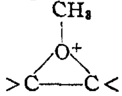
Identification of Alcohols.—This was carried out as indicated in Table I by a comparison of the physical properties of the alcohols and their derivatives with those of authentic specimens. Mixed melting points with the proper authentic derivatives gave no lowering. The physical properties of the alcohols and the melting points of the crude derivatives indicated small but appreciable stereoisomeric impurity.

Attempted Resolution[5f] of 2-Methoxycyclohexyl Bromide.—The halide, 0.3 mole, and 0.1 mole of brucine were mixed and left for twenty-four hours. The bromide, recovered in the usual way,[3] was inactive. The recovered bromide was similarly inactive when the brucine-bromide mixture was kept at 120° for 26 hours.

Summary

The diastereomeric 2-bromo-3-methoxybutanes, 3-methoxy-2-butanols and 2-acetoxy-3-methoxybutanes have been prepared.

The steric result of the reaction of silver acetate in acetic acid with the 2-bromo-3-methoxybutanes and *trans*-1-bromo-2-methoxycyclohexane is retention of configuration. This steric result is ascribed to the participation of the neighboring methoxyl group in the replacement process,  being an intermediate.

Possible participation of the carbomethoxy and carbonyl groups is briefly mentioned.

LOS ANGELES, CALIFORNIA RECEIVED JULY 31, 1943

[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

The Configuration of Starch in the Starch–Iodine Complex. IV. An X-Ray Diffraction Investigation of Butanol-Precipitated Amylose[1]

BY R. E. RUNDLE AND FRANK C. EDWARDS

In the previous papers of this series[2] evidence has been presented that both in the starch–iodine complex and in alcohol-precipitated starch the starch chains assume a helical configuration. X-Ray diffraction diagrams of the starch–iodine complex have revealed the type of packing of the helices and the dimensions of a turn in the helix.[2c] Similar diffraction diagrams of alcohol-precipitated starch might be expected to confirm the information obtained from the starch–iodine complex and perhaps supplement it by providing details of the structure not obtained from the starch-iodine complex, since diffraction patterns from the latter are largely the result of the scattering of the iodine molecules.

Bear[3] has already discussed the possibility of a helical structure for Katz's "V" modification[4] of starch on the basis of three or four diffraction maxima obtained from a sample of ethanol-precipitated whole starch. It is now possible to get much better diffraction diagrams, and hence to obtain considerably more information than was possible at that time.

Preparation of Samples and Diffraction Diagrams.—There is evidence that many of the lower alcohols precipitate starch in the helical configuration. Thus starch precipitated by nearly any alcohol will absorb iodine vapor readily,[2c] and Bear[3] has shown that the dried precipitates yield identical or nearly identical X-ray diffraction patterns of the "V" type. In our experience, however, butanol precipitation produces very superior samples for diffraction purposes. Equally, or even more important in obtaining good diffraction diagrams is the use of amylose or the unbranched component of starch in place of whole starch.

The amylose used in this investigation was prepared by Schoch's fractionation.[5] Since in Schoch's procedure the amylose is precipitated by butanol in excellent crystalline form, samples were taken directly from the precipitated fraction. The precipitated material occurs as highly birefringent rosets, an optical study of which has already been made.[2b] This amylose contains about 10% amylopectin.[6] The purer[6] "crystalline amylose" of Kerr[7] was not superior for diffraction purposes.

Diffraction diagrams were prepared from both wet and dry samples. The wet samples dripping with the saturated butanol solution were sealed in thin glass capillaries. Other samples were dried to constant weight over phosphorus pentoxide in an Abderhalden drier. Diffraction diagrams from samples dried below 80° were best. The dried samples were very hygroscopic, and so were sealed in thin-walled glass capillaries.

Powder diagrams were prepared with Ni filtered Cu K radiation in a camera of 10-cm. radius. Exposure periods were varied from 360 to 1500 ma. hrs. at 40 Kv. peak.

The Unit Cells.—The pattern from the dried precipitate can be indexed on the basis of a hexagonal unit $A_0 = 27.4$ Å., $C_0 = 8.05$ Å., or of an orthorhombic unit $a_0 = 13.7$ Å., $b_0 = 24.8$ Å., $c_0 = 8.05$ Å. (Table I). The relation between the two unit cells is shown in Fig. 1. As will be seen later, the orthorhombic unit is probably the true unit. In either case the packing of the helices approximates the closest packing of cylinders, a packing very similar to that found for the starch–iodine complex.[2c] There are four helices running through the hexagonal unit, two through the orthorhombic unit.

Assuming 6 glucose residues per turn of the

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[1] Journal Paper No. J-1140 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 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); (c) R. Rundle and D. French, *ibid.*, **65**, 1707 (1943).

[3] R. S. Bear, *ibid.*, **64**, 1388 (1942).

