X-RAY AND ELECTRON MICROSCOPE STUDIES OF THE DEGRADATION OF CELLULOSE BY SULPHURIC ACID

by

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The hydrolytic action of sulphuric acid on cellulose has been extensively studied with the object of obtaining information about the degree of degradation of the cellulose chains. One of the most striking set of results is that due to NICKERSON AND HABRLE[1] who showed that the degradation induced by boiling cellulose in 2.5 N H_2SO_4 appeared to reach a limit after a certain time of treatment. Their conclusions were based on estimates of the degree of polymerisation (calculated from viscosity data). Subsequently, attempts were made to correlate their results with the appearance of the degraded cellulose under the electron microscope. Two such investigations have led to noteworthy advances in our knowledge of the texture, on the colloidal scale, of cellulose fibres. MOREHEAD[2], studying the effect of ultrasonic vibrations on normal and acid-degraded fibres, found that the former broke up into fibrils, whilst the latter gave elongated particles apparently consisting of fibrillar fragments and on closer examination appearing to be aggregates of elongated units. RANBY AND RIBI[3] were also inspired by NICKERSON AND HABRLE's results to examine in greater detail the effects produced by boiling cellulose fibres in 2.5 N H_2SO_4, and they found that after such treatment the fibres could be peptized by simple washing in water until, when the pH rose to approximately 4, a colloidal solution was formed. Such solutions were found to consist of elongated particles (aggregated, for the most part, into more complex lamellar bodies) of a size similar to MOREHEAD's units. They showed that the degraded material still gave the X-ray photograph of Cellulose I, so that the residual cellulose had not been changed in crystalline structure. These investigations are of particular importance, therefore, in their implication that the unit particles thus made evident are the cellulose crystallites themselves or their remains. Thus the acid degradation technique shows distinct possibilities of having opened the way for the settlement of all those questions concerning the size, shape, and arrangement of the crystallites which have exercised the minds of cellulose workers for over a quarter of a century.

The present investigations had their origin in an attempt to follow by X-rays the course of the degradation induced by the action of progressively more concentrated solutions of sulphuric acid to which various kinds of cellulose fibres had been exposed at 20° C. Severe "tendering", with a marked reduction in tensile strength, takes place in comparatively dilute acid; for example, after exposure for 48 h at room temperature to sulphuric acid of concentration 550 g/l, the wet strength of jute had fallen to about 6% of the value for untreated fibres. Such treatments, however, are quite ineffective in producing any fundamental change in the structure as revealed by X-rays; in fact, increasing the acid concentration to 900 g/l was still without any appreciable effect on the crystal structure, although the washed fibres were then so weak that they were almost impossible to manipulate. Further increase in the acid concentration introduced experimental difficulties which led to the abandonment of this particular line of attack, for the fibres then started to break up into fragments in the acid. Attempts to collect and wash these fragments were unsuccessful because, as the pH of the wash water rose, fragmentation increased, and at pH 3 a colloidal solution was obtained. The fibres which remained at this stage could not be examined by X-rays, since they still contained so much acid that severe charring took place on drying, and further washing only led to more complete solution. It is now clear that our treatment was leading to something of the same kind of result as was obtained by RANBY AND RIBI in their experiments with dilute acid; our technique, however, seems to give more satisfactory disintegration into the elementary particles, and it is with these that we are mainly concerned.

EXPERIMENTAL PROCEDURE

Samples of ramie and cotton, purified by the usual extraction and dilute alkali boil, were placed in sulphuric acid solutions of known concentration (x g/l) at a constant temperature (T° C) for a period of t h. (In what follows, we shall refer to such a treatment by using a symbol such as ramie (x, T, t).) The treated fibres were collected by centrifuging from the acid, and subsequent washing was carried out by repeated centrifugation after adding distilled water, the supernatant being kept for examination after each run. Even with severe acid treatments no effect, apart from some fragmentation of the fibres, was observed during the first few washings, but as the pH rose the supernatant wash-liquors became more and more opalescent, and with suitable acid treatments all trace of the original fibre structure had disappeared (and no sedimentation occurred when centrifuging at 1000 g) before neutrality had been attained. The final step in the preparatory process was to dialyse the solutions, thus obtained, against distilled water, and this could be done without precipitation even when the final pH was between 5 and 6.

For electron microscope examination the neutral colloidal solution was diluted to a suitable degree, and a specimen prepared by evaporation on the cellulose nitrate film on the specimen grid. For shadowing, a standard technique was adopted, chromium being deposited at an angle of about 14° with the surface. The density of the deposit was kept as low as possible, consistent with the development of adequate contrast, but no quantitative control was attempted. The microscope used was a Metropolitan-Vickers EM3; the accelerating voltage was 75 kV.

