STRUCTURAL UNITS OF STARCH DETERMINED BY X-RAY CRYSTAL STRUCTURE METHOD.

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Among the earliest investigators of starch the idea prevailed that these minute, transparent, spherical grains were built of uniform structural units, the nature, size, shape, and arrangement of which have been the source of a number of theories and of much speculation. Raspail's work in 1825 led him to think that the grains were not crystallization products. Münter on the other hand decided that the grains must be crystals. Nägeli conceived the grain to be made up of concentrically and radially arranged particles which he called at one time molecules, and later micelles, and in one place he speaks of these small particles as consisting of several thousand molecules. In 1863 Kabsch considered starch grains to have a very definite arrangement of molecules, although not sufficiently uniform to have optical axes ascribed to them. Schimper decided that they consisted of radially arranged crystal fibers. In 1895 Meyer completed this idea of a spherocrystal and conceived the grains to be built of radially arranged needle-like branching crystals, which became more and more branched the more nearly they approached the surface of the grain. These crystals he called trichites. The vast amount of work that has been done since then has neither confirmed nor disproved the theory of the trichite or micellar structure, and of the later articles on starch some favor and some oppose this view.

3 Nägeli, C., *Die Stärkekörner, Zürich*, 1858.
Probably all has been done with the microscope and the ultramicroscope that can be done, and no structural unit has been found. If one is to be discovered it must probably be with some new tool, and during the past few years such a new tool has made its appearance, namely the x-ray. It has been used to investigate the building units of crystals, and with it a great deal of work has been done in determining the size and arrangement of these structural units in many inorganic crystals. These units prove to be the atoms of which the crystals are composed. For example, the cubical crystal of common table salt consists of sodium and chlorine atoms arranged alternately in three dimensions. The position with relation to each other and the distance from center to center of these atoms have been very accurately determined. About fifty compounds and a considerable number of metal elements have been investigated in this way, among them the diamond, graphite, carbonates, sulfides, oxides, etc. Very few organic compounds, however, have been studied.

With these investigations in mind it seemed fairly plausible that the structure of the starch grain might be determined, especially since the grains behave towards light as though they were built up in some regular way, and since x-rays are of the nature of light.

The x-ray method of determining the atomic structure of crystals is described in considerable detail in a number of places in the literature, so only a very brief résumé will be given here. For proofs and evidence concerning the various steps the reader is referred to the citations just mentioned.

The method consists in measuring the angle at which x-rays are reflected from a crystal, and computing from that measurement the distance between the planes of atoms which have caused the reflection. When an x-ray wave is incident on the face of a crystal it passes through the surface layer of atoms and through many thousand

layers beneath. Only a minute part of the wave is reflected from each plane. There are several millions of these planes or layers uniformly spaced in each millimeter of depth in a crystal. The distance between the layers and also between the atoms in the layer, varies with the kind of crystal from one to several Ångström units. An Ångström unit is \( \frac{1}{10,000,000} \) millimeter. When the distance between the planes is such that a crest of the minute part of the wave which is reflected from one plane coincides with a crest from that of the next plane, then they will reinforce, and the sum of many thousand such reflections will carry sufficient energy to register visibly on a photographic plate. Thus x-ray reflection depends upon reinforcement from a depth of many planes. The crests of the waves will coincide only when there is a certain relation between the glancing angle, the wave length of the x-rays used, and the distance between the planes. This relationship is expressed by the formula

\[
\lambda = 2d \sin \theta
\]

in which \( \lambda \) is the wave length, \( d \) the distance between planes, and \( \theta \) the glancing angle. If the glancing angle varies by only one part in several thousand the tendency is to annul instead of reinforce, and consequently, reflection can occur only at a very definite angle for a given set of planes and a given wave length.

When a narrow beam of x-rays, consisting primarily of one wave length of known value, is allowed to pass through a small mass of powdered crystals, some of the crystal particles will reflect at one angle, some at another, still others at a third angle, and so on, according to the relation mentioned above between the wave length, the glancing angle, and the distance between planes in the crystal particles. When these reflections are recorded on a photographic film, they will appear as dense lines with a width corresponding to the slit through which the beam of x-rays is allowed to pass before reaching the powder. The arc of the reflecting or glancing angle can be measured in millimeters directly on the film, and since a known wave length is used, the distance between planes can be readily computed. For a more detailed and simpler explanation, as well as
for diagrams and descriptions of the apparatus used in this work, the reader is referred to my paper in the *American Journal of Botany*.

