THE CONFIGURATION AND PACKING OF THE CHAIN MOLECULES OF NATIVE STARCH AS DERIVED FROM X-RAY DIFFRACTION OF PART OF A SINGLE STARCH GRAIN

by

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I. INTRODUCTION

The present communication is the full account announced by the author in brief letters to *Nature* on the same subject[1, 2].

This work on starch had its origin in the availibility of a new micro-method for X-ray diffraction developed during the years 1943 and 1944 for the purpose of studying the submicroscopic fine structure of plant and animal tissues[3, 6]. The method enables microscopic specimens, or regions of such specimens, to be irradiated with narrow X-ray pencils down to about 10 μ diameter, so as to obtain from such a small region a diffraction pattern on which no blackening appears due to diffraction from matter surrounding the region to be studied.

When in September 1944 the development of the method could be regarded as to be complete, the crystal structure of starch grains was one of the first subjects we intended to study.

According to the literature available to us at that time, no conclusive evidence had been gained concerning this problem since KATZ and co-workers had shown that various starches yield different types of X-ray powder diagrams and hence exhibit different crystalline organizations.

However, powder diagrams offer no favourable prospects if we wish to gain an insight into the structure of the crystallites or micells in starch grains. For that purpose fibre diagrams are the first requirement. These diagrams are produced by specimens in which the crystallites lie oriented with corresponding crystal axes in a given direction as *e.g.* in cellulose fibres.

In contrast to fibrous substances like cellulose and *e.g.* chitin, starch is not deposited in living nature as fibres exhibiting a parallel orientation of crystallites. Its microscopic grains possess a radial orientation of crystallites. Hence, X-ray diffraction of even a single whole grain yields a powder pattern as is obtained from powders of crystalline particles, oriented at random.

The difficulty of producing oriented fibres of starch and the lack of satisfactory micro-methods for X-ray diffraction are the reasons why the crystal structure of native starch has long been unapproachable for the crystallographer, whereas that of the other substances mentioned above could be almost completely elucidated.

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It will be evident that on account of the radial orientation of crystallites in starch grains, a small sector of a grain may be expected to contain crystallites exhibiting only a small angular dispersion in their orientation. And if it were possible by means of the new micro-method to select for irradiation such a portion of a grain, we might obtain a fibre pattern of native starch.

Because of war events it was not until the end of 1945 that we were able to undertake attempts in the proposed direction. These attempts resulted in the achievement in February 1946 of a diagram which, though far from being an ideal fibre diagram, showed a clear orientation and permitted suggestion of unit cell dimensions. The latter were mentioned in a brief letter to *Nature*[1] along with some new spacings in both A and B-starch spectra, not observed by KATZ *et al.*, and a suggestion concerning the chain configuration in native B-starch.

During the months following the dispatch of this letter, files of periodicals from overseas countries reached the Delft Libraries, revealing that in U.S.A. much work on starch had been done during the war. It appeared that RUNDLE, DAASCH AND FRENCH[4] had obtained a fibre pattern from artificial films and fibres of the amylose fraction of starch. These preparations yield the same X-ray diagram as native starch in the B-modification and therefore possess the same crystal structure. The suggestions made by RUNDLE *et al.* concerning the chain configuration and the dimensions of the unit cell for their amylose preparations appeared to be essentially the same as the ones we made for native B-starch.

However, the chain configuration proposed in the above papers, containing, like that of cellulose, two glucose residues per identity period, involves difficulties on account of the α-linkage of glucose residues in starch. As already mentioned by RUNDLE *et al.*[4] one would expect a similar chain to be far more crumpled, resulting in a much shorter fibre period than the one actually found. Prof. ASTBURY, during a short conversation on the matter in November 1946, also stressed this difficulty and wondered whether the photographs pointed unambiguously to the period mentioned.

After having paid new attention to the problem we found no reason to change the period considerably, but manipulation of chain models yielded a chain configuration from which the period could be understood without any objections. In contrast to the stretched configuration containing two glucose residues in the period, as suggested before by RUNDLE *et al.* and, independently, in our first communication on the subject, the new configuration shows a spiral containing three glucose residues in the period.

The above result was reported briefly in a second letter to *Nature*[2]. This letter evoked a letter to *Nature* by RUNDLE[5], drawing attention to the work on starch done in U.S.A., and in which the author maintains the configuration and unit cell suggested by RUNDLE *et al.*[4] and by us in our first communication.

We shall now give a detailed account of our work and results and answer RUNDLE's letter at the end of the present communication.

2. MATERIAL AND METHODS

It is evident that in the present investigation the size of the starch grains to be studied is a factor of the highest importance. The bigger the grains the easier it will be to select a portion with small angular dispersion in the position of the crystallites.

Very large starch grains occur in the rhizome of *Canna indica*, in the scales of the

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subterranean shoot of *Lathraea squamaria* and in the pseudo-bulbs of the orchid *Phajus grandifolius*.

Among the *Phajus*-starch grains many are found of a peculiar shape. These show a part that is built like a normal grain and a protruding part of which the layers do not, as they do in normal grains, envelop the whole grain (Fig. 1). In the protruding part the layers possess a relatively small curvature. We also observed grains lacking a normal part and built up wholely in the same way as the above protrusions (Fig. 1a).

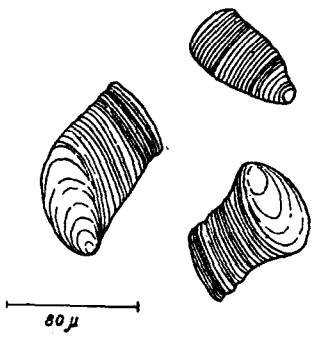

Fig. 1. Starch grains of *Phajus grandifolius* particularly suitable for obtaining a fibre pattern

Under the polarizing microscope it appears that in the protrusions the optical behaviour of the grain is the same as in the normal part. Therefore the orientation of micells with respect to the plane of the layers will be the same as it is in normal starch grains, *i.e.* with the chain direction nearly perpendicular to the layers. (*Cf. e.g.* MEYER[9]).

It will be clear that these *Phajus*-starch grains possess a shape particularly suitable for our purpose, because the protrusions with their comparatively small curvature of the layers and, hence, probably rather high degree of parallel orientation of the micells, may be expected to give a fibre pattern when irradiated with a narrow pencil of X-rays in a direction perpendicular to the main direction of orientation. The shape of the grains of *Canna* and of *Lathraea* is much less favourable. Therefore those of *Phajus* were used, in particular grains with the above protrusions.

The grains were isolated from fresh pseudo-bulbs by mashing a small piece of bulb in a reagent tube. Along with the grains a mucous substance and a great quantity of long spicules are liberated from the broken cells. The latter products were removed by dilution of the pulp with water, shaking up, and subsequently decanting the liquid with the suspended needles from the fast settling grains. When clean the grains were dried in air.

The micro-method for X-ray diffraction applied in this investigation has been described elsewhere[3]. A description in greater detail appears in the book by BOUMAN and others[6]. Therefore we refrain from giving a description here and refer to those publications.

A starch grain with a large protrusion was selected under the dissection microscope and mounted between thin collodion films in the micro-specimen holder. The specimen holder was attached in front of the pinhole in a position permitting the beam to traverse the protrusion only, in a direction parallel to that from which the grains are seen in Fig. 1.

The first photographs obtained already revealed a clear orientation, even though the reflections were very vague. It appeared that this vagueness was due to the fact that dry hydrogen was passed through the camera in order to prevent central diffuse blackening of the photographs caused by air scattering. In accordance with the known fact that starch must be kept moistened to give clear X-ray spectra, much better results were obtained if the hydrogen was saturated with water vapour.

The best photograph obtained is shown in Fig. 2. On this photograph the longest spacing is not shown, however. It is overshadowed by a central blackening due to diffuse

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glass scattering from the pinhole. The spacing is indeed shown by the photograph of Fig. 3. (This has been attained by using a longer secondary pinhole (*cf.* KREGER[3]) than the one used for the preceding photograph and thus confining the diffuse glass radiation to a much smaller angle). In contrast to the preceding one this diagram was made in an atmosphere of dry hydrogen, which explains the vague reflections. The same starch grain was used as for the preceding diagram.