With ramie and cotton fibres the sulphuric acid concentrations, which are effective at 20° in leading to peptization without, at the same time, producing any change to the Cellulose II modification (see below), lie within the range from 900 to 975 g/l. The effect of 900 g/l acid is negligible in 24 h, and relatively slight after 72 h; concentrations of 985 g/l or more lead ultimately to complete solution in the acid, and if the treatment is stopped before this stage is reached the cellulose is found to be partially transformed to Cellulose II. Most of our experiments were, therefore, done with concentrations of 950 or 975 g/l. With the former, the fibres did not dissolve even in times as long as 32 days, but gave colloidal solutions when washed. It was found that the pH range within which peptization occurred was lowered when the time of acid treatment was prolonged. Similar results were obtained with the 975 g/l acid, but the time of treatment required to reach a definite state of disintegration was considerably less. The effect of increasing the temperature of the acid during treatment was also chiefly to hasten the process of disintegration; for example, somewhat similar results were found for ramie (950, 40, 24) and (950, 20, 216).

The dialysed colloidal solutions could be concentrated by evaporation and coherent films could be obtained by drying on glass surfaces previously exposed to the vapour of "Teddol compound" (dichloro-dimethyl silicone), which facilitated subsequent removal of the film from the glass. These films were transparent and rather brittle. Once dried, they could be soaked in water without disintegrating.

Electron microscope and X-ray examination. The action of the milder acid treatments was to lead to electron micrographs of the type shown in Fig. 1. The general appearance is of objects which are clearly aggregates of smaller elongated particles. The modal length of the particles is of the order of 2000 A, and their widths appear to lie between

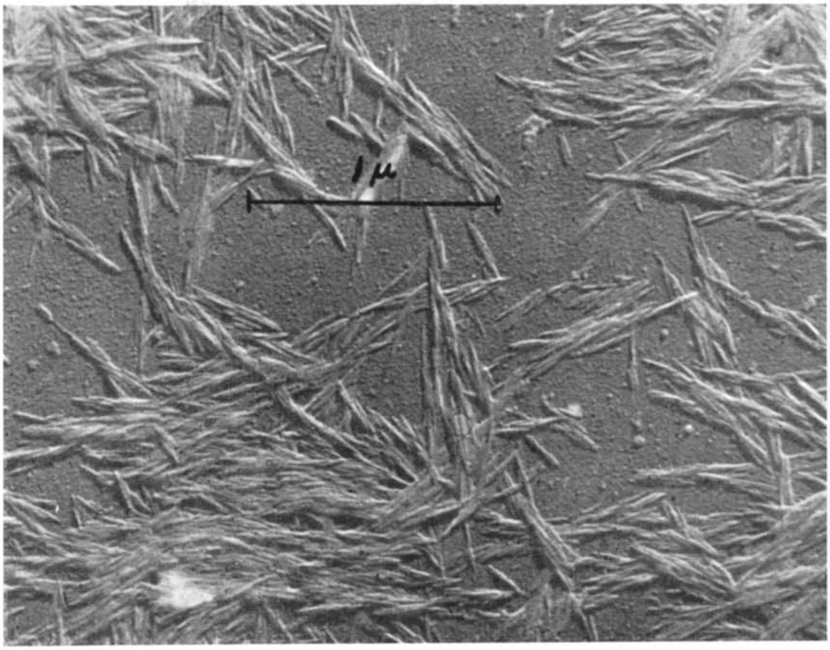

Fig. 1. Ramie, less drastic disintegration, showing aggregates of particles. Photographic magnification, X3. Chromium shadowed 1:4.

100 A and 200 A; a few isolated particles of these dimensions (or shorter in length) usually appear. The aggregates themselves are in the form of sheets not more than a few particles thick; their fine structure is particulate rather than fibrillar, and it is difficult to trace any longitudinal continuity of structure over lengths greater than a few thousand A. Very similar pictures of this stage of disintegration have been given by RANBY[1]; their interest lies in the way in which the clear picture of a fibrillar structure, with fibrils microns long at least, such as has been found by other workers using mechanical or ultrasonic methods of disintegration, is now modified by the apparent cleavage of the fibrils into much shorter lengths. Since the action of acid is to cause, in the end, hydrolytic breakdown of the cellulose chains, such an effect is, perhaps, to be expected; nevertheless, the fact that only comparatively inefficient longitudinal splitting into fibrils precedes the lateral fission into particles, is worthy of note, since interfibrillar consolidation may be supposed to be much more dependent on secondary than on primary valence bonds.