Many demonstrations have been made by a number of investigators to show that the dense lines, as in Fig. 1, are produced by the reflection of x-rays from planes of atoms. These demonstrations consist of two parts. First, that the lines on the photograph are produced by reflecting points arranged in planes; and second, that these reflecting points are atoms. The proof of the first part consists in obtaining an agreement between the values of \( d \) (distance between planes) from measurements of the photograph, and the values obtained from a mathematical consideration of the type of crystal used. The proof of the second part consists in obtaining an agreement between the volume occupied by a reflecting point as computed from the photograph and the volume of the atom or molecule as obtained by the use of the molecular weight, the density, and Avogadro's number. It may be worth while to illustrate these two points briefly, since similar methods are used later in determining the structural units of starch.

Fig. 1 is reproduced from an x-ray photograph of the lines reflected by the crystal particles of powdered sodium chloride. A rhodium anticathode was used, and the rays were filtered through a ruthenium screen so that the beam was practically monochromatic. The blank space in the middle of the photograph is the shadow of a lead shield used to absorb that part of the main beam which was not diverted when passing through the powder. The right and left hand sides are mirror images, and the distances between lines 1 and 1, 2 and 2, 3 and 3, etc., measure the arc of 40° in each case, where \( \theta \) is the glancing angle. By using these measurements and the rhodium \( K\alpha \) wave-length 0.614 Å.u., the distance between the planes of reflecting points was computed from the fundamental formula, \( \lambda = 2d \sin \theta \). The results show that line 1 was reflected from planes which were 2.81 Å.u. apart; line 2, by planes 1.99 Å.u. apart and so on as recorded in Table I.

A striking agreement is obtained when these figures are compared with those which were computed from a cubical space lattice such as Bravais' old theory proposed for the atoms in a crystal. Knowing that sodium chloride forms cubical crystals, we may think of a
unit cube as having an atom at each corner and of the large crystal as being built up of many of these unit cubes with the atoms shared by the adjacent cubes. The atoms then would form a space lattice in which they would occur in many sets of parallel planes. The planes coinciding with the faces of the cubes would be farthest apart, and the distances between the diagonal planes would bear definite relations to this widest spacing. When the sides of the cube are

**TABLE I.**

Sodium Chloride.

<table>
<thead>
<tr>
<th>Line No.</th>
<th>Distance between planes. A.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.81</td>
</tr>
<tr>
<td>2</td>
<td>1.99</td>
</tr>
<tr>
<td>3</td>
<td>1.62</td>
</tr>
<tr>
<td>4</td>
<td>1.41</td>
</tr>
<tr>
<td>5</td>
<td>1.26</td>
</tr>
<tr>
<td>6</td>
<td>1.14</td>
</tr>
</tbody>
</table>

**TABLE II.**

Sodium Chloride.

<table>
<thead>
<tr>
<th>Line No.</th>
<th>Distance computed from angle and wave-length. A.u.</th>
<th>Computed from cubic lattice based on 2.81 A.u.</th>
<th>Ratio of planes in a cubic lattice.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.81</td>
<td>2.81</td>
<td>1.000</td>
</tr>
<tr>
<td>2</td>
<td>1.99</td>
<td>1.99</td>
<td>0.707</td>
</tr>
<tr>
<td>3</td>
<td>1.62</td>
<td>1.62</td>
<td>0.577</td>
</tr>
<tr>
<td>4</td>
<td>1.41</td>
<td>1.41</td>
<td>0.500</td>
</tr>
<tr>
<td>5</td>
<td>1.25</td>
<td>1.25</td>
<td>0.447</td>
</tr>
<tr>
<td>6</td>
<td>1.14</td>
<td>1.14</td>
<td>0.408</td>
</tr>
</tbody>
</table>

1.00 unit apart the various sets of diagonal planes are spaced 0.707 unit, 0.577, 0.500, etc. Now if we accept line 1 as being reflected by the planes which have the widest spacing, then if a cubical arrangement exists, line 2 would be reflected by planes which are spaced $0.707 \times 2.81$; line 3, $0.577 \times 2.81$, etc. Table II gives the ratio of spacings of planes in a cubic lattice and the distance between planes based on 2.81 A.u. as the possible distance between cube faces. Table I is incorporated in it for comparison.
Such close agreement between these two sets of figures necessarily leads one to conclude that the "reflecting points" must be arranged in a cubic space lattice.

