[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA]

THE STRUCTURE OF MERCERIZED CELLULOSE. I. THE SPACE LATTICE OF MERCERIZED RAMIE CELLULOSE AS DEVELOPED FROM X-RAY DATA[1]

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It has been noted by Herzog[2] and by Katz and Mark[3] that mercerized cellulose gives a diffraction pattern with x-rays which differs somewhat from that of untreated cellulose, but no clearly defined space lattice for mercerized cellulose has been heretofore worked out.[3a] Based upon new x-ray data that we have obtained for mercerized ramie fibers, we have developed a space lattice which appears to agree with all of the observed facts. In the present paper this structure is described and suggestions are made in regard to the probable mechanism of mercerization.

Several lots of ramie fibers were extracted with a mixture of alcohol and benzene and then mercerized by treating for thirty minutes with solutions containing 1, 8, 14, 17.5 and 28%, respectively, of sodium hydroxide. The alkali was removed by washing for a long time with distilled water, then digesting for a few minutes in very dilute acetic acid and again washing thoroughly with water. Finally the samples were dried in an oven. In order to keep the fibers from becoming tangled during these treatments, each sample was wound on a glass frame and tied in position, where it remained during all of the operations.

After mercerization the fibers were cut from the frames, laid parallel and cemented with dilute celloidin into tablets from which small blocks were cut. These blocks were used for obtaining the diffraction patterns. A molybdenum Coolidge tube was used as the source of radiation, and a monochromatic beam of x-rays was obtained by using screens of zirconium oxide. The procedure is described in greater detail in an earlier paper.[4]

By revolving the block of fibers through known angles, it is possible to determine the position of the atomic planes with reference to the long axis of the fibers. When that axis, designated here as the *c* axis, is parallel to the line of propagation of the x-ray beam,

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[1] This paper is a joint contribution from the Department of Botany, University of California at Los Angeles, California, and the Division of Plant Nutrition, University of California Experiment Station, Berkeley, California.

[2] Herzog, *J. Phys. Chem.*, **30**, 460 (1926).

[3] Katz and Mark, *Z. Elektrochem.*, **31**, 105 (1925).

[3a] Since this paper was written, a paper by Meyer and Mark, *Ber.*, **61**, 593–614 (1928), has appeared in which is proposed a structure for native cellulose resembling in many ways the structure proposed by the present authors in 1926 (see ref. 6), but differing in several respects from the earlier structure. Based partly upon the data of Herzog, and partly upon new data of their own, Meyer and Mark have calculated lattice dimensions for mercerized cellulose and have made suggestions as to the probable orientation changes accompanying mercerization. The lattice dimensions given by these authors as well as their conclusions are at variance with those of the present paper. Additional data will probably be required before it will be possible to show how far these conflicting views are capable of being reconciled.

[4] Sponsler, *J. Gen. Physiol.*, **9**, 221–233 (1925); **9**, 677–695 (1926).

the position is called the 0° position; when the beam cuts the fibers at right angles, the position of the *c* axis is referred to as the 90° position. The interplanar spacings calculated from the diffraction lines obtained from the 0° position are the spacings between planes of atoms which are parallel to the fiber length; when obtained from the 90° position, they are the spacings between planes which are perpendicular to the fiber length.

In Table I the interplanar values obtained from the 0° position for the various mercerization treatments are listed for comparison.

TABLE I

INTERPLANAR VALUES FROM 0° POSITION RAMIE FIBERS

Untreated, Å.	8% NaOH, Å.	14% NaOH, Å.	17.5 NaOH, Å.	28% NaOH, Å.
6.10	6.08	7.55	7.53	7.64
5.40	5.45	4.49	4.48	4.51
3.98	3.98	4.10	4.10	4.09
2.65	2.64	2.22	2.22	2.24
1.98	1.96	..	..	..
1.93	1.88	..	..	..