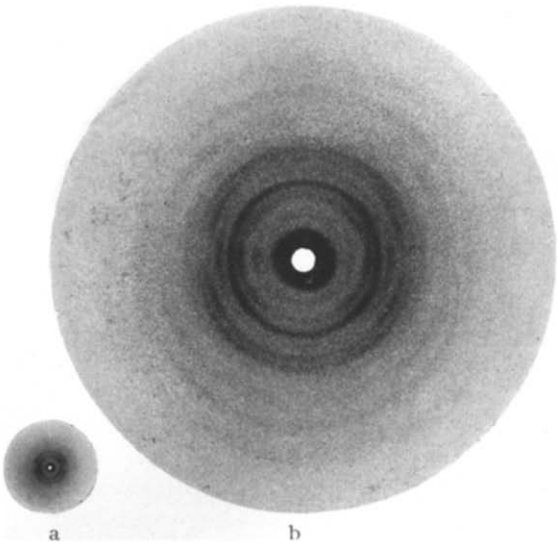

Fig. 2. Fibre pattern of part of a starch grain of *Phajus grandifolius*: a. micro-film at natural size; b. enlarged. The longest spacing is not shown

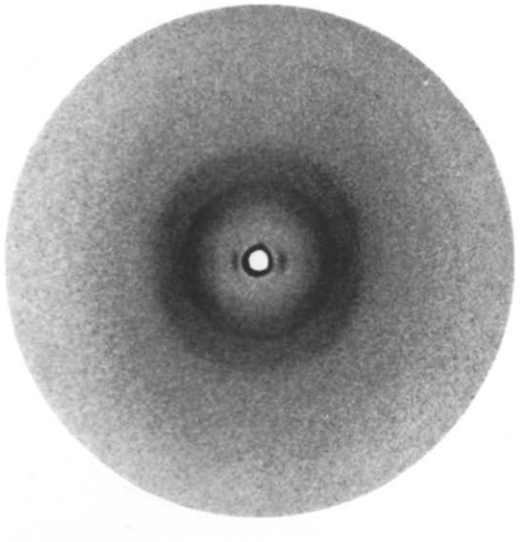

Fig. 3. Fibre pattern of part of a starch grain of *Phajus grandifolius* in dry hydrogen, showing the longest spacing

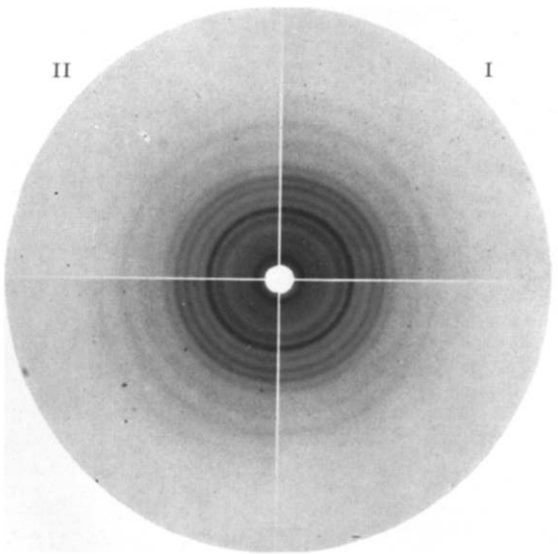

Fig. 4. Powder patterns of potato starch grains (I) and *Phajus* starch grains (II)

In Fig. 4 a powder diagram of *Phajus* starch grains (I) is shown matched against one of potato starch grains (II). These diagrams were not made with the micro-technique but according to the usual method. It is seen that there is an almost complete agreement between the diagrams of *Phajus* and those of potato starch grains. *Phajus* starch belongs therefore to the same type as potato starch, *i.e.* the B-type according to KATZ AND VAN ITALLIE[7].

Technical details of the photographs are as follows: —
Fig. 2. Pinhole: conical lead glass capillary, 1 cm long, 40 μ diameter at the narrow end and

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290 μ at the wide; secondary pinhole (lead) 80 μ wide by 370 μ long; specimen-to-film distance $\pm$ 4.5 mm; exposure 10 h at 25 kv/100 ma, rotating anode.

Fig. 3. Pinhole: as above, but 20 μ at the narrow end and 145 μ at the wide; sec. pinhole 40 μ wide by 550 μ long; specimen-to-film distance about 2.5 mm; exposure 3 h at 25 kv/100 ma, rotating anode.

Fig. 4. Pinhole: cylindrical capillary 0.25 mm wide by 4 cm long; specimen-to-film distance 3 cm; exposure 24 h for each pair of quadrants at 45 kv peak/25 ma, sealed-off Philips tube; specimen in air saturated with water vapour.

3. THE EVALUATION OF THE X-RAY DIAGRAMS

a. *Calculation of the fibre period*

The fibre diagram shown in Fig. 2 exhibits reflection rings with rather strongly elongated arcs of increased intensity. The position of the arcs enables four layer lines to be distinguished. It will be recognised that the arcs are too much elongated to determine their position exactly and, hence, to permit the fibre period to be calculated very accurately. Nevertheless we have endeavoured to compute the fibre period from the positions of their centres.

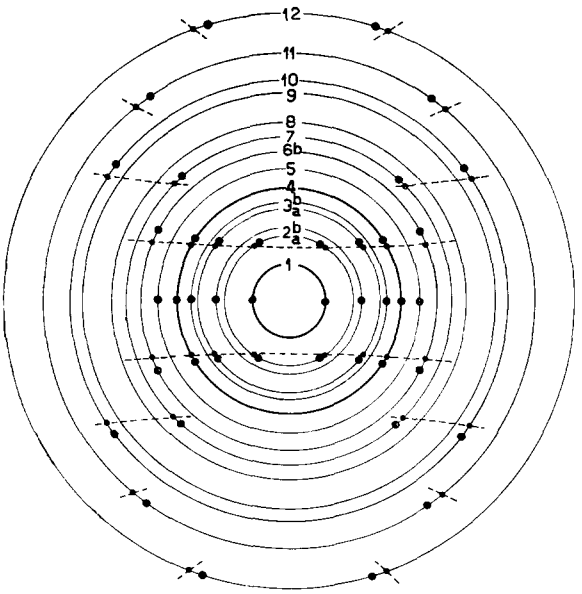

Fig. 5. Schematic representation of the fibre diagram shown in Fig. 2. Explanation in the text

For that purpose the micro-diagram was enlarged on a photographic plate to an arbitrary convenient scale. The centres of the arcs were estimated visually and marked by ink dots whose distances to the equator were measured. After wiping out the ink marks this was repeated several times, so that the distances to the equator could be determined as the means of several independent measurements.

In Fig. 5 a schematic representation is given of the fibre diagram of Fig. 2. The centres of the dark arcs in the rings, determined as mentioned above, are marked by the large black dots. The meaning of the small black dots will be discussed later. The diffraction ring diameters have been taken from the powder diagram of *Phajus* starch grains shown in Fig. 4, because it allows their measurement to be carried out more accurately than does the enlarged micro-diagram.

We need not explain that if the ring diameters on the enlarged micro-diagram are denoted by $2f$, the distances of the centres of the dark arcs to the equator by z and the ring diameters of the powder diagram for a distance r between specimen and film by $2f_r$, the distance of the centres of the dark arcs to the equator in a given ring for a distance r between specimen and film can be found as:

$$z_r = \frac{2f_r \cdot z}{2f}$$

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The fibre period T is then calculated as

$$T = n\lambda \frac{\sqrt{f_r^2 + r^2}}{z_r}$$

valid for a flat film, in which n is the order-number of the layer line at which the maxima of the reflection ring considered are situated and λ the wave length of the X-radiation.

It turned out that the fibre periods calculated from the maxima in the different rings showed rather considerable differences. This could be expected on account of the considerable elongation of the arcs of enhanced intensity on the fibre diagram and the accordingly ill-defined layer line positions. The periods vary between 8.85 and 10.44 Å.