The second part of the demonstration, showing that the reflecting points are atoms, is given briefly in the following paragraphs.

It is a well established fact that the molecular weight of any compound in grams contains a definite number of molecules; the accepted figure is $6.062 \times 10^{23}$. This is called Avogadro's number. Sodium chloride contains that number of molecules for each 58.5 gm. of the salt. The volume of 58.5 gm. of NaCl is 26.95 cc., since its specific gravity is 2.17.

$$\frac{58.5}{2.17} = 26.95$$

That volume then contains $6.062 \times 10^{23}$ molecules, and the volume of 1 molecule of sodium chloride would be $\frac{26.95}{6.062 \times 10^{23}}$ or $44.4 \times 10^{-24}$, or 44.4 cu. Å.

The photograph shows that in the unit cube the faces are spaced 2.81 Å apart. Each point, then, might be considered as having a volume of 2.81³ cu. Å, and if we assume each to be an atom, then the volume of two of them should be the volume of a molecule of sodium chloride.

$$2.81^3 \times 2 = 44.4 \text{ cu. Å.}$$

Agreement as close as that both in spacing and in volume makes it difficult to believe anything else than that the reflections are due to atoms arranged in a cubic space lattice.

**Interpretation of the Starch Spectrum.**

In an earlier article it was shown that an x-ray spectrum can be obtained from a mass of starch grains somewhat similar to that obtained from the crystal powder of sodium chloride. In later work, which is described in the present paper, the nature and the size of the reflecting unit have been determined and a definite structure has been ascribed to the starch grain. The demonstration of these conclusions following somewhat the same lines of reasoning as just used for sodium chloride, involves the several steps which are now to be presented.
Nature of Reflected Lines.

When compared with a line photograph of a common crystalline substance such as sodium chloride, the negatives from starch exhibit several striking features (Figs. 1 and 2). The background is very dense and the lines are only slightly denser, consequently the definition of the lines is poor; they seem to blend in with the background instead of being clear cut, and wherever they occur close together they often overlap so much that two lines make a broad band in which they are scarcely separable. These features tend to make measurements, both of distance and of comparative density between lines, very difficult. They also militate against a satisfactory reproduction of the photographs by means of half-tones.

About a dozen negatives were made from three different kinds of starch—potato, corn, and cassava. On all of them two or three of the lines are noticeably prominent and can be measured with a
fair degree of accuracy, several more are visible only when carefully
studied in properly adjusted light, and still two or three more can
be detected only with a photometer. The first two lines are some-
times blended into a single broad band, but on several negatives they
appear clearly separated and there they can be readily measured.
Line 4 (Table III), the third prominent line from the center of the
negative is by far the most sharply defined and has yielded consis-
tent measurements on all of the ten or eleven negatives. Of the
other lines, 6, 7, 8, 9, 11, and 12 are distinct enough on a half dozen
or more negatives to be fairly consistently measured. The actual
existence of some of the lines was often questioned on account of
their faintness, but several months after this paper was written an
opportunity was presented for having an energy curve made on a
recording micro photometer,10 and the position of the lines as shown
by the curve agreed so well with the measurements of the negatives
that further doubt of their existence was dispelled. The curves, in
addition to verifying the visual location of the lines, brought out two
lines, 3 and 5, which had been predicted but had not been distinguished
by the unaided eye.

The fact that lines are present on the negatives indicates the
existence of reflecting points arranged in some regular way forming
a space lattice. In a space lattice the units form many different
sets of parallel planes. Each set, having its own particular value of
do, the distance between planes, produces one of the lines on the pho-
tographic film. The value of that do may be determined by using the
formula $\lambda = 2d \sin \theta$, in which the value used for $\theta$ is obtained from
measurements of the lines on the negative. In this way the value
of $d$ for every line found on the negatives was obtained and listed in
Table III, Columns 2 and 3. The value of $\lambda$ used in these computa-
tions was 0.614 Å.u., the wave length of the $K\alpha$ line of rhodium.
The figures, then, in the table represent the distances between
the parallel planes of the various sets for an unknown space lattice.