The first and second columns are practically identical; similarly, the third, fourth and fifth columns. Apparently no change had taken place in the first two; while in the remaining three columns the change produced by the alkali was the same regardless of the concentrations used. A critical concentration is indicated between 8 and 14%. From data which we are not presenting completely at this time, that critical point was found to be very close to 13%. For convenience we are using the term "unmercerized" as associated with treatments below the critical concentration, and "mercerized" for all above that. We found that fibers which have been subjected to concentrations near 13% may produce lines of both groups. The significance of that observation is as yet uncertain, but studies now under way may determine whether indvidual fibers have slightly different critical points or whether the same fiber wall may contain both mercerized and unmercerized cellulose.

In Table II values from Table I are summarized into the two groups which we have called "unmercerized" and "mercerized." Instead of tak-

TABLE II

INTERPLANAR VALUES FOR MERCERIZED AND UNMERCERIZED RAMIE FIBERS FROM 0° POSITION

Unmercerized. Treated with 1 or 8% NaOH or untreated		Mercerized. Treated with 14, 17½ or 28% NaOH	
Spacing, Å.	Density of line	Spacing, Å.	Density of line
6.10	Strong	7.55	Medium
5.40	Medium	4.50	Strong
3.98	Very strong	4.10	Strong
2.65	Weak	2.23	Weak
1.98	Very weak		
1.93	Very weak		

ing the averages, however, we have used the values for the strongest clean-cut lines which were obtained, on the assumption that they are most nearly correct.

It may not be out of place to assume at this time that the various planes of atoms producing the diffraction lines have shifted from the spacings given in the first column to those given on the same line in the third column. This assumption will be amply justified later by the facts. In the table it will be noted that with the shift in positions, changes also occur in the densities of some of the lines. Especially significant is the change in density of the line corresponding to the 5.40 spacing into a stronger 4.50, and that of the 3.98 to a weaker 4.10. These density changes are of considerable importance in determining the orientation of the constituent C_6 units in the structure for mercerized cellulose, as will be shown further on.

The patterns from the 90° position of the fibers are identical in all cases regardless of the concentration of sodium hydroxide used, so far as the interplanar spacings are concerned. However, there is a very evident difference in the density of at least three lines, between the mercerized and unmercerized groups; the 5.15 line is slightly stronger, the 3.40 considerably weaker and the 2.58 much weaker from the mercerized material.

TABLE III

INTERPLANAR VALUES FOR MERCERIZED AND UNMERCERIZED RAMIE FIBERS FROM 90° POSITION

Unmercerized. Treated with 1 or 8% NaOH or untreated		Mercerized. Treated with 14, 17$^1/_2$ or 28% NaOH	
Spacing, Å.	Density of line	Spacing, Å.	Density of line
5.15	Strong	5.16	Strong
3.40	Medium	3.36	Very weak
2.58	Very strong	2.59	Strong
2.03	Strong	2.02	Strong
1.70	Strong	1.69	Strong

From the intermediate positions, between 0 and 90°, the mercerized fibers produced fewer lines than the unmercerized. Their values and densities are given in Table IV.

TABLE IV

INTERPLANAR VALUES FOR MERCERIZED RAMIE FIBERS FROM POSITIONS BETWEEN 0 AND 90°

Position of fibers	Spacing, Å.	Density of line
70 to 80°	2.46	Weak
60 to 70°	3.15	Strong
60°	2.19	Weak
55°	4.38	Strong
40 to 50°	2.62	Medium
60 to 70°	1.89	Very weak

Development of Space Lattice

The interplanar spacings for mercerized material given in these tables are in agreement with the calculated spacings for a lattice the elementary cell of which is slightly monoclinic and has the axial ratios, $a:b:c$ = 0.595:1:1.352 (a = 4.53 Å., b = 7.61, c = 10.30).

The angle made by the axes, a and b, is approximately 83°. We have departed here from the conventional nomenclature of crystallography, since, consistent with the terms employed in our earlier work on untreated cellulose, we have found it convenient to retain the long axis of the fiber as the c axis.