A survey of data of the diagrams is given in Table I, columns 3–6. In column 3 the spacings derived from the powder photograph of *Phajus* starch grains are listed. The numbers of the corresponding reflections are added in brackets. Reflection 6*a* is not observed on diagrams of *Phajus* starch grains. We did observe it on diagrams of potato starch grains. In column 4 the reflection intensities are denoted as s (strong), m (medium), f (faint), vf (very faint). In column 5 the numbers of the layer lines at which the reflection rings show a maximum are given. Finally, in column 6, the fibre periods calculated from the position of the maxima in the rings are mentioned.

TABLE I

DATA OF THE X-RAY DIAGRAMS OF FIG. 2, 3 AND 4

1	2	3	4	5	6	1	2	3	4	5	6
(*hkl*)	$d_{(calc)}$	$d_{(obs)}$	Int.	*n*	*T*	(*hkl*)	$d_{(calc)}$	$d_{(obs)}$	Int.	*n*	*T*
001	15.60	15.6 (1)	s	0		113	4.14	4.11 (6a)	f		
010	10.60					211	4.01	4.00 (6b)	m	1	8.8[5]
100	9.00					122	3.94				
011	8.77	8.8 (2a)	vf	1	10.1	023	3.71	3.68 (7)	m	2	10.1
101	7.82	7.8 (2b)	vf	0		031	3.45	3.41 (8)	f	?	
002	7.80					123	3.44				
110	6.85					220	3.42				
111	6.29	6.29 (3a)	m	1	9.9	203	3.41				
012	6.29					114	3.40				
102	5.90	5.89 (3b)	m	0		132	3.03	2.99 (9)	f	?	
020	5.30					015	3.00				
003	5.20	5.17 (4)	s	0,1	9.6	301	2.95				
112	5.15					223	2.87	2.86 (10)	f	2	9.8
021	5.01					232	2.63	2.61 (11)	f	3	9.9[5]
013	4.67					034	2.63				
120	4.56					142	2.41	2.34 (12)	f	4	10.4[5]
200	4.50	4.51 (5)	m	0		240	2.28				
103	4.51					241	2.27				

The numbering of the spacings, mentioned in brackets in col. 3, is different from the numbering used by KATZ AND VAN ITALLIE[7]. The values for d mentioned in col. 2 are calculated on the basis of a unit cell with $a = 9.0$ Å, $b = 10.6$ Å, $c = 15.6$ Å; $a \perp b \perp c$. Further explanation in the text.

b. *Considerations on the dimensions of the unit cell*

It is striking that in the fibre diagrams the number of reflections showing equatorial maxima is rather large. It therefore seems appropriate to consider first the equatorial maxima in order to find the indices of the net planes (*hOl*), *i.e.* the planes parallel to

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the crystallite axis that is oriented perpendicular to the layers of the starch grain. It appears that these reflections can be indexed on the basis of an orthorhombic unit cell with axes $a = 9.0$ Å and $c = 15.6$ Å in the basal plane.

If, now, we assume the unit cell to be orthorhombic with the above axes in the basal plane and $b = 9.8$ Å, *i.e.* the mean of the fibre periods mentioned in Table I, it appears very difficult to index the other reflections. If for b the greatest value found for the fibre period is chosen (10.44 Å), there is rather good agreement between theoretical and observed spacings. If, however, a value of 10.6 Å is taken for b all spacings can be indexed with still better agreement between theoretical and observed spacings. The difference is smaller than 1% for every reflection. The accurate fibre period is therefore assumed to be 10.6 Å.

In Table I the theoretical d values for a number of net-planes of an orthorhombic cell with axes $a = 9.0$ Å, $b = 10.6$ Å and $c = 15.6$ Å are listed in column 2. The indices are mentioned in column 1. From a comparison of columns 2 and 3 the agreement between the calculated and observed spacings is evident. A further factor in favour of the correctness of the indexing is the agreement between the indices k in column 1 and the layer line numbers n in column 5.

On the assumption that a value of 10.6 Å for the fibre period is correct, it is now possible to calculate the exact positions of the maxima in the Debije-Scherrer rings starting from this period. These positions are indicated in Fig. 5 by the small black dots. Broken lines drawn through these dots indicate the theoretical layer-line positions.

It is striking that the observed positions of the maxima are all at somewhat greater distance from the equator than the positions corresponding to a period of 10.6 Å and, accordingly, that all fibre periods derived from the observed positions are somewhat shorter than the supposed true period. One may wonder at the cause of this phenomenon.

We thought it likely that the phenomenon is caused by the fact that the directions of the b axes of the crystallites are scattered through a rather great angle. This might effect an elongation of the arcs of increased intensity along the reflection rings that is greater in the direction of the meridian than it is in the direction of the equator. Thus the estimated centres of the arcs would undergo a slight displacement in the direction of the meridian as compared to their positions in the case of perfect orientation of the b axis. The supposition may be elucidated by the following considerations.

Let us suppose the directions of the b axis to be regularly scattered through an angle 2ε. Indicated by lines joining in a given point, the directions form a conus with a vertical angle 2ε. Let us call the axis of this conus the fibre direction and let the incident beam be perpendicular to that direction.

It will be clear that if the b-axis were oriented perfectly parallel to the fibre direction, sharply defined spots would be formed on the photograph. We shall now consider how these spots are drawn out into arcs by deviations of the direction of the b-axis from the fibre direction, first by deviations in a plane perpendicular to the incident beam and then in a plane parallel to the incident beam and the fibre direction.

It will be recognised that in the first case deviations of b from the fibre direction up to $+\varepsilon$ and $-\varepsilon$ degrees will result in elongation of the spots into arcs stretching over ε degrees on both sides of the original places of the spots, along the reflection rings corresponding to the spacings in question in the case of a powder specimen.

Since the elongations to both sides are equal, the centres of the arcs will coincide with the spots appearing at perfect orientation. Hence the deviations of the b-axis from the fibre direction in a plane perpendicular to the incident beam cannot explain the displacement of the centres of the arcs.

The effect of the deviations in the plane parallel to the incident beam and the fibre direction is more difficult to interpret. For that purpose it is convenient to make use of the reciprocal lattice and reflectation sphere.

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For details concerning these concepts we must refer to the textbooks on X-ray crystallography.

In Fig. 6 a plane is represented that contains the origin O of the reciprocal lattice and the fibre axis. O is at a distance λ, *i.e.* the radius of the reflection sphere, from the centre of the reflection sphere M in the specimen. The specimen and centre of the reflection sphere are not shown. Directions of the reciprocal b-axis (b^*) in the plane under consideration are drawn parallel to the fibre axis and at angles of $+\varepsilon$ and $-\varepsilon$ degrees.

Furthermore we have indicated for the different directions of b^* the projections of the reciprocal lattice plane containing the points hkl on the plane under consideration. The reciprocal lattice plane projects itself as a line because it is normal to b^*.

The broken lines are projections of the circles of intersection of the reflection sphere and the coni of diffracted radiation that arise in a powder specimen of B-starch from the spacings reflecting in the first layer line in the fibre diagram. These are the spacings 2a, 3a, 4 and 6b, *cf.* Table I. The projections of the circles belonging to spacings reflecting in other layer lines have not been drawn since this is unnecessary for our purpose. The figure is drawn in the right proportions.

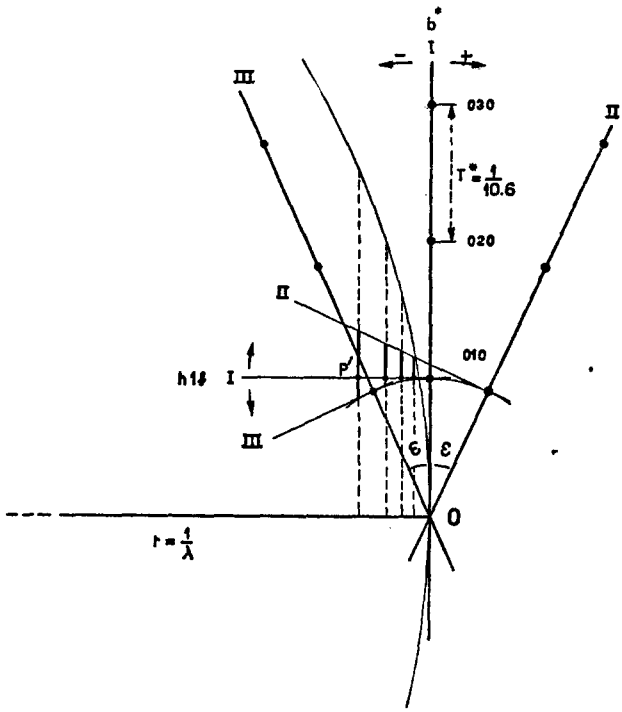

Fig. 6. Diagram explaining the difference between the observed and theoretical layer-line positions in Fig. 5

If, now, b^* is in position I—and the reciprocal lattice takes up all positions arising on rotation around b, as is the case in a fibre specimen—it is known that the diffracted radiation of the spacings (hkl) passes the reflection sphere in the places where the points hkl of the reciprocal lattice penetrate the reflection sphere on rotation around b^*. For a given point hkl the place of penetration, P, must of course lie on the circle of intersection of the reflection sphere and the conus of radiation belonging to the spacing (hkl) in the case of a powder specimen of the substance under consideration. In our drawing the projection P' of this place on the plane under consideration is at the crossing of the projection of the "powder circle" and the line representing the projection of the reciprocal lattice plane containing the points hkl.