[4] J. Katz, *Z. physik Chem.*, **A150**, 60 (1930), applied this term to gelatinized starch precipitated by alcohol. Starch so treated produces a characteristic diffraction pattern, distinct from granular and retrograded starch.

[5] T. J. Schoch, THIS JOURNAL, **64**, 2957 (1942).

[6] F. Bates, D. French and R. Rundle, *ibid.*, **65**, 142 (1943).

[7] R. Kerr and G. Severson, *ibid.*, **65**, 193 (1943).

helix, the X-ray density is 1.23 g./cc. This calculation assumes that all butanol and water have been removed from the amylose. The observed density, measured by flotation of the material in several mixtures of organic solvents, is about 1.34 g./cc. The difference in these values would be just explained if one water molecule per glucose residue remained in the amylose, but it is possible that varying amounts of both water and butanol remain. It also appears that the dry butanol precipitate absorbs many organic substances readily. It differs from ordinary starch in this respect just as it differs in its ability to absorb iodine vapor,[2c] and this absorption doubtless increased somewhat the observed density. At any rate we feel that the above factors tend to make the observed density higher than the density calculated for completely solvent-free starch. The density calculated for seven glucose residues per turn in the helix is 1.45 g./cc.; from the above considerations this density would seem to be too high.

TABLE I

POWDER PATTERN FROM DRY BUTANOL PRECIPITATE—CuKα RADIATION

Indices Hexagonal	Indices Orthorhombic	$\sin^2 \Theta$ (calcd.)	$\sin^2 \Theta$ (obsd.)	Intensity[a]
(200)	(110)	0.00421	0.00422	M
	(020)			
(101)	(011)	.01018	.01026	VW
(220)	(130)	.01264		
	(200)	.01264	.01261	VS
(111)[b]	(101)[b]	.01229		
(310)	(210)	.01369		
	(111)[b]	.01334	.01374	M
(201)[b]	(021)[b]	.01334		
(400)	(040)	.01685	.01687	VW
	(220)			
(221)	(131)	.02177	.02161	W
	(201)			
(401)	(041)	.02598	.02618	W
	(221)			
(420)	(150)	.02948	.02955	VS
	(310)			
(510)	(320)	.03264	.03258	S
(600)	(060)	.03790		
	(330)	.03790	.03791	MS
(331)[b]	(301)[b]	.03757		
(511)	(321)	.04177	.04203	VW
(601)	(061)	.04703	.04690	W
	(331)			
(530)	(410)	.05160	.05153	VW
	(070)			
(620)	(420)	.05476	.05480	W
	(170)			

[a] Intensity notation—S, strong; M, medium; W, weak; V, very. [b] Reflection (*hkl*) probably very weak compared with (*hk*0).

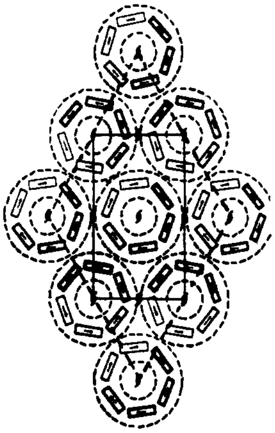

Fig. 1.—Structure proposed for the dried butanol-precipitated amylose. Dotted lines outline the pseudo-hexagonal cell, solid lines the orthorhombic unit. The symmetry relations are probably those of the space group $P2_12_12_1$ (Fig. 2).

Four of the maxima on the diagrams from the dried butanol precipitate appear to be identical with those from the "V" configuration of starch,[3] and it is likely that the structures of the dried butanol precipitate and the dried ethanol precipitate are identical. Since we were unable to get any further data on the ethanol precipitate the correspondence of the two patterns cannot be tested further.

The diagram from the wet butanol precipitate is clearly not hexagonal, yet comparison of the observed values of $\sin^2 \Theta$ for the two patterns reveals a great deal of similarity (Tables I and II). The correspondence of the reflections at low angles must indicate a simple relation between the two structures. Since powder diagrams from structures with large unit cells and low symmetry can seldom be indexed with certainty, reliance was

TABLE II

POWDER PATTERN FROM THE WET BUTANOL PRECIPITATE—Cu Kα RADIATION

Indices	$\sin^2 \Theta$ (calcd.)	$\sin^2 \Theta$ (obsd.)	Intensity[a]
(110)	0.00406	0.00412	MS
(120)	.00676	.00667	VS
(011)	.01075	.01088	S
(200)	.01264	.01267	M
(111)	.01391	.01393	S
(121)	.01661	.01678	VVW
(230)	.02074	.02059	VW
(201)	.02249	.02278	VW
(041)	.02425	.02450	W
(221)	.02609	.02607	VW
(310)	.02934	.02995	VS
(231)	.03059	(very broad)	
(060)	.03240	.03260	M
(250)	.03514	.03460	S
(241)	.03689	(.03760)	W
(301)	.03829	(doublet)	
(340)	.04284	.04285	VW
(161)	.04541	.04580	VW
(400)	.05056	.05060	VW

[a] Intensity notation as in Table I.

placed in the resemblance of the two patterns in obtaining a unit cell for the wet butanol precipitate.

