SOME NOTES ON THE STRUCTURE OF B-STARCH

by

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The publication of a recent paper on the structure of starch by KREGER[1] has suggested the advisability of giving a brief report of some work on amyloses which was carried out some years ago[2] in the Department of Biomolecular Structure at Leeds under Professor W. T. ASTBURY.

The X-ray diffraction pattern of starch, it should be noted, is due to the unbranched fraction known as amylose, which can be separated from the branched-chain fraction, amylopectin, and therefore only the former is considered here, although the terms amylose and starch are used almost interchangeably.

During the course of the research it became necessary to construct skeleton chain models of the cellulose, alginic acid and amylose types. In the first two the fully-extended straight chains, as is now well known, had repeat periods containing two residues in 10.3 A and 8.7 A, respectively. It was noticed that by making suitable rotations about the bonds of the bridge oxygen atoms, straight chains could be produced having repeat periods which varied continuously between 7.2 A and 10.3 A for residues in the cellulose configuration, and between 7.2 A and 8.7 A for residues in the alginic acid configuration. It must be stressed that there were no side-groups on these models and that their presence would restrict structures otherwise possible.

The situation is a little more complex in the case of amylose as two types of residue are possible; they may be considered to be derived from the cellulose and alginic acid structures and are illustrated in Figs 9b and 9a of KREGER[1]. It follows that several types of chain molecule have to be considered. Straight chains containing either type of residue may be constructed having periods lying between 5.4 A and 8.4 A. Straight chains in which the two types of residue alternative have a period of 7.2 A.

Straight chains with three or more residues in the repeating unit are rather flexible but were not investigated further because it was thought that possible configurations were not limited by the geometry of the skeleton but rather by the nature of the particular side-groups and perhaps by side-to-side packing of the chains in crystallites.

Turning to the observations on amylose itself, X-ray work on many amyloses, both natural and synthetic, emphasised that the type of diffraction pattern obtained depends more on the treatment of the material than on its source. Conversion from B to V, for example, was frequently observed. More recently it has been found that the B-starch normally present in the seta of *Pellia*[4] is converted to the V structure when the material is preserved in 70% alcohol and that the B-form may be regenerated by soaking in water for 12 hours.

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Oriented photographs of the V type were obtained from amylose prepared by Professor HIRST of Manchester. The results supported the unit cell (orthorhombic a = 13.5 A, b = 7.8 A, c = 26 A) proposed by RUNDLE AND EDWARDS[3] based on powder photographs only. The orientation, however, was unusual and indicated that the b (fibre) axis lay in the shortest dimension of tablet- or ribbon-shaped crystallites. This sort of arrangement is more consistent with the proposed helical structure than with one involving straight chains. A good B pattern was obtained from this material after it had been moistened with water and allowed to dry.

It is now fairly certain that the unit cell of the B structure is orthorhombic with a = 9 — 9.2 A, b = 10.6 A, and c = 15.6 — 16 A[1, 5], and that it contains eight or nine glucose residues and some water, though the arrangement of the residues in the unit cell is still very hypothetical. Density considerations do not appear to be very critical because there is 5% (or more) uncertainty in the volume of the unit cell, the amount of water present can be chosen as required, and there is no satisfactory method of correlating observed densities with theoretical values deduced from X-ray data. In the case of cellulose observed densities are 1.53–1.55 in toluene and 1.604–1.61 in water; the calculated value is 1.59[6]. Similar relationships would suggest a value of roughly 1.55 for the 'X-ray density' of starch. Thus KREGER's calculated value seems to be on the large side, and more reasonable values, 1.52–1.59, are obtained for a cell containing eight glucose residues and eight water molecules. These eight residues must be arranged in two chains with four residues in each repeat unit. It would be difficult to quote an accurate value for the external diameter of the chains, but a value about 8 A or 9 A would be reasonable. Two such chains would fit very well into the unit cell. This structure is not very different from that proposed for the V modification, and it is conceivable that water may stabilise the first form and the larger alcohol molecules the larger helices of the V structure. The two chains passing through each unit cell cannot be identical; there are, however, many ways in which this may be brought about: they may run in opposite directions, they may be constructed from different types of residues, or they may be enantiomorphous spirals.

While a structure of this kind does not account very well for the observed reflection intensities, it is probably as good in this respect as those proposed by KREGER and has the advantage of requiring a much smaller and simpler unit cell. The cells illustrated in Fig. 13 of KREGER's paper cannot be considered very satisfactory because in the first the distribution of chains over the base of the unit cell is very uneven and in the second the true (monoclinic) cell is too small to have a spacing of 15.6 A.

I agree with KREGER that much more work is needed to determine the space-group and details of the structure of B-amylose.

I should like to thank Professor W. T. ASTBURY, F.R.S. for permission to publish this note.

SUMMARY

1. Skeleton chain models of the cellulose, alginic acid and amylose types were constructed; the fully-extended straight chains have repeat periods, containing two residues, of 10.3 A, 8.7 A and 8.4 A, respectively. Shorter straight chains are also geometrically possible.

2. A well-oriented X-ray diffraction photograph of V-amylose supports the unit cell proposed by RUNDLE AND EDWARDS. The unusual orientation is in agreement with a helical structure.

3. A possible structure for B-starch is suggested, two chains each containing four residues in 10.6 A pass through the cell.

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RÉSUMÉ

1. Nous avons construit des modèles pour les squelettes des chaînes des types cellulose, acide alginique et amylose; les chaînes droites, tout à fait étendues, ont une période contenant deux résidues, de 10.3 A, 8.7 A et 8.4 A respectivement. Des chaînes droites, plus courtes sont également possibles géométriquement.

2. Une photographie bien orientée de diffraction de rayons-X du V-amylose est en favour de la cellule élémentaire proposée par RUNDLE ET EDWARDS. L'orientation peu commune est en accord avec une structure hélicoïdale.

3. Nous proposons une structure possible pour l'amidon-B; deux chaînes, contenant l'une et l'autre quatre restes par 10.6 A passeraient à travers la cellule.

ZUSAMMENFASSUNG

1. Modelle für das Skelett der Zellulose-, Alginsäure- und Amyloseketten wurden konstruiert; die voll ausgezogenen geraden Ketten haben Identitätsperioden welche zwei Reste enthalten, von resp. 10.3 A, 8.7 A und 8.4 A. Kürzere gerade Ketten sind auch geometrisch möglich.

2. Eine gut gerichtete X-Strahlendiffraktions-Aufnahme von V-Amylose stützt die von RUNDLE UND EDWARDS vorgeschlagene Elementarzelle. Die ungewöhnliche Orientierung stimmt mit einer Spiralstruktur überein.

3. Eine mögliche Struktur für B-Stärke wird vorgeschlagen; dabei würde die Zelle zwei Ketten umfassen die je vier Reste pro 10.6 A enthalten.

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