10 Through the courtesy and kind assistance of Mr. Edison Pettit of the Mount
Wilson Observatory at Pasadena, California, the energy curves referred to were
made on the registering micro photometer described in a paper by Pettit and Nich-
ments, 1923, vii, 187).
The problem now is to determine the type of this unknown space lattice and the dimensions of its elementary cell. The solution was influenced by the one well established fact concerning the formation of the starch grain in the plant cell; that is, that the starch substance is deposited on the grain at the interface between the grain and the protoplasm. Since the grain assumes a more or less spherical form it seems probable that the particles are deposited at equally spaced points on the surface of the grain. This would make two dimensions of the lattice equal and the value would be the largest obtainable from the negatives; that is, 5.94 Å. The third dimension would be likely to be the next larger spacing, 5.05 Å. and the elementary cell of the lattice then would have the dimensions, 5.94 × 5.94 × 5.05. If this cell is a rectangular figure, a square prism, then it would have for its various planes the values of d as given in Column 4 of Table III. The indices of the planes are given in Column 5 and the position of the planes in the cell is shown in Fig. 3.

The agreement between these values and those obtained from the measurements of the negatives is sufficiently close to justify our acceptance of the shape and the size of the elementary cell as assumed above, and we may now say that the lines on the negatives indicate that planes of reflecting units are spaced 5.94 Å apart, and that other planes at right angles to those are spaced 5.05 Å apart, forming elementary cells of the size mentioned in the last paragraph. The lattice would look somewhat like Fig. 4.

![Diagram of elementary cell structure](image)

**Fig. 3.** Position of the more important planes in the elementary cell.

**Fig. 4.** Elementary cells from the lattice of the starch grain.

**Fig. 5.** Elementary cells in two positions.

*Size and Nature of the Reflecting Unit.*

The atoms which cause the reflection from starch grains are those of carbon and of oxygen. The former are 1.50 Å in diameter and the latter, 1.30 Å. The reflection from hydrogen is too weak to make any appreciable difference in this work. It seems very probable that the units which form the lattice are not single atoms, for a structure with so great a distance as five or six
Ångström units between atoms, which are no larger than those of carbon and oxygen, would take the form of some other state of matter than that of a solid with the density of starch. It follows then that there must be a group arrangement of the atoms around each corner of the elementary cell. An arrangement of this nature is not unusual. Very convincing evidence has been brought forward to show that the benzene ring acts as a unit in crystals of anthracene, naphthalene, and their compounds, that the CO$_2$ group retains its identity in crystals of carbonates, and that 3 molecules of silicon dioxide are associated with each point in the lattice of quartz crystals.

The group of atoms in starch, of which one would naturally think first, is that indicated by the empirical formula, C$_8$H$_{10}$O$_5$. The volume of that group as computed from the density of starch, 1.50, the sum of the atomic weights, 162, and Avogadro's number, 6.062 × 10$^{23}$, is 178.2 cubic Ångström units.

\[
\frac{162}{1.50} \times \frac{1}{6.062 \times 10^{23}} = 178.2 \times 10^{-21} \text{ or } 178.2 \text{ cu. Å. u.}
\]

If that is the group which is associated with the corners of the cells, then its volume, 178.2 cu. Å. u. should be equal to the volume of the elementary cell. Although we have thought of the groups as being identified with the corners of the cells, that is the points of the lattice, the imaginary boundary lines may be shifted so that a group will be seen to occupy a space equal to that of the cell. In Fig. 5 the dotted lines indicate the positions of the new cells after the shift has been made. The volume of this cell is almost exactly that of the group, 178.2 cu. Å. u.

\[
5.94 \times 5.94 \times 5.05 = 178.2
\]

This agreement between the volumes of the elementary cell and the group of atoms is perhaps closer than is consistent with the degree of accuracy of the measurements; on the other hand, it is not likely that it is merely coincidental. It seems to me that we may accept the figures as indicating the probable structure and that we

may consider the starch grain as built up of *groups* of atoms, each group being associated with each point in the lattice, that is a group acting as a unit of the lattice; and further, that each group consists of 6 carbon, 5 oxygen, and 10 hydrogen atoms.