A second point of interest concerns the morphology of the aggregates which are the disintegration products of the milder acid treatments. They are, as we have said, in the form of thin sheets. When a film is formed by drying a suspension of such objects, they will, of course, tend to lie down with their surfaces parallel to the film surface. Films made in this way were found, on examination by X-rays, to be in the Cellulose I configuration, and to show very clearly the effects of the orientation tendency. In fact, the 101 planes of the cellulose crystallites tend to lie parallel to the film surface. In photographs taken with the X-ray beam perpendicular to the film (Fig. 2a) the intensity of 101 was considerably less than that of $10\bar{1}$, whereas in the normal powder photograph

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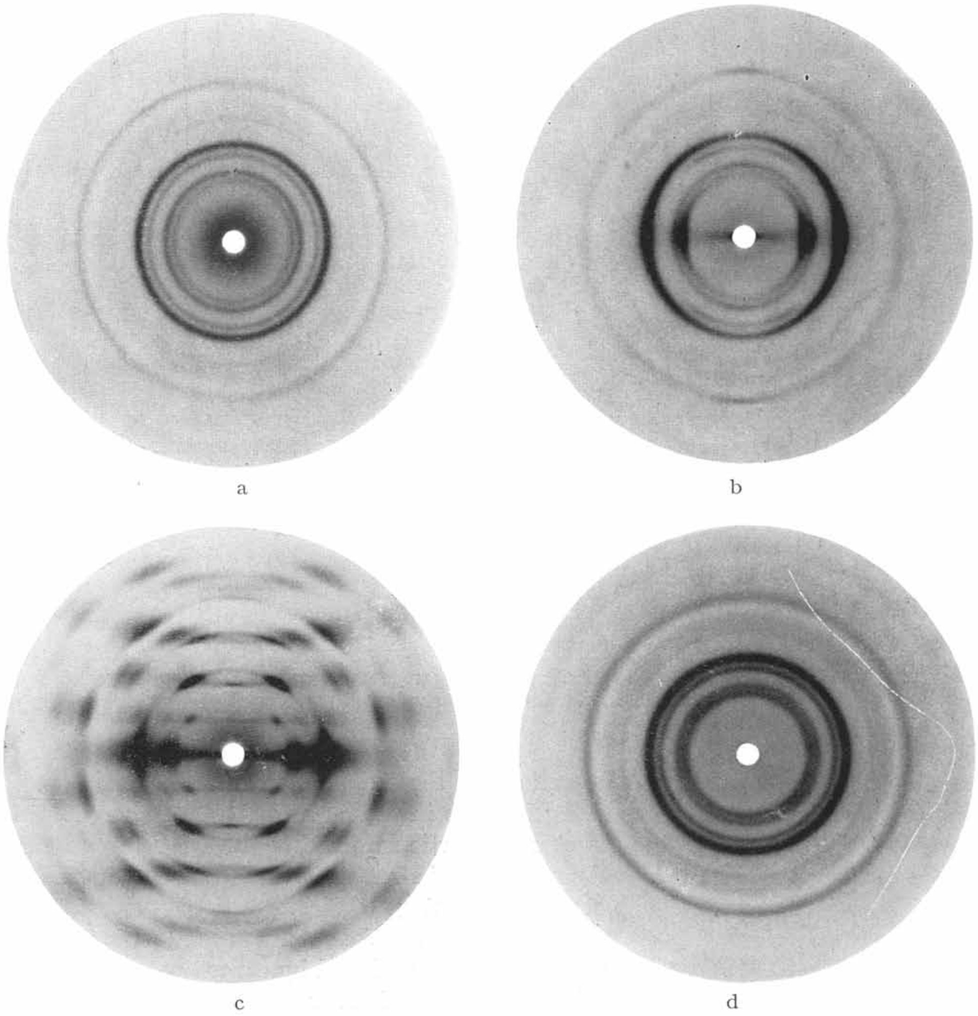

Fig. 2. (a) and (b) X-ray photographs of film of ramie particles. (a) Beam perpendicular; (b) beam parallel. (c) and (d) Fibre and powder photographs of ramie.

of cellulose (Fig. 2d) the reverse is the case. In the pseudo-fibre-photograph taken with the beam parallel to the surface (Fig. 2b) the complementary effect is seen; now, the 101 reflection is strong and $10\bar{1}$ weak, with a tendency to orient on the "meridian". In a film in which the cellulose crystallites are perfectly oriented with their 101 planes parallel to the surface, the "perpendicular" photograph should have the 101 reflection absent, and the "parallel" photograph should have a strong equatorial 101 and a weaker $10\bar{1}$ appearing as a meridianal arc. In the actual films we have not attained such a perfect degree of orientation, but there is partial orientation of the type described, and this is, perhaps, as much as can be expected in view of the irregular shape and size of the aggregates. These aggregates are not, of course, single crystals; nevertheless, the observed orientation effects show that crystallographic orientation persists throughout them, and we must conclude that in the fibre there are extended regions within which the crystallites lie side-by-side in regular conjunction. The lamellar nature of the disintegration products suggests that this type of structural continuity may be associated with the surface of the cell wall, and our results may, therefore, be taken as lending some support to suggestions previously put forward by others that the wall itself has a layer structure with a tendency towards regular conjunction of the crystallites within the layers.