It will be clear that if b^* is moved through an angle $+\varepsilon$ into the position II, P' moves along the projection of the powder circle upwards, and if b^* is moved through an angle $-\varepsilon$ into the position III, P' moves downwards.

It appears from the drawing that for an angle of deviation $+\varepsilon$ of b^* from the fibre direction the upward displacement of P' is much greater than the downward displacement for an angle of deviation $-\varepsilon$. Of course a difference in displacement also appears for P on the reflection sphere and for the place in which the produced part of MP incides upon the film. In Fig. 6 the drawn parts of the projections of the powder circles indicate the stretches over which the points P' for each reflection move up and downwards.

Thus it may be shown that in the plane under consideration deviations of the b axis from perfect orientation result in a non-symmetrical elongation into arcs of the diffraction spots appearing at perfect orientation. The upward elongation is greater than the downward—the reverse is, of course, true for spots below the equator, and the elongation is symmetrical for spots on the equator—, which must cause a displacement of the centre of the spot away from the equator.

The fibre period of 10.6 Å is in accordance with that found by RUNDLE *et al.*[4] in their artificial amylose threads showing B-starch spectra.

SENTI AND WITNAUER[8] have obtained fibre diagrams of artificial amylose threads

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showing the A-starch spectrum, which yield the same fibre period. However, suggestions on the basis of these diagrams concerning the dimensions of the unit cell for the A modification of starch have not hitherto been made.

The spacings in the basal plane mentioned by RUNDLE *et al.*[4] for B-amylose viz. 9.2 Å and 16 Å, are slightly different from those we found for B-starch (9 Å and 15.6 Å). Also the indices of certain spacings mentioned by these authors are different from those we have assigned.

Meanwhile it should be noticed that although the spacings of B-starch can be indexed from an orthorhombic unit cell of dimensions as mentioned above, the possibility remains that this unit does not represent the actual cell. In this connection it is striking that the ratio of the axes in the basal plane is $\sqrt{3}:1$. This is the ratio of the orthorhombic axes in the basal plane of a hexagonal unit cell. Hence, there is a good reason to suspect that the cell has to be outlined as a hexagonal or rhombohedral one. Further on in this paper (section 6) we shall return to this point.

4. FIBRE PERIOD AND CHAIN CONFIGURATION

From the foregoing it will be clear that there is little doubt as to the correctness of the fibre period found, and it will now be discussed what chain configuration might explain this period. Let us for that purpose first reproduce in Fig. 7 the structural formulae generally accepted at present for starch and cellulose chains. For references and details *cf. e.g.* MEYER[9].

The starch chain is considered to consist of α-glucose residues. In these the glucosidic oxygen bonds project from the ring on the same side and consequently take up a "cis" position with reference to the plane of the ring.

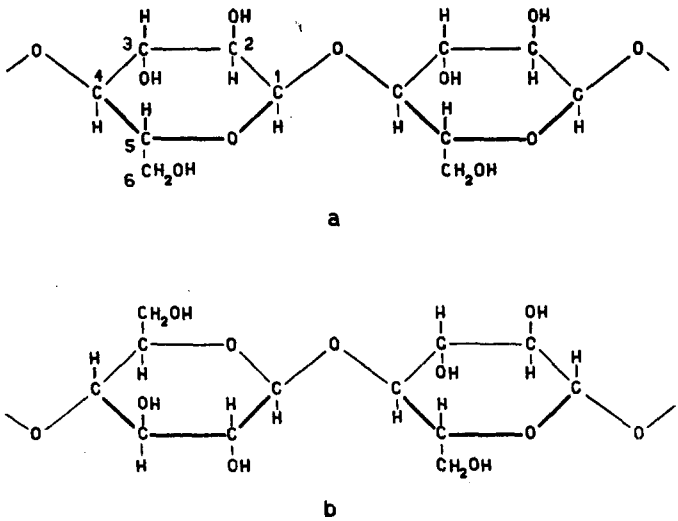

Fig. 7. Structural formulae of starch (a) and cellulose (b)

The cellulose chain consists of β-glucose residues. In these the glucosidic oxygen bonds project to opposite sides from the ring and take up a "trans"position with reference

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to the plane of the ring. On account of the "trans"-position in the latter case, the successive glucose residues in the cellulose structure are linked in digonal screw axis.

These structural formulae leave room for various configurational possibilities, and to elucidate our views concerning the starch configuration we will start from what is known of cellulose.

The configuration of the pyranose ring is of particular interest. A flat ring is inconsistent with the normal interbond angles and interatomic distances. Of several possibilities for the form of the ring the well-known strainless so-called armchair form (*cf.* Fig. 8) is at present accepted by most investigators in this field.

ASTBURY[10, 11], in connection with his study of alginic acid, has drawn attention to the fact that pyranose rings in the armchair form, linked by oxygen atoms in the "trans"-position, as in cellulose, may theoretically form two essentially different configurations of straight chains, because for the glucosidic oxygen bonds there are two directions possible with reference to the plane of the ring. In Fig. 8 these configurations are shown

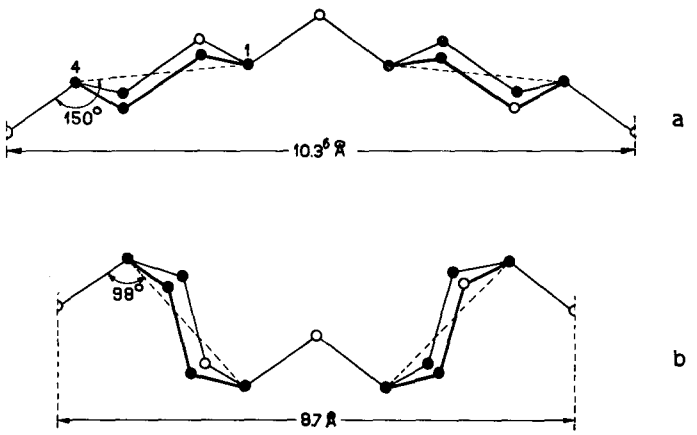

Fig. 8. Diagrams of the two configurational possibilities of straight strainless chains of β-glucose residues. Only the pyranose rings and the glucosidic oxygen atoms are drawn. Further explanation in the text

as constructed in the right proportions on the bases of theoretical principles to be mentioned below. In this construction, for the sake of simplicity, the ring oxygen atom is taken as a carbon atom, and in the following considerations the fact that it is actually smaller is neglected. For each configuration one chain period is shown. The centres of carbon atoms and oxygen atoms are indicated by black dots and white circles respectively. Broken lines have been drawn between the carbon atoms 1 and 4 of the rings. The difference between the chains may be sufficiently clear from the figures.

It will be understood that these chains proceed in a constant direction because the glucosidic oxygen bonds in C_1 and C_4 meet the line joining C_1 and C_4 at the same angles. Constructed on the basis of theoretical principles, *i.e.* bond lengths C — C = 1.54 Å and C — O = 1.42 Å, the tetra-hedral angle for the carbon bonds and 110° for the oxygen bonds (PAULING[12]), we find for type *a* a fibre period of 10.36 Å and for type *b* of 8.7 Å. The former period is in close agreement with the fibre period found in cellulose (10.3 Å), the latter with that mentioned by ASTBURY for alginic acid (8.7 Å). Hence, the fibre periods of cellulose and alginic acid both containing pyranose rings linked by oxygen

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atoms in the "trans"-position can be understood without any difficulty on theoretical grounds.