It is highly probable that each group \((\text{C}_6\text{H}_10\text{O}_5)\) has a definite configuration, and further, that all of the groups, at least a large percentage of them, are oriented in the same way with respect to the surface of the grain. These assumptions are based on the dark cross-effect with polarized light, a common phenomenon produced by starch grains. What the configuration of that group is we have no means of knowing at the present time, but we may assume a form for illustration which has a slight basis in the chemistry of starch. The end-product of many starch reactions is glucose \((\text{C}_6\text{H}_{12}\text{O}_6)\). The structural formula generally accepted for glucose shows the 3rd and 6th carbon atoms linked together through an oxygen atom.

\[
\begin{align*}
\text{CH}_2\text{OH} \\
\text{CH} \\
\text{O} \\
\text{CH}_2\text{OH} \\
\text{CH}_2\text{OH} \\
\text{CH}_2\text{OH}
\end{align*}
\]

In the starch group the 6 carbon atoms are attached, without doubt, in the same way and it is not improbable that the 3rd and 6th carbon atoms are linked also through an oxygen atom. On that assumption a model of the starch group was made to scale.

Fig. 6 gives two views of the model. The dark balls represent the carbon atoms, the light ones the oxygen atoms, and the small loops indicate the position of the hydrogen atoms. So many arrangements of the atoms and so many orientations of the whole group inside of the elementary cell are possible that no specific conclusions can be made, but nevertheless certain rather convincing impressions are left with one after a short study of this hypothetical structure.

The size of the structure corresponds to the size of the elementary cell, the boundary lines of which are represented in the model by the rectangular wire cage. The group fits in the cell loosely enough.
to suggest the low specific gravity of starch and at the same time extends far enough towards each face of the cell to make the rather weak cohesion, which is characteristic of the starch grain, seem possible.

In Fig. 6 the diagrams below the pictures of the model are intended to help make clear the kind of reflection which occurs when a group of atoms acts as a unit of the lattice. Parallel to each face of the cell there are several possible planes which contain atoms of the unit group. In the 100 view the plane marked $p$ in the diagram contains 4 atoms, the others marked $s$ contain only 1 each, or in one case, 2 atoms. In the 010 view the principal plane, $p$, has 2 atoms in it and each of the secondary planes, $s$, has only 1. The reflection which produces a line on the negative comes from the principal plane, but its reflecting power may be partially annulled by waves from the secondary planes. The tendency of secondary planes in
general is to annul each other, depending upon the spacing and the number of atoms occurring respectively in them. Thus the reflecting power of a particular set of planes depends not only on the number of atoms in a unit area of the principal plane, but also upon the conditions of spacing and number of atoms occurring in the secondary planes. It is evident from this and the two views of the model that for the same group of atoms the reflection from one set of planes will not necessarily be as strong as that from another set. The reflection from the 010 planes would probably be very weak, while that from the 100 planes would be stronger. Curiously, that is exactly the appearance of those two lines on the negatives. The core of heavier atoms occurring near the center of the cell would favor strong reflections for the 110 and 011 planes, and very weak for the 111 planes, while the somewhat flattened effect of the core facing the 010 planes would favor weak reflections for those planes as well as for the 101 planes, and stronger reflections for the 100 planes. It is interesting to see how favorable this particular shape and position of the model is to the lines actually obtained on the negatives, but since the data from which the model was built are so meager, the structure must not be taken too seriously. The importance attached to the model lies in the fact that a model can be built which seems to fulfill most of the conditions necessary for reflections such as those obtained from the starch grains.

Concentric Layers.

Up to this time the data have been used as though starch were without question a crystalline substance, while as a matter of fact starch does not have the appearance nor the properties of common crystals. The grains are spherical bodies which have grown by additions at the interface between the grain and the plastid, that is they are built up of concentric layers; they have no ordinary cleavage planes; and further, the polarized light phenomenon is not that of ordinary crystals. These statements immediately raise several questions. How could spherical grains produce line photographs similar to those of ordinary crystals? How could a lattice such as that ascribed to starch occur in a sphere?
These questions may be answered best perhaps by comparing the photographs from starch with the results of an assumption that the grains are built up of concentric layers, each layer having the thickness of the $\text{C}_6\text{H}_{10}\text{O}_5$ group which, from the lattice worked out above, would be 5.05 Å thick, and the groups in each layer located 5.94 Å apart. In other words the layers would be sheets of elementary cells, one cell thick. Of course the inner layers would have to contain a smaller number of cells than the outer ones, and in order to retain the rectangular lattice there would have to be slight readjustments. The result of these readjustments may be the so called lamellae of starch grains.