Examination of the disintegration products of the milder acid treatments showed that the cellulose fragments ranged in size down to what appeared to be elementary particles whose widths lay between 100 A and 200 A, although, for the most part, the number of such unit particles which appeared was not very large. It was found, however, that more drastic acid treatments, involving longer times or higher temperatures, were effective in breaking down the aggregates fairly successfully, and we therefore considered the possibility of obtaining preparations which contained only unit particles or small aggregates. Attempts were made to fractionate our colloidal solutions, and trial runs on an ultracentrifuge showed that this should be possible. We were not, however, able to command the use of an ultracentrifuge for extended investigations, and the application of this method has had to be temporarily deferred. Electrodialysis was found to be more effective as a cleaning than as a fractionating technique, and simple electrophoresis was even less efficient. We therefore fell back upon a technique of controlled washing of the acid-treated fibres, since our experience with the milder treatments indicated that the solutions obtained at low pH tended to have smaller aggregates than those formed later. This trend was found to be even more strongly shown after the more drastic acid treatments, and solutions formed at approximately pH 1 contained relatively large numbers of the unit particles. Fig. 3 shows the type of disintegration obtained in such experiments. Although we have not, as yet, been able to eliminate aggregates completely, our best preparations contained few very large aggregates.

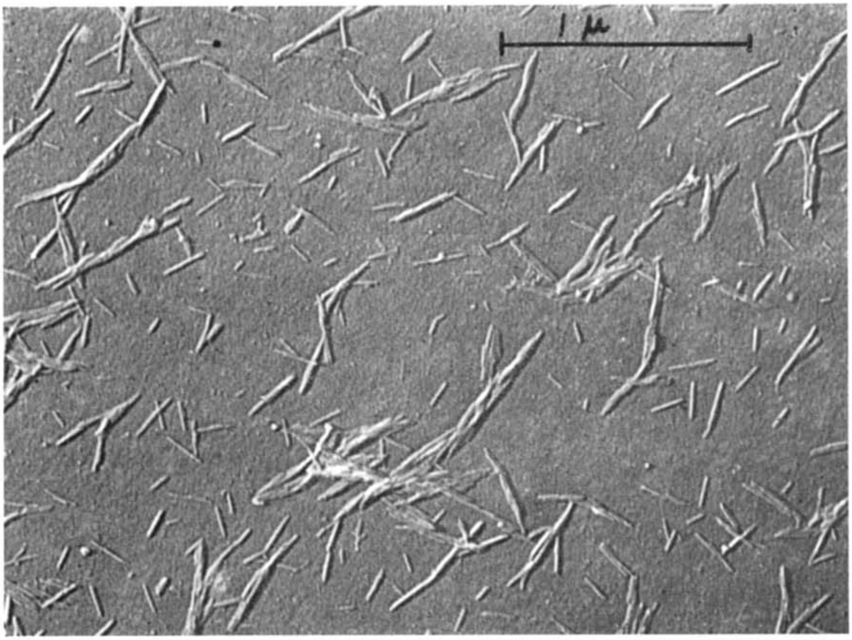

Fig. 3. Cotton, more drastic disintegration. Photographic magnification, X3. Chromium shadowed 1:4.

A cursory glance at Fig. 3 suggests that the single particles are of remarkably uniform width, although they show a very wide range of lengths. It will be observed, too, that the widths of the shadows of the single particles are approximately equal to the widths of the particles; since the shadowing angle was 1 in 4, the thickness of a particle is thus about a quarter of its width. More precise data were obtained by measurement of the widths of the particles and their shadows on the original electron micrographs. For a particular type of cellulose fibre the particles were found to have specific lateral dimensions, which were not affected very much by the severity of the acid treatment, which, as far as the individual particles were concerned, seemed only to cause a shortening in length. In some preparations particles as long as 2500 A have been observed, but the lower limit of length may be as little as 100 A. We have also noticed a process of shortening to go on when the neutral colloidal solutions were stored for some months, and our most successful electron micrographs have been obtained with freshly prepared material. The lateral dimensions of the particles from some types of native cellulose are given in Table I. The particles are tabular, and lie down on their largest faces; the width: thickness ratio averages about 4.5.