At first sight more difficulties seem to arise when we try to understand the fibre period of starch from α-glucose residues. The pyranose ring with its glucosidic oxygen bonds for α-glucose in the strainless configuration, *i.e.* based on the same principles as mentioned before for the pyranose rings in β-glucose units, is constructed in Fig. 9a and b. As in β-glucose there are theoretically two possibilities. In each of these configurations, one of the glucosidic oxygen bonds meets the line joining C_1 and C_4 at angles as in Fig. 8a, the other as in Fig. 8b. Hence, in both configurations the distance between the glucosidic oxygen atoms is the same. And it will be evident that in order to explain the fibre period it is of no importance from which of these configurations we start.

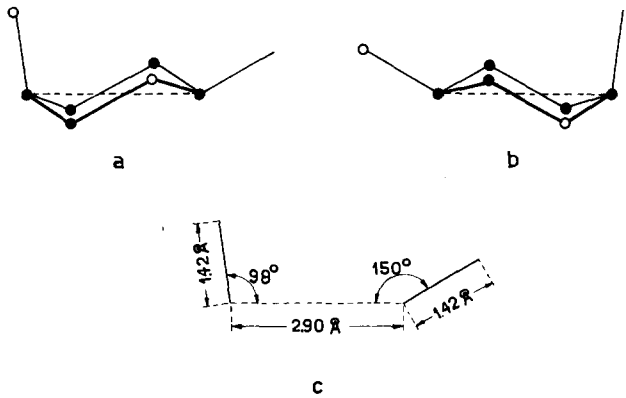

Fig. 9. Two possibilities of configuration of the pyranose ring in α-glucose residues (a and b) and the schematic α-glucose residue (c) used for the construction of the starch-chain configurations presented in Fig. 10 and 11

The problem of understanding the starch fibre period may now be reduced to the question how flat units of a shape as given in Fig. 9c can be arranged to form chains running forward in a constant direction with a period of 10.6 Å. It appears that a chain of these units, one linked to the other in the same position, is inconsistent with a bond angle of 110° in the glucosidic oxygen atom and does not yield a fibre period of 10.6 Å. Even though the units can be arranged to form straight strainless chains with two units in the period—*cf.* Fig. 10—, the periods of these chains do not reach 10.6 Å either.

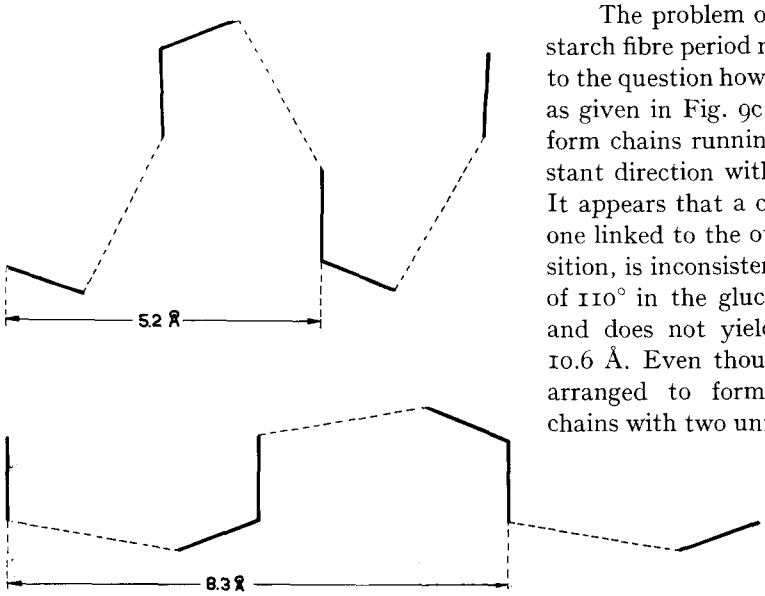

Fig. 10. Two possibilities of "flat" straight strainless chains with two of the units presented in Fig. 9c in the period

Without departing from the principle of strainlessness, it appears impossible to reach in any other way with one or two α-glucose units per period a period of 10.6 Å.

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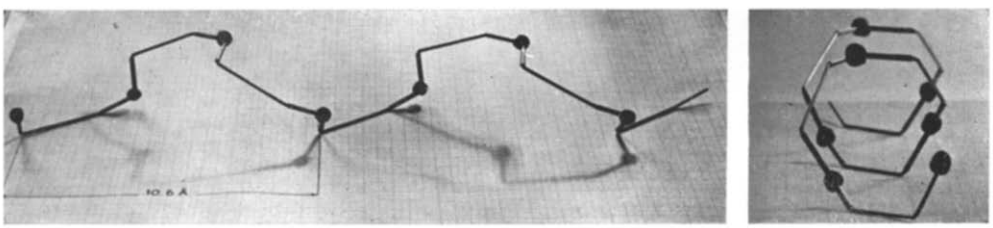
Therefore we tried if it might be reached by three units. It was then found that without any departure from the conditions required, this period can be reached if the units are arranged in such a way that the chain possesses a three-fold screw axis. This can be done by rotation of the units about the glucosidic oxygen bonds. This is shown in Fig. 11a by a wire model built up from the schematic α-glucose units of Fig. 9c constructed to scale. For the sake of clearness the centres of the glucosidic oxygen atoms are marked by small balls. The model shows $2^1/_3$ period and it represents a left hand spiral. Of course its reflected image, *i.e.* a right hand spiral, can be constructed equally well. In Fig. 11b the three-fold symmetry of the model appears more clearly.

Meanwhile, a spiral configuration in starch resulting from the α-linkage of glucose units in the "armchair"-form has been put forward by CAESAR AND CUSHING[13]. A spiral configurations for starch chains consisting of α-glucose residues in the "bed"-form has been suggested by FREUDENBERG *et al.*[14]. HANES[15] has also proposed a spiral structure to explain the breakdown of the chains by α-amylase. These spirals, however, contain six glucose residues in the period. As regards native starch, a spiral structure with six glucose residues in the period has to be rejected. For although such a spiral may be



a b

Fig. 11. Model showing that the schematic α-glucose units of Fig. 9c, if linked in threefold screw symmetry, permit a strainless chain to be constructed with a period of 10.6 Å running forward in a constant direction. a. The chain in side view; b. The chain seen at a small angle to the direction of the axis. The model represents a left-hand spiral. $2^1/_3$ periods are shown

compressed or stretched so as to yield a period of 10.6 Å, its diameter would then grow to dimensions inconsistent with the equatorial spacings, and it would not allow a packing to be realised consistent with the experimental density of starch grains discussed further on. However, starch precipitated by alcohol, *i.e.* the "V"-modification according to KATZ *et al.*, appears to yield X-ray and optical evidence in favour of a spiral configuration with six glucose residues per turn (RUNDLE AND EDWARDS[16]). This structure might also occur in solution. It will be clear, therefore, that our conception of the spiral structure in grains is not contradictory to HANES' explanation of the action of α-amylase on starch chains in solution.

In order to complete our picture of the chain configuration we now have to replace the schematic wire units by α-glucose residues in either one of the configurations *a* or *b* of Fig. 9. For that purpose we used flat cardboard models representing the projection of α-glucose residues without the glucosidic oxygen atoms on a plane parallel to the lines C_1–C_4 and C_3–C_5 of the pyranose ring. As glucosidic oxygen atoms separate discs were used. Hydrogen atoms have been omitted. Up to the present ball models have not been built.

The flat models were attached to a copper wire bent to the shape represented in

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Fig. 11. In this manner chain models are obtained as shown in Fig. 12. Chain *a* is built up of α-glucose residues in configuration *a* of Fig. 9, chain *b* of those in configuration *b* of Fig. 9. White discs represent oxygen atoms. Black and grey discs are carbon atoms; grey if they lie "on top" in the ring, black if they lie "underneath". Two periods and a glucosidic oxygen atom of the next one are shown.