The volume of this elementary cell is $4.53 \times \sin 83° \times 7.61 \times 10.30 =$ 353 cu. Å. The volume of the cellulose unit, $C_6H_{10}O_5$, assuming that no chemical change has taken place, is $162.1/1.57 \times 1/(6.062 \times 10^{23}) = 170 \times 10^{-24}$ cm.^{3} or 170 cu. Å., where 162.1 is the sum of the atomic weights of $C_6H_{10}O_5$, 1.57 is the value for the specific gravity of mercerized cellulose determined by us by the de Mosenthal method[5] and 6.062×10^{23} is Avogadro's number. There are then two of these C_6 units per elementary cell. 353/170 = 2.08 groups per unit cell.

In Table V the data from the previous tables are brought together for

TABLE V

INTERPLANAR SPACING VALUES FOR MERCERIZED AND UNMERCERIZED RAMIE FIBERS

Basis, $a:b:c$ = 4.53:7.61:10.30, aob = 83°

Unmercerized treated with 1 or 8% NaOH or untreated. Obs. values, Å.[a]	Mercerized treated with 14, 17½ or 28% NaOH				
			Angular position of fibers		
	Obs. values, Å.	Calcd. values, Å.	Obs. approx.	Calcd.	Indices
6.10	7.55	7.55	0°	0°	(010)
5.40	4.50	4.50	0°	0°	(100)
3.98	4.10	4.10	0°	0°	(110)
..	2.23	2.22	0°	0°	(210)
2.65	..	..	...	...	(120)
..	..	10.27	...	90°	(001)
5.15	5.16	5.13	90°	90°	(002)
3.40	3.36	3.42	90°	90°	(003)
2.58	2.59	2.56	90°	90°	(004)
2.03	2.02	2.05	90°	90°	(005)
1.70	1.69	1.71	90°	90°	(006)
4.35	4.38	4.37	55°	58°	(114)
2.17	2.19	2.18	60°	58°	(114)
2.62	2.62	2.63	45°	50°	(113)
2.35	2.46	2.44	75°	71°	(014)
2.97	3.15	3.13	65°	65°	(013)
1.94	1.89	1.88	65°	65°	(105)

[a] Figures in this column are taken directly from an earlier paper, *J. Gen. Physiol.*, **9**, 221–233 (1925).

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[5] H. J. de Mosenthal, *J. Soc. Chem. Ind.*, **26**, 443 (1907).

comparison, and the corresponding crystallographic indices and calculated values for the interplanar spacings and for the angular positions have been added. The observed angular position refers to a relationship between the long axis of the fiber and the path of the beam, the calculated position to the angle between the long axis and the diffracting plane as determined from the elementary cell. These two values should agree within a few degrees. The calculated values are based upon the axial dimensions as given above and upon the value of 83° for the angle between the axes *a* and *b*.

The close agreement between observed and calculated values seems to indicate that the space lattice for mercerized ramie cellulose, which we have described, meets the requirement of the x-ray data.

Discussion

A comparison of the lattice which we have just deduced for mercerized ramie cellulose with our earlier lattice for unmercerized cellulose[4,6] reveals rather definitely, we believe, the rearrangement of the structural units which has taken place during mercerization of the fiber.

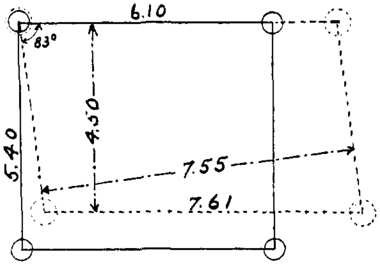

Fig. 1.

In the earlier paper[6] it was shown that untreated ramie cellulose is apparently made up of glucose units arranged in parallel chains of indefinite length running lengthwise of the fiber, the C_6 units of the chain being united throughout by glucosidal linkages. The chains themselves, in a cross section of the fiber, are rectangularly spaced 6.10 by 5.40 Å.