TABLE I

DIMENSIONS OF CELLULOSE PARTICLES

Type of fibre and treatment	*Width*		*Thickness*	
	Mean (A)	*C.V. (%)*	*Mean (A)*	*C.V. (%)*
Norman & Jenkins cellulose from jute (900, 24, 40)	85	13	20	13
Cotton (950, 216, 20)	130	6	25	3
Hemp (900, 144, 20)	130	12	30	9
Ramie (950, 216, 20)	155	13	35	12

Thin films of the more severely disintegrated cellulose were made in the way described above, and they gave, in general, the same types of X-ray photographs as the films of aggregates. Assuming, therefore, that in the later experiments there was a high enough proportion of the unaggregated particles to allow us to draw conclusions about them from the photographs, we can say the orientation effects are now a consequence of the tabular shape of the particles, and that the 101 planes lie parallel to the largest face. This type of orientation is similar to that observed by SISSON[5] for films of bacterial cellulose prepared by drying on a glass surface.

Although we cannot place too much reliance on the absolute values of the figures in Table I, because of the necessarily limited accuracy of this kind of measurement (this refers particularly to the thickness figures), it appears that in the thinnest particles there must be 4 or 5 layers of the glucose residues. It is tempting, but would be unwise, to read anything more into the thickness values—the mean thickness increases in steps of about the thickness of a glucose residue in the 101 direction (*ca.* 6 A); the accuracy of our measurements, however, hardly warrants such close examination of the results. The data, nevertheless, are suggestive of the possibility of obtaining a direct microscopical measure of d_{101}, and further work on these lines is projected.

RANBY AND RIBI[6] claimed that their degradation products gave somewhat sharper X-ray photographs than the original fibres. We have made corresponding measurements of the widths at half maximum intensity of the 002 reflections (the only equatorial ones which are properly resolved) in cotton, ramie, and jute cellulose fibres and particles. In cotton and ramie there is a small, but definite, increase in width of the reflections in the particle photographs: for cotton, 0.032 radians for the particles and 0.027 for the fibres; for ramie, 0.027 and 0.024 radians, respectively. Bearing in mind the exceptionally drastic treatment to which our cellulose had been subjected, the observed line-broadening must be regarded as remarkably small; that the photographs of the particles are slightly more diffuse may be evidence of some loss of cellulose from the surfaces of the crystallites, possibly from their larger faces preferentially. In view of the constant size of the particles obtained after different acid treatments, it is hardly possible to assume that any such piecemeal attack had proceeded very far, otherwise we should have expected a wider range of particle sizes, although, bearing in mind what we have said about the accuracy of our measurements, this argument does not apply with full force to the case of attack on the largest faces.

In this connection we must mention the rather low yield of particles in our experiments. As we have said, our treatment can be made effective in dispersing completely into a colloidal state all of the fibres in the sample used. Nevertheless, our attempts to collect the colloidal particles have never been successful in giving a final yield of more than about 30% of the weight of the original fibres. Such a low figure is difficult to reconcile with the idea that the particles thus obtained are substantially the same in size and structure as in the original fibres, since, if they are the cellulose crystallites, they should have comprised a much greater proportion of the fibre than 30%, according to current ideas of the amount of crystalline material in cellulose fibres[7]. We must, therefore, suppose that continued action of the acid does ultimately cause complete dispersion of the cellulose in the crystallites (or in an important fraction of them), and if this does not take place by lateral "erosion", we are left with only one reasonable alternative, that there is a progressive shortening of the particles, until, at some critical length, they disperse spontaneously and completely. The positive evidence is, in fact, very much in favour of such an idea; for there is nothing like the specificity in the length of the particles as there is in the lateral dimensions, and, as we have mentioned above, we have found that a process of shortening goes on slowly even in acid-free preparations of the particles. The idea that there is some critical length below which the cellulose crystallite is unstable under the conditions of our experiments is reasonable, since the cellulose chains are held together laterally by secondary valence forces.

It is, in any case, clear that the loss in weight following the acid treatment and washing is closely connected with the breakdown of the fibres into the colloidal condition. We found, for example, that ramie loses only about 3½% in weight when treated at 20° C for 48 h in 800 g/l H_2SO_4, compared with the 70% loss in 950 g/l acid in the same time. If we assume that in the more drastic experiment all of the non-crystalline cellulose (say, about 35% of the fibre weight) has been hydrolysed to a soluble sugar, we are still faced with the loss of some 50% of the crystalline material. We are not, however, satisfied that our procedure for isolating the particles is the best that can be devised, and further attempts are being made to improve the technique and thus obtain more satisfactory yields.