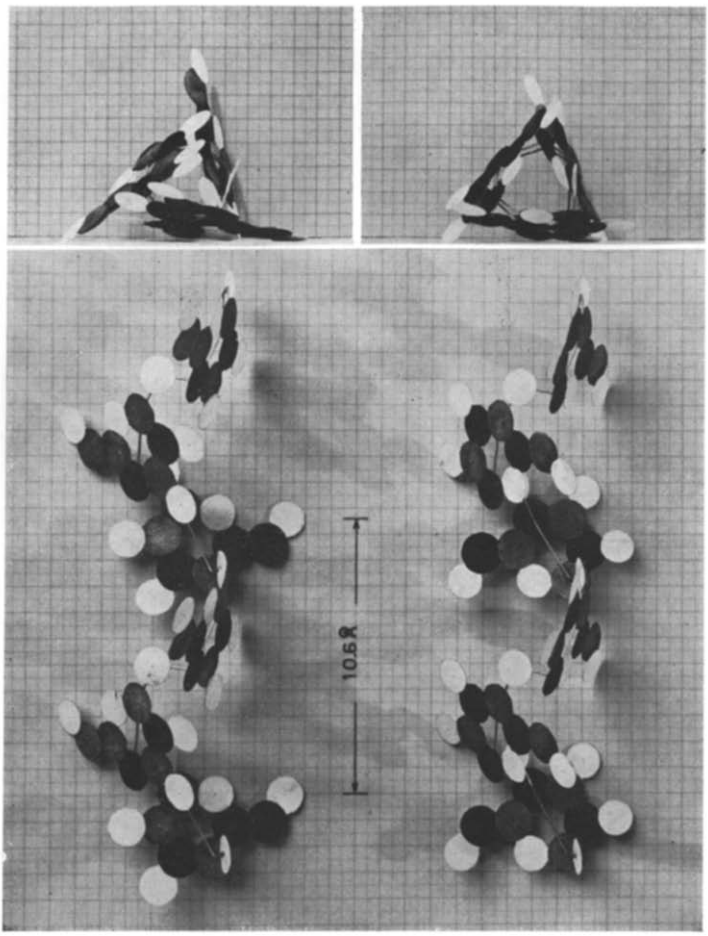

Fig. 12. More complete chain models based on the left-hand spiral shown in Fig. 11, and their projections along the axis. a. Chain of α-glucose residues based on the ring configuration a in Fig. 9; b. Chain of α-glucose residues based on the ring configuration b in Fig. 9

The projections of the chains along their axes are also represented in Fig. 12. The projection of chain *a* fits in a triangle with sides of about 9–10 Å, that of chain *b* in a triangle with sides of about 7.5–8.5 Å.

Finally it should be noted that two further configurations arise if a right-hand spiral is chosen instead of the left-hand spiral pictured in Fig. 11. One might suppose that the configurations then obtained are the reflected images of those already shown.

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This is not the case, however. For although the wire model to which the α-glucose residues have to be attached is the reflected image of that pictured in Fig. 11, the glucose residues themselves must remain the same because the reflected image of the glucose residue does not represent the α-d-glucose residue characteristic of starch but its optical antipode.

For both the *a* and *b* type of pyranose ring (Fig. 9) the projections of the right-hand spiral chain on the basal plane fits in a triangle of side somewhat different from that belonging to the projection of the chain with a left-hand spiral. The projection of a right-hand chain of glucose residues with the ring configuration *a* of Fig. 9 fits in a triangle of sides 7.5–8.5 Å, that of a chain of glucose residues with the ring configuration *b* fits in a triangle of sides 8.5–9.5 Å.

One might distinguish the four possible configurations as a_l, a_r, b_l and b_r respectively, depending on whether left-hand (Fig. 12) or right-hand spirals are meant.

5. THE DOUBLE REFRACTION OF STARCH GRAINS

It is known that starch grains, when examined under the polarising microscope between the crossed nicols, show a spherite cross. After inserting a gypsum platelet red I with the long axis n'γ of the effective refractive index ellips in the diagonal position, the bright sectors of the grain parallel to n'γ show the blue addition colour and those perpendicular to it appear in the yellow subtraction colour. This can be understood if it is assumed that in the starch grains uni-axially and positively birefringent micells are oriented with the long axis of the index ellipsoid in radial position.

In cellulose micells the direction of the long axis of the index ellipsoid is parallel to the direction of the chain molecules. And, on account of the fundamental agreement between starch and cellulose chains as regards their chemical structure, it has been assumed also for starch that the long axis of the index ellipsoid is parallel to the chain direction.

Hence, on account of their optical behaviour, it has been assumed that in the starch grains the micells are oriented with the chains in the radial directions. For references *cf.* MEYER[10]. The assumption is confirmed by our fibre diagram of part of a starch grain.

NOW, HANES[15], FREUDENBERG *et al.*[14] and CAESAR AND CUSHING[13]—on grounds acceptable with reference to native starch as long as no fibre diagram of the substance was available—have proposed spiral models for the starch chain with six glucose residues per turn. In these spirals the axis of the chain forms an angle much greater than 45° with the axis of the spiral. Therefore, if a similar configuration should appear in native starch, the direction of the chains would be nearly tangential with reference to the starch grains. As FREY-WYSSLING[17] points out, on account of this tangential direction one should expect the long axis of the index ellipsoid to be oriented tangentially in the grains, and this is not in agreement with the facts.

To meet this inconsistency of the spiral chain models proposed by the authors mentioned above and the observed optical behaviour of the starch grains FREY-WYSSLING has suggested that the spherite cross of starch might be due to tension birefringence and that it gives no information about the orientation of submicroscopic elements. FREY-WYSSLING gives support to this opinion by the fact that on conoscopic observation of grains crushed under a cover glass no spherite cross is observed.

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However, it is known that under pressure the crystalline regions in starch grains are easily disturbed; the rings of the X-ray diagram pass into diffuse haloes if the grains are ground in a mortar. And on account of the ramification of the amylopectine complete molecular disorder and anisotropy may arise in crushed grains. Therefore, in our opinion, the absence of a spherite cross in such preparations is no proof that in the native grains we have to do with tension birefringence.

Furthermore it will be clear from Fig. 12 that in a spiral configuration of the chains with three glucose residues per turn and a period of 10.6 Å, the direction of the chain axis forms an angle smaller than 45° with the spiral axis. On account of this configuration we may therefore indeed expect a radial orientation of the long axis of the index ellipsoid for the micells in native grains. For this spiral, the birefringence may be expected to be considerably smaller, however, than it is for the stretched chains of glucose residues present in cellulose.

Now, according to FREY-WYSSLING[17], the intrinsic positive double refraction of air-dry starch grains is about one quarter of the intrinsic double refraction of cellulose. It may be clear therefore that the optical behaviour of starch grains is in harmony with our new conception of the chain configuration in native starch, whereas it is not explained by spirals with six glucose residues per turn—the long axis of the index ellipsoid would then be oriented tangentially—, nor by a stretched chain as proposed by RUNDLE *et al.*[4] and formerly also by KREGER[1], for in that case the double refraction may be expected to be stronger.

6. THE PACKING OF THE CHAINS

The next point to be considered is how the spiral chains with three α-glucose residues per period can fill a unit cell of dimensions as mentioned before. For that purpose we must first consider the density of starch. Very accurate determinations in this respect were carried out by RODEWALD[18]. Very thoroughly dried starch (what kind of starch is not mentioned by RODEWALD) was found to have a density of 1.43 g/ccm when determined under chloroform or petroleum ether and of 1.60–1.63 g/ccm when determined under water. The increased value of the latter density must probably be ascribed to the fact that under water the starch crystallizes and water is taken up in the lattice.

It will be clear that the experimental densities must be expected to be lower than the X-ray density, because only part of the starch is crystallized and the rest will show a less orderly and, hence, a less dense packing.

If now the X-ray density is calculated for 2, 3 or 4 chains running through the unit cell, *i.e.* for a cell of the dimensions mentioned in section 3b containing 6, 9 or 12 glucose residues respectively, either without water or containing one water molecule per glucose residue, the following densities are found:

without water: 1.08 – 1.62 – 2.16 g/ccm.
with water: 1.20 – 1.80 – 2.40 g/ccm.