In the present paper the data indicate that during mercerization the chains are moved bodily in such a manner that the 6.10 Å. spacing has become 7.55 Å., while the 5.40 Å. spacing has become 4.50 Å. This is illustrated in Fig. 1, which shows a section through the unit cells perpendicular to the *c* axis. The solid circles indicate the centers of the C_6 groups as they occur in the unmercerized fibers; the dotted circles show the new positions after mercerization.

As pointed out in our earlier paper,[6] each of the constituent glucose units of cellulose contained a six-membered ring which gave the unit a flattened structure having a maximum dimension of about 7 Å. at right angles to the *c* axis. In the unmercerized fibers this dimension was regarded as lying along one of the diagonals of the 6.10 by 5.40 rectangle as indicated in Fig. 2.

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[6] Sponsler and Dore, "Fourth Colloid Symposium Monograph," Chemical Catalog Company, New York, **1926**, pp. 174–202.

This view is in agreement with the x-ray data, since the diagonal 3.98 line is much denser than either the 6.10 or the 5.40 lines. The density of the lines from the mercerized fibers, however, forces a different interpretation in regard to the position of the flattened C_6 units. Here the 4.10 line, a diagonal, is of equal density to the 4.50 line, which may correspond to the 5.40 of the unmercerized material. The equality of density of these two lines strongly suggests that in the mercerized material one-half of the number of C_6 groups have their long dimension (7 Å.) along the diagonal and the other half along the 4.50 planes, that is, parallel to the *b* axis. This may be more clearly seen from Fig. 3, where several possible arrangements are shown, each diagram representing a section through the unit cell perpendicular to the *c* axis. In A and B the long dimensions of all the C_6 units of any one chain lie in the same direction, but all those of two of the chains lie along the 4.50 planes and of the other two chains along the diagonal planes. By either arrangement a given chain would contribute mostly to one line or to the other, but by the arrangement shown in C every chain would contribute equally to each line. Here the dotted circles indicate a level below the solid circles. A study of three-dimensional models seems to indicate the C arrangement as the most probable one.

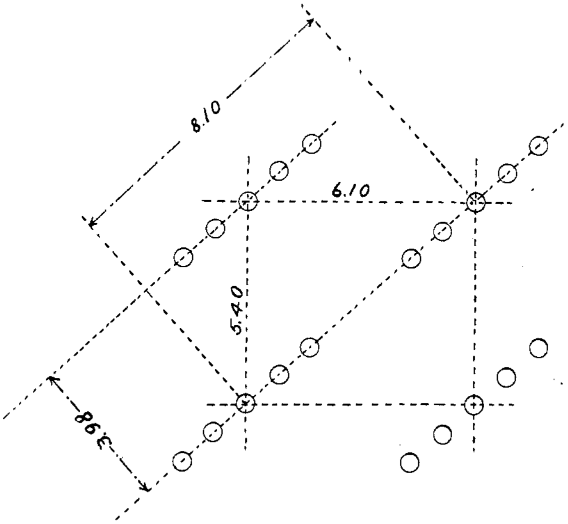

Fig. 2.

In attempting to fit a three-dimensional model of the glucose unit to our original elementary cell of untreated cellulose, we were forced to place the long dimension of the unit (7 Å.) on a diagonal of the cell because the axial dimensions were too short (6.10 and 5.40). This diagonal position furnished very satisfactory agreement with the densities of the diffraction lines produced. A similar agreement between position of the units and density of lines should occur, of course, with the mercerized cellulose. It is interesting to note that the density of the lines demanded that about half of the units should change their position from the diagonal to the *b* axis, and then to find that the axial dimension along that axis had actually increased sufficiently (to 7.61 Å.) to allow for the new orientation of the long axis of the glucose unit.