Moisture absorption and density. We have considered the water-absorbing capacity and the density of the films of particles. These films, once dried, do not disperse when placed in water, and show no measurable swelling (in area, at least), when so treated.

They do, however, absorb water, which presumably penetrates into the spaces left between the particles by virtue of the imperfect packing which must occur when the film is formed. We have found that the amount of water taken up at low humidities is less than that absorbed by fibres under the same conditions; for example, at 26% relative humidity ramie fibres absorbed 3.36%, and films, 2.84%, of their dry weight. This trend is in the direction which we should expect if some of the non-crystalline material had been eliminated. The dry density of the films is roughly the same as that of the fibres, but, in general, slightly higher. Here, again, the imperfect packing of the particles in the films make quantitative comparisons difficult; if we are dealing with crystalline cellulose a perfectly packed film should have a density near 1.59 g/cc, but, in fact, the greatest value which we have observed is 1.562 g/cc for a ramie film, which must be compared with 1.553 g/cc for ramie fibres[7]. That packing can affect the density

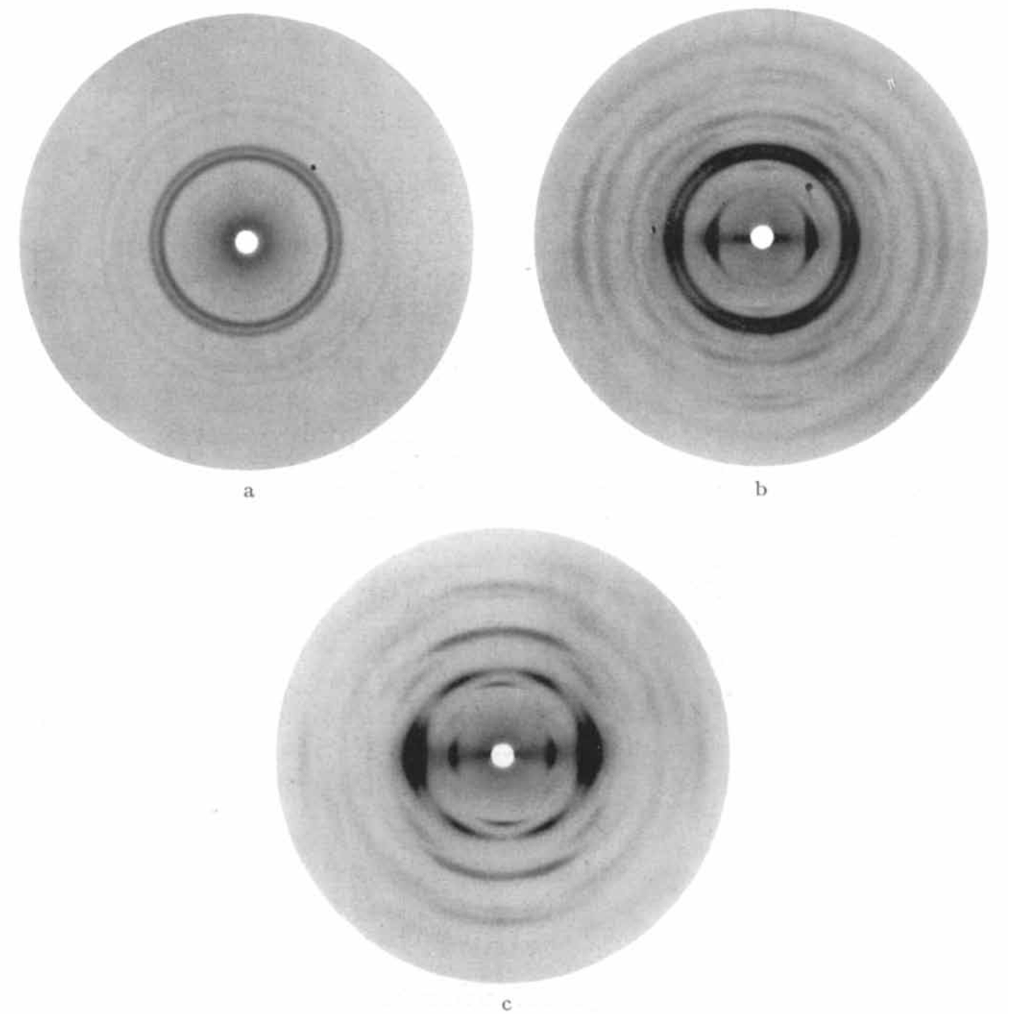

Fig. 4. (a) and (b) X-ray photographs of film of particles from mercerised ramie; (a) Beam perpendicular. (b) beam parallel. (c) Fibre photograph of mercerised ramie.