To gain a better conception of this arrangement one may imagine the elementary cells to be the size of common building bricks, and then build up a set of concentric circles to represent a cross-section of a starch grain. Now in the average starch grain there are about 20,000 elementary cells along one diameter. (The grains are about 100,000 Å in diameter.) So the concentric circles of bricks would be built out until the diameter is 20,000 bricks. This would make the outside circle about 1½ miles in diameter.

One can see that the rearrangement of elementary cells in the inner circles, in order to keep a rectangular lattice, would be comparatively insignificant; and that large regions would closely approach the parallel layers of a rectangular lattice, such as that of ordinary crystals. It seems then not improbable that starch grains built proportionally in a somewhat similar way would reflect x-rays from certain regions of the grain. Each spherical grain, unlike the particles of a crystal powder, however, would reflect from a great many regions. From this point of view it is interesting to examine into the possibilities of reflection from a powder composed of such spherical grains.

In Fig. 7 suppose the large circle to be a cross-section of one of these spherical grains placed in the path of a beam of x-rays. The regions indicated by the letters are drawn to show four elementary cells. The reflecting planes are made somewhat heavier than the other lines. Of course the cells are enormously out of proportion to the diameter of the circle.
The strongest reflection would be that from the 3.85 planes since every grain would reflect from at least the four regions C, C, C, C, and many of them which happen to be revolved into certain positions would reflect from four additional regions, one above and one below each B. On all of the negatives this line is actually the most prominent line.

Every grain would reflect also from the 5.05 planes from two regions, B, B. This line too should be a strong line, about as dense as the 3.85 line. The negatives actually show these two lines to be about equal in intensity.

The 5.94 planes would be in the proper position to reflect in only a comparatively few grains and on that account should give a much weaker line than the 5.05 planes; but when in that position, the reflecting region would completely encircle the grain passing through A, A, and consequently the density of the reflected line should approach that of the 5.05 line. This is in fairly satisfactory agreement with the negatives.

![Fig. 7. X-ray reflection from a starch grain.](image-url)
The 4.17 planes would reflect in similar positions to those of the 5.94 planes and should be, as in ordinary crystals, somewhat weaker. On the negatives the lines are actually weaker than one is lead to expect from the diagram.

The 3.20 planes, which would reflect from four or eight positions just as it was shown the 3.85 planes would do, actually produce much weaker lines than would be anticipated.

In making these comparisons no consideration was given to the probable fact that the principal planes of the different positions are not equal in reflecting power, nor to the possible effect of the secondary planes in reducing the reflection. Both the position of the secondary planes and the number of atoms in them are very important factors in determining the density of the lines, but there are absolutely no data so far obtained which could be used in this connection. On the whole the agreement between the negatives and the expectations from the diagram is fairly satisfactory.

There is another factor which may tend to make the lines less dense and so diminish the difference in intensity between the lines and the background. The 21 atoms of the starch group, while they occupy a space equal to 178 cubic Ångström units, undoubtedly do not completely fill that space. On the assumption that the carbon and oxygen atoms are the same size in starch that they appear to be in many crystals, that is 1.5 Å.u. and 1.3 Å.u. in diameter respectively, and guessing that the hydrogen atoms are about 1 Å.u. in diameter, the total space which these atoms would fill is less than 50 cubic Ångström units. The unoccupied space in the elementary cell would be four or five times as much as that actually filled with atoms. The group then is loosely constructed and is likely to be strongly influenced by temperature. In fact, an increase of about 150°C. over room temperature produces profound changes in dry starch, and in water at about 60°C. the grains undergo a kind of disintegration. Based on that, one might expect considerable thermal agitation in dry grains even at room temperature. It has been shown that there is a very decided reduction in intensity of reflection from sodium chloride when raised

in temperature about half way up to its melting point. The experimental proof of the thermal effect in the case of starch seems comparatively simple but has not yet been attempted.