In the above discussion we have attempted to show that the chains of C_6 units have been shifted in their relative positions and that the individual units in each chain have assumed new relative positions with respect to one another. It now remains to be considered whether in addition to these larger shifts there have also occurred internal rearrangements in the structure of the chain and of the C_6 unit.

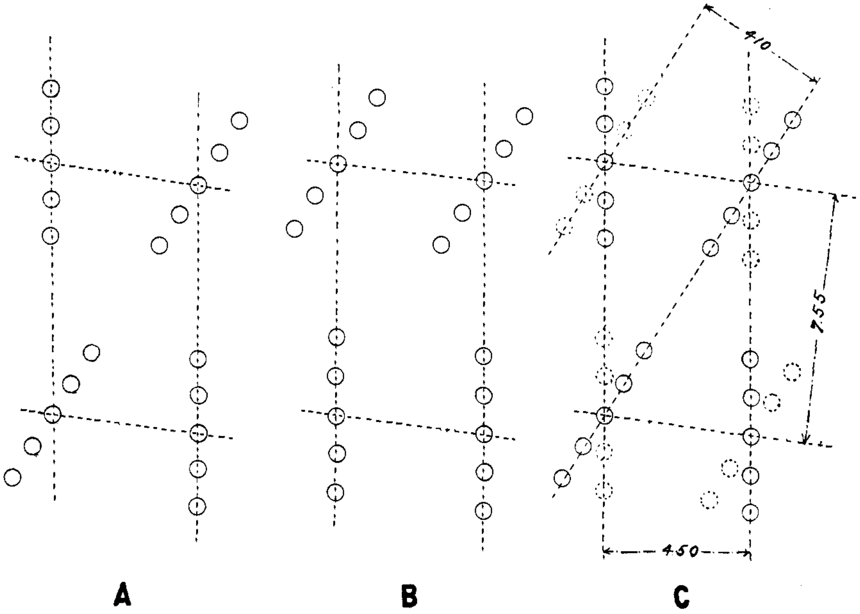

Fig. 3.

The fact that identical diffraction lines were obtained from both untreated and from mercerized fibers in the 90° position shows that the planes of atoms at right angles to the *c* axis have not shifted during the mercerization process. • Since it has been shown in our earlier paper that the arrangement of these particular planes of atoms is produced by the arrangement of atoms in the amylene oxide ring of the constituent glucose units, the absence of change in the arrangement of the planes would appear to indicate that the ring formation has not been disturbed. Although the same planes of atoms exist after as before mercerization, a distinct change in the intensities of three lines shows that there has been some change in the spacial relationship of some of the constituent atoms of the C_6 group. An adequate explanation may be found in the mobility of the hydroxyl group attached to the sixth carbon atom. An examination of the three-dimensional model[7] will show that while the rest of the atoms in the molecule are in practically fixed positions, this particular hydroxyl is capable of rotation about the axis of the bond joining the fifth and sixth carbon atoms. A rotation from position A to position B, as shown in Fig. 4, would have a tendency to produce the changes observed, namely, a decrease in the density of the 2.58 and the 3,40 lines and an increase in that of the 5.15 line.

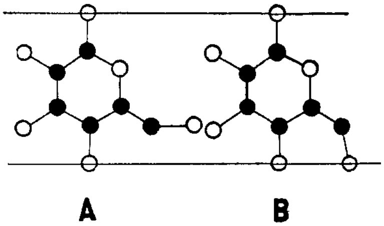

Fig 4.

The Nature of the Mercerization Change

From the preceding considerations mercerization appears to be the result of rearrangements in three different ways: (1) a shift in the position of the chain with respect to the neighboring chains, (2) a partial rotation of the alternate glucose units in each chain and (3) a shift in the position of the hydroxyl attached to the sixth carbon atom. We are not prepared to discuss at present either the time relation or the causal relation of these three events; that is, we do not know whether the movement of the whole chain is due to the partial rotation of the alternate glucose groups nor whether those movements are influenced by the probable shifting of the hydroxyl mentioned.