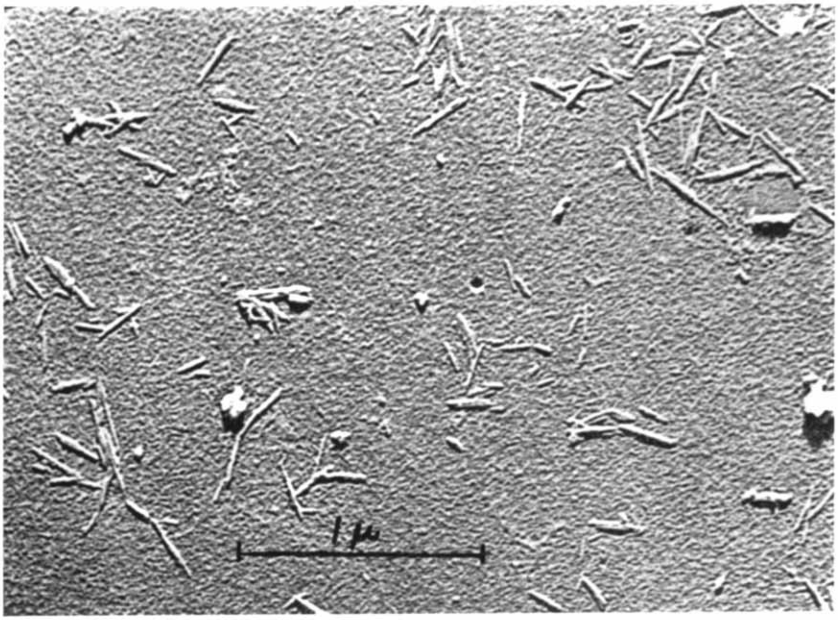

Fig. 5. Fortisan, disintegrated by boiling in 2.5 N H_2SO_4. Photographic magnification, X3. Chromium shadowed 1:4.

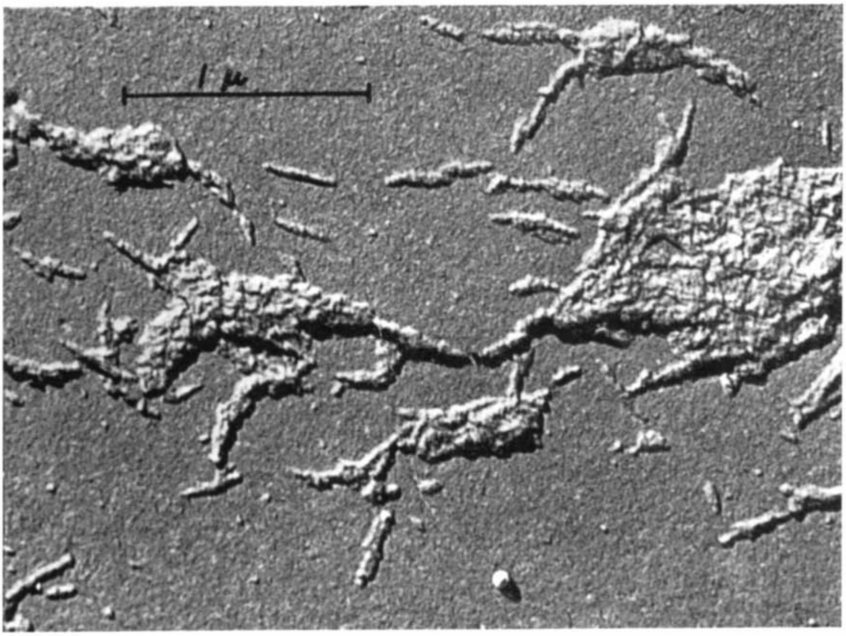

Fig. 6. Cellulose acetate rayon, details as in Fig. 5.