It was found that if the orthorhombic unit found for the dried precipitate was modified by increasing b_0 and decreasing c_0 somewhat a unit was obtained which would account satisfactorily for the observed reflections from the wet precipitate. The unit cell dimensions are a_0 = 13.7 Å., b_0 = 25.6 Å., c_0 = 7.8 Å. A comparison of observed and calculated values of $\sin^2 \Theta$ is given in Table II.

It seems impossible to determine accurately the density of the wet precipitate or its water and butanol content, since the diffraction diagram is altered somewhat as soon as the mother liquor is removed from the precipitate. From the size of the unit cell it is apparent, however, that there are two helices running through the unit, and the unit must contain 12 glucose residues.

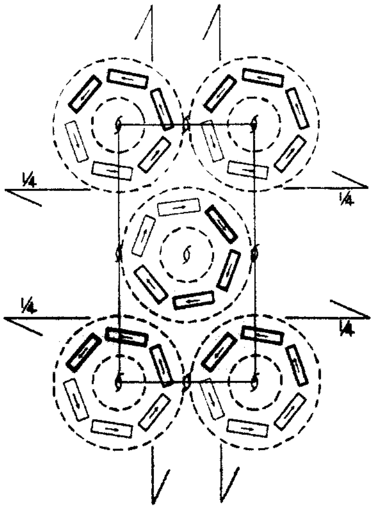

Fig. 2.—Structure of the wet butanol-precipitated amylose based on the space group P2$_1$2$_1$2$_1$. Arrows within rectangles indicate direction of the starch chain; shading of the rectangle represents the relative level of glucose residue along c_0, which is normal to the diagram. Positions of the screw axes are shown by symbols similar to those used by the "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935, Band I, p. 92.

Discussion of the Structures.—The unit cells of the wet and dry precipitates establish beyond a doubt that the hexagonal-type packing found in the starch–iodine complex is due to the starch and not to the arrangement of the iodines alone. They also provide additional evidence that the iodine molecules are within the helices, for on comparing the space required for a turn of the helix in the dry butanol precipitate and in the starch–iodine complex it is found that the space required in the latter is actually smaller. Thus the distance between helices is 13.7 Å. in the dry precipitate, 13.0 Å. in the iodine complex; a turn in the helix is 8.0 Å. in the dry precipitate, 7.9 Å. in the iodine complex.[2c] The dry precipitate will absorb 26% of its own weight of iodine.[2c] In so doing it actually contracts in volume. If the iodine molecules were to occupy space outside the helices it seems unlikely that this contraction could occur. It appears that the formation of the complex tightens and stabilizes the helix.

It is interesting to note that the wet butanol precipitate also has a shorter period along the helix, 7.8 Å., than that of the dry butanol precipitate, 8.0 Å. On the basis of this apparent tightening of the helix in the presence of butanol, and on the basis of the excellent crystalline properties of the wet butanol precipitate,[2b] we suggest that the starch forms with butanol a complex in which the butanol is present within the helices. Indeed we feel that the rather remarkable ability of butanol-precipitated starch to absorb organic molecules may be attributed to the capacity of the helices. Confirmation of this point requires further study.

If either the wet or dried butanol precipitate has an orthorhombic structure the space group must be isomorphous with D_2, since the molecules are optically active and the structure can contain no planes of symmetry. Of the space groups isomorphous with D_2 only those based on a primitive lattice are permitted by the observed reflections. Since the helix itself can have no two-fold axes it appears that the only orthorhombic space group providing a satisfactory arrangement of two helices per unit is D_2^4-P2$_1$2$_1$2$_1$. In this space group each helix axis would be coincident with one of the two-fold screw-axes running through the lattice, and alternate chains would be running in opposite directions (Fig. 2). This space group and structure is permitted by the observed reflections from both the wet and dried precipitate.

If the above structure is correct for either the wet or dried precipitate, then certainly half the helices are directed in one direction, half the other, in the dried butanol precipitate. This equal division in direction of chains seems all the more probable since it has been found for other long chain molecules, such as chitin and cellulose. An examination of the structure of the dried precipitate reveals that with alternately directed helices the structure cannot have true hexagonal symmetry; the true unit must then be the orthorhombic unit.

Since the starch–iodine complex can be prepared from the dried precipitate by treatment with iodine vapor, it would appear that in the iodine complex, too, half the helices must be oriented in one direction, half in the other. The unit reported for the starch–iodine complex[2c] must then be a pseudo unit. The true unit must contain at least two helices and have only pseudo-hexagonal symmetry.