Still another factor which should be mentioned in connection with the density of the reflected lines is one embodied in the spherical shape of the grain. While certain large regions of the grain act as ordinary crystal particles, there are other regions which just miss the exact angle for reflection and in which there are not enough planes to annul completely the reflection. This would produce a broadening of the reflected lines and increase the density of the background by blending into it.

SUMMARY.

A few brief statements summarizing the foregoing conclusions may make a picture of the structure of the starch grain somewhat clearer.

1. The presence of lines on the negatives indicates a regular arrangement of the planes of atoms.
2. The lines are in close agreement with lines which would be produced by a lattice of the tetragonal system, the elementary cell of which is a square prism with the dimensions $5.94 \times 5.94 \times 5.05$ Å.u.
3. The unit of the lattice occupies a space equal to the volume of the starch group, $C_{6}H_{12}O_{6}$.
4. The large number of atoms in the unit makes it highly probable that principal planes and secondary planes of atoms occur for every reflecting position.
5. The effect of the secondary upon the principal planes may readily account for the differences in the density of the lines produced on the negatives.
6. From theoretical considerations, reflections, such as those obtained, would occur if starch grains were built up of concentric layers of units.
7. Two other factors which might affect the density of the lines are thermal agitation and the curvature of the concentric layers.
8. A model of the starch group was constructed to scale based on the accepted sizes of the atoms involved and upon rather meager chemical evidence. The model apparently fulfills the requirements necessary to produce reflections such as were obtained.
9. The model fits the elementary cell loosely enough to suggest a low density and to allow for considerable thermal movement. At the same time, parts of it approach the faces of the cell closely enough to make cohesion seem possible.

10. The model makes clearer the basis for the assumption that reflection from certain positions would be stronger than from others.

If the interpretation of the data is correct and if the assumptions made are sound, then the starch grain is built up of units arranged in concentric layers, and the units are groups of atoms, each containing 6 carbon, 10 hydrogen, and 5 oxygen atoms. Such a structure is certainly not an amorphous structure, and on the other hand it is not crystalline in the common sense of the term. Parts of the grain, it is true, act as crystals in that for certain distances the layers of units are in planes, but taken as a whole the layers are curved.

As to the validity of the conclusions, those pertaining to the type of lattice and to the size of the unit may be accepted as sound in our present knowledge of x-rays and crystal structure; those, however, pertaining to the nature and the spherical arrangement of the units, while they seem convincing, need the support of further investigation into the various structures deposited by living protoplasm.

In conclusion, the assumption that the units form a sort of spherical space lattice, gives a picture of the starch grain which leads us to ponder over the nature of the activity in protoplasm when it is depositing solid substances. Starch, cellulose, and pectic bodies are about the only solid deposits made directly by the living substance of plants, and all three have the same proportional formula, $C_{6}H_{10}O_{5}$. Investigations, as yet incomplete, indicate that cellulose also consists of a regular arrangement of $C_{6}H_{10}O_{5}$ groups, each acting as a unit, but the spacing ($5.14 \times 6.14 \times 5.55$) is slightly different from that of starch. Pectin has not been studied. Protoplasm may be thought of as being composed of molecules of many different sizes, polypeptides, or even proteins forming the larger, and amino-acids the smaller, if water and electrolytes are ignored. The smaller molecules, such as those of the amino-acid, leucine, are approximately equal in size to the $C_{6}H_{10}O_{5}$ group of starch. That being the case, what can be the state of affairs at the interface when the starch particles are being deposited? Is it probable that protoplasm is
homogeneous to the extent of being able to deposit these particles at 6 Å intervals?

From quite another view-point a clear picture of the units of structure and their arrangement in cellulose should give a new point of attack on the many problems connected with osmosis. And from still a different view-point, it might lead perhaps, to a solution of problems connected with swelling.

Another line of thought is suggested by the uniformity of the groups in the starch grain. Since the C₁₀H₁₆O₅ group occurs as an individual unit, one is inclined to suspect that it is really the molecule. Generally the starch molecule is considered to be very large, to be composed of several dozens of such groups, and to have a molecular weight of 7,000 or much more. No one figure, however, seems satisfactory to the different authorities. There is already at hand considerable evidence which will be assembled in a later paper favoring the single group, C₁₀H₁₆O₅, as the molecule.

Finally, problems in polarized light may receive more satisfactory explanations through a clearer notion of the molecular structure of the carbohydrates.

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