Independent of whether the densities with or without water are considered, it appears from these values that if three chains are running through the cell, the experimental density is about 10% lower than the X-ray density, and this difference could

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be expected. In the other cases, however, the density differs too much from the experimental density to regard these as true possibilities.

We must now consider how three chains with basal projections fitting in triangles of side either 9–10 Å or 7.5–8.5 Å, can fill a unit cell with a basal plane of 15.6 by 9.0 Å. This is found to be impossible. In fact an arrangement is possible in which three chains, or rather 2 chains and 2 half chains, run through a similar area, but it can not be repeated in the axial directions. It is therefore likely that the unit cell has to be chosen as a multiple of that calculated previously. And, in addition, on account of the threefold symmetry of the chains and the hexagonal ratio of the above-mentioned axes, already noted before, it is most likely that we are dealing with a hexagonal (or trigonal) unit cell.

In such a cell with axis $a = 18.0$ Å in the basal plane, *i.e.* twice the axis a of the provisional cell, the spirals can indeed be arranged in such a manner that two chains

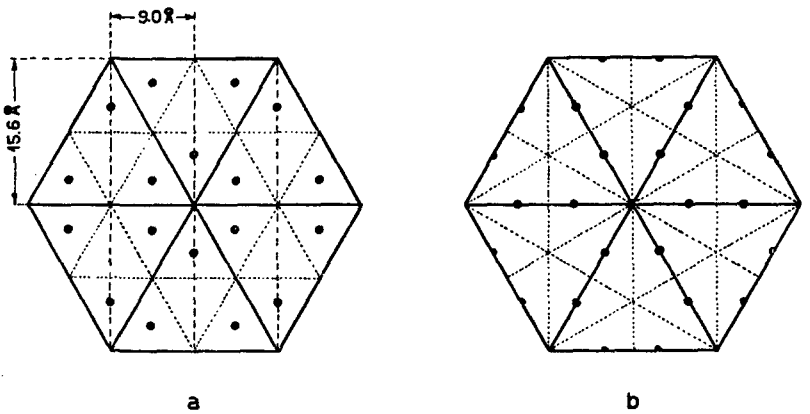

Fig. 13. Two possibilities for the packing of the chains in accordance with the spacings observed and consistent with the experimental density of native starch. Black dots indicate the positions of the chain axes

and two half chains run through a space equal to that of the provisional cell, so that the density is consistent with the experimental density. Two possibilities are shown in Fig. 13a and b. In these figures the basal plane of the hexagonal cell is divided into triangles in two manners. The dimensions of the triangles are sufficiently large to contain the projection of either chain b_l or a_r (Fig. 13a), or each of the four types of chains possible (Fig. 13b). The supposed positions of the spiral axes are marked by black dots in both cases.

At the present state of the problem of packing of the chains we must end with the following remarks. The type of arrangement of Fig. 13a might explain the appearance of an equatorial spacing of 4.5 Å, rather than that of Fig. 13b. This might give some indication that at least for the B-modification of starch we have to deal with chains of the configurational type b_l or a_r arranged as in Fig. 13a, even though it is remarkable that no equatorial spacing of 9.0 Å can be observed. But it is, of course, a matter of further investigation whether such packings may explain the intensities and which space group is the most probable one. Interest also centres upon the question whether the

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occurence of the A and B-modification in native starch is connected with the fact that 4 chain configurations are possible.

Finally, in reply to RUNDLE's letter[5], the following may be remarked.

We fully admit that in our letters it was not the first time that a fibre period for starch in the B-modification derived from fibre diagrams could be mentioned. The absence of references in these letters to the papers of RUNDLE *et al.*[4] and of SENTI AND WITNAUER[8] is due to the fact that, when our first letter appeared, we were ignorant of these papers owing to post-war conditions. The second letter, at the request of the editors of *Nature*, has been abridged to a statement of the utmost brevity. Therefore these references, though initially mentioned, have been omitted.

Furthermore, we agree that if the B-modification does indeed contain *two* water molecules per glucose residue in the crystalline portions, the X-ray density of the structure suggested first by RUNDLE *et al.* would be 1.67 for a unit cell of dimensions as calculated by RUNDLE *et al.* For a unit cell of the dimensions we have calculated (section 3b) it would become 1.76. And these values are in satisfactory agreement indeed with the observed density of starch under water of 1.60–1.63. But the packings of spiral chains with three glucose residues per period and *one* water molecule per residue as we have proposed, satisfy the observed density equally well. And there is no conclusive evidence for the presence of *two* water molecules per glucose residue.

We also agree that the difficulty of understanding the fibre period of starch has been discussed before by RUNDLE *et al.* But this difficulty has not been solved by these authors, whereas from the configuration we have proposed the fibre period can be understood without any difficulty. In addition, this configuration explains the hexagonal ratio of the equatorial spacings and is in satisfactory agreement with the intrinsic birefringence of starch mentioned by FREY-WYSSLING[17]. We therefore do not see any reason to adhere to the chain configuration suggested by RUNDLE *et al.*[4], also accepted in our letter of 1946[1].

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Prof. G. VAN ITERSON Jr for his stimulating interest in this work. His thanks are due also to Prof. H. B. DORGELO for hospitality in the laboratory of Technical Physics and for his interest shown, as well as to his colleages of the Delft X-ray group for valuable discussions on the subject.

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SUMMARY

To elucidate the crystal structure of native starch, an X-ray fibre diagram of the substance is indispensable. On account of the smallness of the starch grains and the radial orientation of their crystallites, the usual techniques for X-ray diffraction are unsuitable for obtaining such a diagram from the grains. For that purpose a micro-technique enabling part of a grain to be irradiated by a narrow X-ray pencil is required.

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By means of a new micro-method for X-ray diffraction[3, 6]—not described in this communication—a fibre diagram of a native starch grain could be obtained for the first time from part of a starch grain of the large type occurring in the orchid *Phajus grandifolius*.

This result and the conclusions drawn from the diagram were published briefly in earlier papers[1, 2]. The present paper is a more detailed account, and at the end an answer is given to the remarks made by RUNDLE[5] with regard to the above-mentioned papers.

The fibre diagram obtained yields conclusive evidence that in starch grains, according to the assumptions made on the basis of their optical behaviour, the chain molecules are oriented radially.

The powder diagram of *Phajus* starch is almost identical with that of potato starch. Its crystalline modification is therefore the B-modification according to KATZ AND VAN ITALLIE[7].

The fibre diagram obtained may be indexed provisionally on the basis of an orthorhombic unit cell with axes: $a = 9.0$ Å, b (fibre period) $= 10.6$ Å, $c = 15.6$ Å. The dimensions of a and c axes are slightly different from those calculated by RUNDLE *et al.*[4] from a fibre diagram obtained from artificial threads of the amylose fraction of native starch yielding the same—but possibly on account of this difference not quite the same—X-ray spacings as native starch in the B-modification.

The difficulty of understanding the fibre period from a chain of α-glucose residues, already mentioned by RUNDLE *et al.*[4], has been discussed. It appears that the period can be understood without any difficulty from a spiral chain with three α-glucose residues per turn, whereas important objections can be raised against the configuration with two glucose residues per period proposed before by RUNDLE *et al.*[4], and independently by the present author in 1946[1].

Also spiral configurations for starch with six glucose residues per turn, as proposed by HANES[15], FREUDENBERG *et al.*[14] and CAESAR AND CUSHING[13] cannot be present in native starch in the B-modification.

It is shown that four different spiral configurations of chains with three α-*d*-glucose residues per turn can be built up.

A spiral configuration with three glucose residues per turn not only explains the fibre period, but also the hexagonal ratio of the axes in the basal plane of the provisional unit cell and the intrinsic birefringence of starch grains mentioned by FREY-WYSSLING[17].

The spiral chains cannot be packed in the provisional unit cell in such a manner that the X-ray density is consistent with observed experimental densities of native starch. Therefore, and on account of the hexagonal ratio of the axes in the basal plane, a hexagonal unit cell is suggested with $a = 18$ Å and $b = 10.6$ Å, through which 18 chains are running; *i.e.* the cell contains 54 glucose residues and water molecules. The X-ray density of such a packing is consistent with observed densities of starch grains.