Regardless of the relationship existing between these three rearrangements, the new positions taken by the chains and by the constituent units and parts seem to dispose of several suggestions which have appeared in the literature concerning the nature of mercerization. It seems extremely unlikely that the mercerization process involves (*a*) a migration of an oxygen bridge,[8] (*b*) an enolization,[9] (*c*) an isomeric change,[3] or in fact any type of molecular rearrangement of the constituent glucose, since any such change would almost certainly produce a different diffraction pattern than that which is obtained from the 90° position of the fibers.

It appears also unlikely that mercerization is a progressive change varying in degree with the strength of the alkaline solution employed, as Herzog[2] contended. Herzog recognized three stages of mercerization; the first with 8 to 10% NaOH, the second with about 14% and the third or "total mercerization" with 28% NaOH.

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[7] Ref. 6, Fig. 3, p. 179.

[8] Herzog and Londberg, *Ber.*, **57**, 329 (1924).

[9] Gebhard, *Chem.-Ztg.*, **37**, 663 (1913).

Our data indicate that there is a critical concentration of alkali below which the treatment does not produce a permanent effect on the arrangement of the C_6 units. This critical concentration is in the neighborhood of 13% for sodium hydroxide. Material treated with alkali of about that concentration is quite likely to give diffraction lines of both the mercerized and unmercerized fibers, as previously mentioned. It is probable that certain discrepancies between our data and those of Herzog are due to this partially mercerized condition. In his data from the 14% material, the interference points A_1 and A_2 were apparently produced by the parts of the fibers which were unmercerized, since they appeared from the 8% and not from the 28%; while opposed to this the A_3 and A_4 lines were produced by the mercerized parts of the fibers since they appeared from the 28% and not from the 8% treatments. With that explanation his data, but not his conclusions, are in agreement with ours with one further exception. Apparently he has made the error of accepting interference points produced by K_β wave lengths as though they were of K_α origin. His point A_3 from 8% treatment is quite clearly of K_β origin, while A_4 is of K_α origin from the same set of planes. Of course that A_3 point should be discarded and, without that, there is no basis for Herzog's conclusion that mercerization is a progressive change.[10] On the other hand, both his data and ours seem to indicate that only two general types of x-ray diffraction patterns are obtainable, one from unmercerized and the other from mercerized material, and that the spatial rearrangement of the groups of atoms which exist in mercerized material is produced by a definite concentration of the alkali. Although the fibers are swollen to a different extent with different concentrations of alkali, the component chains, upon washing, seem to behave in only two ways: for concentrations below 13% they return to their original position, for those above that concentration they take on new positions as described above.

We desire to call attention here to the additional support which the observations recorded in the present paper give to the conception of a cellulose structure as being made up of continuous chains of glucose units which are held together by primary valence linkages. As we have shown, mercerization produces a separation of the chains and a partial rotation of the units within the chains. This rotation is definitely a rotation about an axis which is parallel to the long axis of the chain. Throughout these changes the chains as such remain intact; that is, the C_6 units have not become detached from the chain.

If the units were held together by secondary valence forces only,[11] then the alkali treatment should produce a separation of the units lengthwise of the fiber, just as it produces the separation of the chains laterally.

[10] Sponsler has discussed this error in greater detail in *Nature*, **120**, 767 (1927).

[11] K. Hess and others, *Ann.*, **435**, 1–144 (1923); **443**, 71–112 (1925).

Our x-ray evidence, however, shows that no separation of the C_6 groups occurs lengthwise of the fiber, but that the chains have become separated, indicating that the forces existing between the units in the chain must be greater than those exerted laterally from chain to chain. We consider that the greater forces holding unit to unit correspond to primary valences and the lesser ones between the chains to secondary valences.

