Our most satisfactory glass apparatus was constructed with an inner cylinder of 2.27 cm. diameter, a distance between cylinders of 0.29 cm., and a cylinder length of 2.20 cm. The arrangement shown in Fig. 3 was found to be useful in eliminating all bubbles from the line of vision. With this apparatus dichroism of flow of viscous pastes stained with iodine was easily visible at 1500 r. p. m.

Observations were made parallel to the axis of rotation through windows provided for the purpose (Fig. 3). An intense, unpolarized, parallel beam of light was directed through the solution, and the components of the emerging beam with electric vectors parallel and normal to the flow lines were examined with polaroid or a Nicol prism. The difference in absorption of the two components was easily observed, and could be confirmed using a photoelectric cell. In most cases reliance was placed on visual observation which is quite sensitive if the Nicol or polaroid is rotated rapidly through 90°.

Dichroism of flow is most easily observed using heavy (5%) potato starch pastes stained with iodine. In these pastes swollen starch granules are present. To be sure that the dichroism was due to the dispersed starch and not to the swollen granules, well dispersed starch solutions were prepared from starch fractions in which the granules no longer existed. Dilute solutions of such fractions showed dichroism of flow which was made much more easily visible by adding corn sirup or some other medium to increase the viscosity of the solution. Swollen granules provide an extraordinarily high viscosity, and their effect on the dichroism may be attributed to that property.

In the study of the starch fractions care was taken to disperse the unbranched component thoroughly, and dilute solutions of low viscosity were examined. In all cases these solutions showed dichroism of flow. The branched component would show no dichroism of flow in dilute solution. Here the viscosity was built up by adding corn sirup, but with no positive dichroism observable. The waxy starches, waxy maize and waxy barley, were prepared as the 5% pastes. These pastes can be prepared with viscosities comparable with potato starch pastes. Even with the iodine-stained pastes, however, any dichroism of flow was doubtful. The tre-

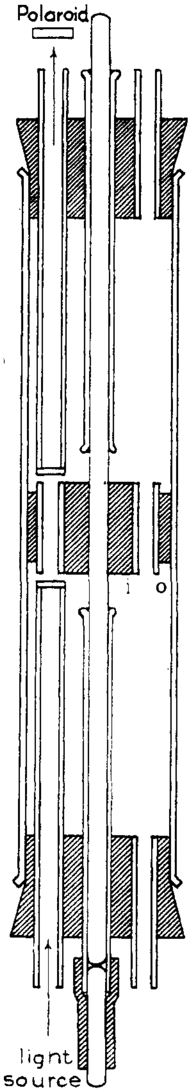

Fig. 3.—Concentric cylinder apparatus for observation of dichroism of flow: i is inner cylinder; o is outer cylinder.

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(18) Meyer has given the terms "amylose" and "amylopectin" structural significance which they have not possessed in the older literature; see (7).

(19) K. Meyer and M. Fuld, *Helv. Chim. Acta*, **24**, 1404 (1941).

(20) K. Meyer, *et al.*, *ibid.*, **24**, 58, 375, 389 (1941).

(21) See review by J. T. Edsall, "Advances in Colloid Science," Interscience Pub., Inc., New York, N. Y., 1942, p. 269.

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.

Ames, Iowa Received August 14, 1942

[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,

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[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).