It is to be noted that the helical configuration of the starch chains occurs only in certain modifications of starch. The chains are fully extended in granular and retrograded starch.[8] The differ-

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(8) R. Rundle, L. Daasch and D. French, THIS JOURNAL, in press.

ence in the configuration of the chains is probably due to rotation of the glucose residues about the glucosidic link. The helical configuration would suggest that the (CH_2OH) groups on neighboring glucose residues are *cis* to each other, while the extended form of the chain must represent a *trans* arrangement.[8]

Little further can be said of the actual arrangement of the glucose residues in the helices. However, models built by Freudenberg, *et al.*,[9] indicate that it is possible to construct helical starch chains only if the normals to the planes of the glucose rings are normal to the helix axis. The periodicity along the helix should then equal the width of a glucose residue. Space models of a glucose ring have a width of about 8 Å., the periodicities found for the helix in the wet and dried precipitates and in the starch–iodine complex[2c] are in good agreement with this value. This width was also found for the glucose residue in the extended starch chains of the "B" modification.[8] Freudenberg's model of the helix is then very probably correct in the above particular.

Summary

Diffraction patterns from wet and dried butanol-precipitated amylose confirm a helical starch chain with a helix diameter of about 13.7 Å., a length per turn of about 8 Å., and six glucose residues per turn. The helices approximate a close-packed arrangement in both the wet and dried precipitates, with alternate helices directed in opposite directions. The space group for both structures is probably D_2^4–$P2_12_12_1$.

The spacial relations between the starch–iodine complex and the dried butanol precipitate confirm the proposal[2] that in the starch–iodine complex the iodines occupy the interior of the helices, and it is suggested that in butanol-precipitated amylose the butanol occupies the interior of the helix.

The cell previously reported for the starch–iodine complex[2c] must be a pseudo-cell with only pseudo-hexagonal symmetry.

AMES, IOWA RECEIVED AUGUST 16, 1943

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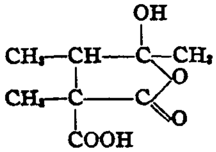
[9] K. Freudenberg, E. Schaaf, G. Dumpert and T. Ploetz, *Naturwissenschaften*, **27**, 850 (1939).

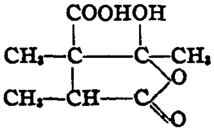
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Structure of Monocrotaline. X. Monocrotalic Acid[1]

BY ROGER ADAMS AND J. M. WILKINSON, JR.[2]

Monocrotalic acid, which is obtained by the hydrogenolysis of the alkaloid monocrotaline,[3] was assigned three possible structural formulas I, II and III. The failure of either ethyl α-carbethoxy-α,β-dimethyllevulinate (IV) or ethyl β-carbethoxy-α,β-dimethyllevulinate (V) to yield monocrotalic acid but instead dimethyllevulinic acid on acid saponification, introduced some doubt as to the correctness of either I or II as possible structures.[1b]


I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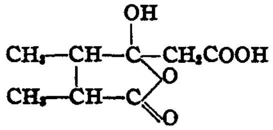
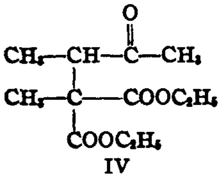
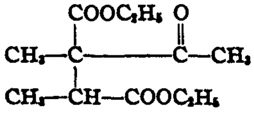
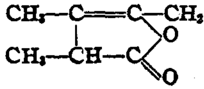

III


IV


V

After the initial researches,[1a,3] two reasons for not favoring structure III for monocrotalic acid were offered. The first was the difficulty encountered in attempting to esterify the acid with methanol and sulfuric acid or with methanol saturated with hydrogen chloride.[1a] Such behavior seemed indicative of a tertiary carboxyl group. The second was that methyl anhydromonocrotalate (VI), which is the unsaturated ester derived from monocrotalic acid of structure III, did not give a Legal test which was considered to be specific for β,γ-unsaturated γ-lactones containing a free hydrogen in the α-position.[4]


VI

Recent investigations have cast doubt as to the specificity of the Legal test for β,γ-unsaturated lactones.[5] As to the esterification, it now appears that the failure to obtain satisfactory yields of the ester by the use of methanol and hydrogen chloride may be attributed not to the unreactivity of the carboxyl group in monocrotalic acid but rather

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[1] For previous papers see (a) Adams, Rogers and Long, THIS JOURNAL, **61**, 2822 (1939); (b) Adams and Long, *ibid.*, **62**, 2289 (1940).

[2] An abstract of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[3] Adams and Rogers, THIS JOURNAL, **61**, 2815 (1939).

[4] Jacobs and Hoffman, *J. Biol. Chem.*, **61**, 333 (1925).

[5] Paist, Blout, Uhle and Elderfield, *J. Org. Chem.*, **6**, 273 (1941).