Again, if cellulose were composed of detached C_6 units held in space by secondary valence only, it is scarcely conceivable that the forces which produce mercerization would be exerted so as to produce partial rotation on one axis only and that axis the long axis of the chain. It would seem more likely that rotation would occur on several axes rather than only one which happens to be always the long axis of the chain, and, further, it would seem that the units would be forced out of their linear arrangement unless the forces which hold the units together, and incidentally act as pivots, are stronger than the laterally acting forces.

The x-ray evidence which we have brought forward points very strongly to a linear arrangement of the units and shows that the mercerization process produces rotation of some of the units about the long axis of the chain but does not disturb their linear arrangement. This evidence indicates that the forces holding the units together in a linear chain are too strong to be overcome by the mercerization process and that, on the contrary, the forces acting laterally unquestionably have been overcome. These stronger linear forces correspond to our conception of primary valence forces; the weaker lateral forces, to secondary valences.

We have not yet attempted to correlate the gross changes of swelling, shrinking and twisting which accompany mercerization with the changes observed in the lattice structure.

We have so far been concerned with the structure of mercerized cellulose rather than with the mercerization process. Accordingly, we have as yet no insight into the mechanism by which treatment of cellulose fibers with strong sodium hydroxide solution is able to produce the changes we have been discussing, but studies are now under way with swollen fibers which may give some suggestion as to the mechanism involved in mercerization.

Summary

1. X-ray diffraction data are given for ramie cellulose which has been subjected to mercerization processes with various strengths of sodium hydroxide solutions. The evidence shows that there is a critical concentration of the alkali at about 13%, above which the fibers are mercerized, below which they remain unmercerized.

2. From the diffraction patterns of mercerized ramie cellulose a space lattice has been developed. When compared with the unmercerized lattice the *c* axis is seen to be unchanged while the *a* and *b* axes have been

changed from $a = 5.40$ in the unmercerized to $a = 4.53$ in the mercerized and from $b = 6.10$, to $b = 7.61$ Å. The angle between axes a and b has been changed from 90 to 83°.

3. As a result of mercerization the chains of glucose units have been shifted laterally in the wall of the fiber and have remained unbroken.

4. Within the chain the original glucose unit has remained unchanged except for a shift of the hydroxyl of the sixth carbon atom. The x-ray diffraction patterns indicate that there has been a partial rotation of some of the glucose units about the long axis of the chain.

5. A comparative study of the structures of mercerized and unmercerized cellulose has produced additional support to the view that the constituent units of cellulose are united in chains by primary valence linkages.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XIV. POLYMERIZATION OF ALDEHYDES

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The nature of polymerization, aggregation and disaggregation is one of peculiar importance in relation to the valence, surface tension, crystal and absorption forces which come into play in the formation of large crystalline and colloidal aggregates in plant and animal life, since "permanence of form" and "capacity to exist" are both dependent on the ability of specific substances to exhibit the pheonomenon of "aggregation." The nature of the forces through which this increased permanence and stability are attained is, as yet, quite unknown, as is evident from the work of Bergmann,[3] R. O. Herzog,[4]

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[1] Presented to the Faculty of the Graduate School, McGill University, June, 1927, in candidacy for the degree of Master of Science.

[2] Taken in part from the thesis of R. E. Montonna as presented to the Graduate School of Yale University in June, 1924, in candidacy for the degree of Doctor of Philosophy.

[3] Bergmann, "Allgemeine Strukturchemie der complexen Kohlenhydrate und Proteine," *Ber.*, **59**, 2973 (1926); "Beiträge zur Chemie hochmolekularer Stoffe," *Ann.* **445**, 1 (1925); "Über den hochmolekularen Zustand von Kohlenhydraten und Proteinen und seine Synthese," *Z. angew. Chem.*, **38**, 114 (1925); *Naturwissenschaften*, **1925**, p. 1045; "Über ein assoziierendes Hexosan," *Ann.*, **448**, 76 (1926).

[4] Herzog, "Published Researches from the Kaiser Wilhelm Institut für Faserstoffchemie," **1920–1927**.