RÉSUMÉ

Pour élucider la structure cristalline de l'amidon natif il faut disposer d'un diagramme de rayons-X de fibre de cette substance. A cause des dimensions réduites des grains d'amidon et de l'orientation radiale de leurs cristallites les techniques habituelles de diffraction des rayons-X ne permettent pas d'obtenir un tel diagramme des grains. A cet effet une microtechnique est nécessaire, permettant d'irradier une partie d'un grain par un faisceau étroit de rayons-X.

A l'aide d'une nouvelle micro-méthode de diffraction des rayons-X[3, 6] (méthode que nous ne décrivons pas dans cette communication) nous avons pu obtenir pour la première fois un diagramme de fibre d'un grain d'amidon natif. Nous nous sommes servi pour cela d'une partie d'un grain du type à grosses dimensions que l'on trouve chez l'orchidée *Phajus grandifolius*.

Nous avons publié ce résultat et les conclusions que l'on peut tirer du diagramme ainsi obtenu dans deux communications précédentes[1, 2]. La présente communication représente un compte-rendu plus detaillé et contient également une réponse aux remarques faites par RUNDLE[5] aux sujets de nos publications antérieures.

L'orientation radiale des molécules à chaîne dans les grains, supposée précédemment à cause des propriétés optiques des grains, est maintenant démontrée par notre diagramme de façon définitive.

Le diagramme de poudre d'amidon de *Phajus* est à peu près identique à celui d'amidon de pomme-de terre. Sa modification cristalline est donc la modification-B d'après KATZ ET VAN ITALLIE[7].

L'on peut dériver provisoirement de notre diagramme une maille élémentaire orthorhombique aux axes: $a = 9.0$ Å, b (période de fibre) $= 10.6$ Å, $c = 15.6$ Å. Les dimensions a et c sont légèrement différentes de celles calculées par RUNDLE *et coll.* à partir d'un diagramme de fibre obtenu de fils artificiels de la fraction amylose de l'amidon natif, fils qui donnent les mêmes —ou, d'après ces différences, peut-être pas tout-à-fait les mêmes— distances réticulaires que la modification B de l'amidon natif.

Nous avons discuté la difficulté signalée précédemment par RUNDLE *et coll.*[4] d'interpréter la période de fibre par une chaîne de restes d'α-glucose. Il paraît que l'on peut expliquer sans difficultés la période trouvée par une chaîne en forme de spirale comprenant trois restes d'α-glucose par tour,

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tandis que la configuration à deux restes de glucose par période proposée précédemment par RUNDLE *et coll.*[4] et indépendemment par l'auteur en 1946, est sujète à de sérieuses objections.

Des configurations à six restes de glucose par tour de spirale, telles que celles proposées par HANES[15], FREUDENBERG *et coll.*[14] et par CAESAR ET CUSHING[13] ne peuvent pas exister non plus dans la modification B de l'amidon natif.

Nous avons montré que l'on peut construire quatre configurations en forme de spirale à partir de chaînes comprenant trois restes d'*α-d*-glucose par tour.

Une configuration en forme de spirale contenant trois restes de glucose par tour explique non seulement la période de fibre, mais aussi le rapport hexagonal des axes dans le plan de base de la maille-unité admise provisoirement et la biréfringence intrinsèque des grains d'amidon mentionnée par FREY-WYSSLING[17].

Les chaînes en forme de spirale ne peuvent pas être disposée dans la maille élémentaire provisoirement admise de telle manière que la densité soit en accord avec les densités observées expérimentalement pour l'amidon natif. Pour cette raison et à cause du rapport hexagonal des axes du plan de base nous proposons une maille élémentaire hexagonale avec $a = 18$ Å et $b = 10.6$ Å, traversée par 18 chaînes; cela signifie que la maille contient 54 restes de glucose et molécules d'eau. La densité d'une telle disposition est en accord avec les densités observées des grains d'amidon.

ZUSAMMENFASSUNG

Zur Aufklärung der Kristallstruktur von nativer Stärke ist ein Röntgen-Faserdiagramm der Substanz unbedingt notwendig. Da die Stärkekörner klein und ihre Kristallite radial angeordnet sind, kann man mit den üblichen Aufnahmeverfahren der Röntgenspektrographie solche Diagramme von den Körnern nicht erhalten. Man benötigt dazu eine Mikromethode, welche erlaubt, einen Teil eines Stärkekornes mit einem sehr feinen Röntgenbündel zu bestrahlen.

Mit Hilfe einer neuen röntgenographischen Mikromethode[3, 6], die hier nicht beschrieben wird, konnte zum ersten Mal ein Faserdiagramm eines nativen Stärkekornes durch Bestrahlung eines Teiles von einem der grossen Stärkekörner der Orchidee *Phajus grandifolius* erhalten werden.

Dieses Ergebnis und die davon abgeleiteten Folgerungen wurden schon früher in Kürze veröffentlicht[1, 2]. Die vorliegende Mitteilung ist ein eingehender Bericht und beantwortet ausserdem die zu der obenerwähnten kurzen Mitteilungen erschienenen Bemerkungen von RUNDLE[5].

Das erhaltene Faserdiagramm liefert einen endgültigen Beweis dafür, dass in den Stärkekörnern die Kettenmoleküle radial angeordnet sind, wie schon früher auf Grund ihrer optischen Eigenschaften angenommen worden war.

Das Pulverdiagramm von *Phajus*-Stärke ist fast identisch mit demjenigen von Kartoffelstärke. Seine Kristallform entspricht daher der B-Modifikation nach KATZ UND VAN ITALLIE[7].

Das Faserdiagramm kann vorläufig indiziert werden auf Grund einer orthorhomischen Elementarzelle mit Achsen $a = 9.0$ Å, b (Faserperiode) $= 10.6$ Å, $c = 15.6$ Å. Die Achsenlängen a und c sind ein wenig verschieden von den Werten, die RUNDLE und Mitarb. berechnet haben aus einem Faserdiagramm das sie erhielten von künstlichen Fäden aus der Amylosefraktion der nativen Stärke, welche dieselben (aber möglicherweise auf Grund dieses Unterschiedes nicht *ganz* dieselben) Netzebenenabstände aufweisen wie native Stärke in der B-Modifikation.

Die schon von RUNDLE und Mitarb. erwähnte Schwierigkeit, die Faserperiode durch eine Kette von α-Glucoseresten zu erklären, wird erörtert. Es geht hervor dass die Faserperiode ohne Schwierigkeit durch eine spiralförmige Kette von drei Glucoseresten per Windung erklärt werden kann, während gegen die von RUNDLE und Mitarb.[4] und unabhängig von diesen auch vom Verfasser im Jahre 1946 vorgeschlagene Konfiguration von zwei Glucoseresten per Periode wichtige Einsprüche erhoben werden können.

Spiralkonfigurationen mit sechs Glucoseresten per Windung, wie sie von HANES[15], von FREUDENBERG und Mitarb.[14] und von CAESAR UND CUSHING[13] vorgeschlagen wurden, können nicht in nativer Stärke in der B-Modifikation vorkommen.

Es wird gezeigt, dass man aus Ketten von *α-d*-Glucose-Resten vier verschiedene Spiralkonfigurationen mit je drei Glucoseresten per Windung aufbauen kann.

Eine Spiralkonfiguration mit drei Glucoseresten per Windung erklärt nicht nur die Faserperiode, sondern auch das hexagonale Achsenverhältnis in der Grundebene der vorläufig angenommenen Elementarzelle und die von FREY-WYSSLING[17] erwähnte Eigendoppelbrechnung der Stärkekörner.

Die Spiralketten können in der angenommenen Elementarzelle nicht so angeordnet werden, dass die Dichte mit den experimentell beobachteten Dichten von nativer Stärke übereinstimmt. Aus diesem Grunde und wegen des hexagonalen Achsenverhältisses in der Grundebene, wird eine hexagonale Elementarzelle mit $a = 18$ Å und $b = 10.6$ Å vorgeschlagen, durch die 18 Ketten laufen; d.h. dass die Zelle 54 Glucosereste und Wassermoleküle enthält. Die Dichte einer solchen Anordnung ist mit den beobachteten Dichten von Stärkekörnern vereinbar.

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