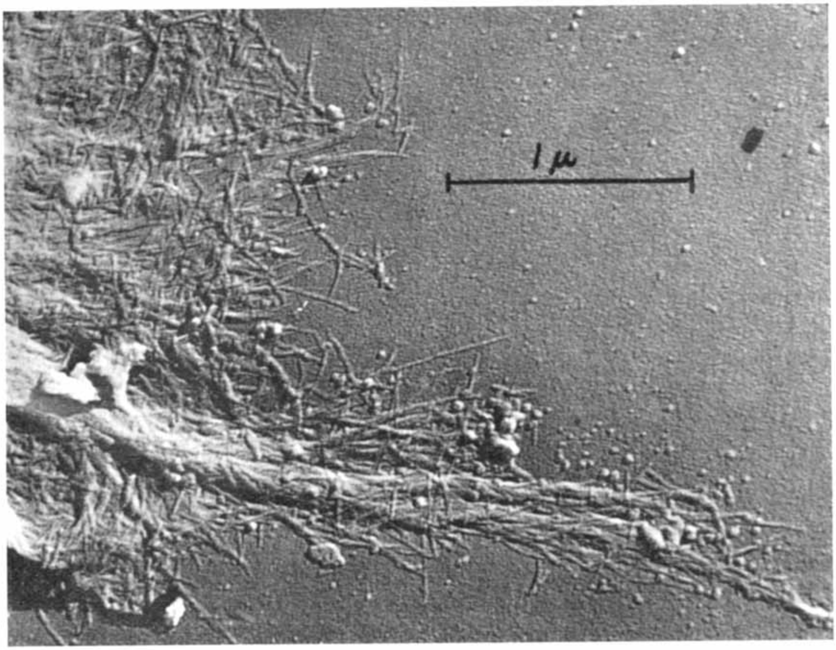

Fig. 7. Jute, squashed after mild acid treatment.

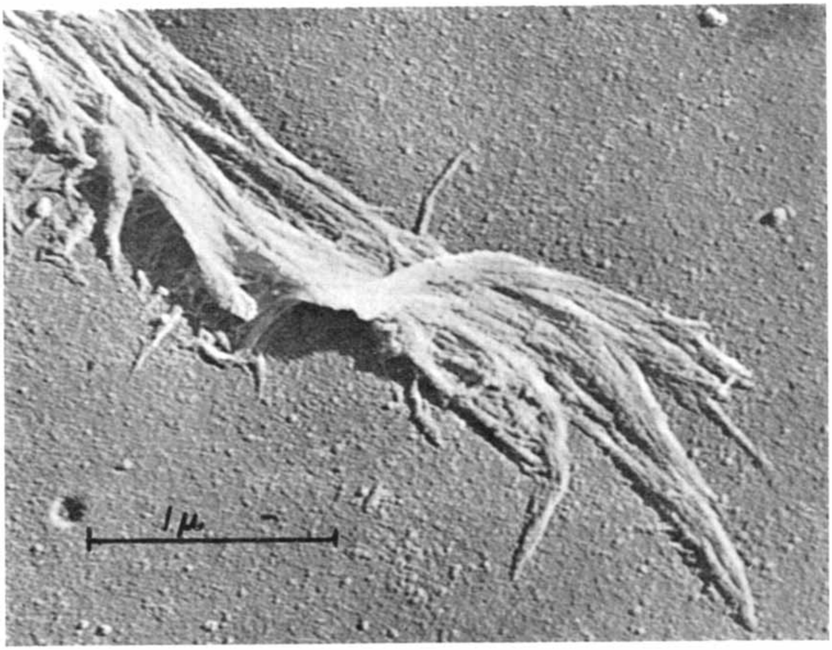

Fig. 8. Ramie, squashed after mild acid treatment.

is shown by the fact that we always obtained higher values for very thin films than for thicker ones. All we can say about the density, therefore, is that the change is in the right direction, but the amount of change is smaller than we might have expected. Later experiments with films of particles from mercerised fibres (see below) gave a more positive result; the density of the film was 1.560 g/cc, which must be compared with 1.526 g/cc for mercerised ramie fibres[7].

Cellulose II particles. Particles in the Cellulose II modification have been prepared by mercerising the fibres before subjecting them to the acid treatment, and by treating the Cellulose I particles with caustic soda of mercerising strength. Preparations obtained by the former technique showed that the cellulose disintegrated into particles very similar in appearance to those obtained from native fibres; somewhat milder acid treatments were, however, effective. The X-ray results were also similar to those already described, but the orientation effect was rather more perfect; in the Cellulose II preparations the 101 planes were parallel to the film surface (Fig. 4). It may be recalled that SISSON also found more perfect orientation in films of mercerised bacterial cellulose. We did not find any great difference in the width: thickness ratio, so that the better orientation cannot be a purely geometrical effect. It is, therefore, probably due to the enhanced surface activity of the modified particles.

The experiments in which the native particles themselves were subjected to the mercerisation process were more complicated, because of the necessity of removing the alkali after treatment. The procedure followed was to add concentrated caustic soda solution to the solution of the native particles in water, until the resultant solution had the desired caustic soda concentration. After 2 h the solution was neutralized by adding, slowly, dilute hydrochloric acid. This caused precipitation of the cellulose, but resolution occurred after the electrolyte had been removed by electrodialysis. Experiments were done with caustic soda concentrations of 5, 10, and 15%. The first of these produced no evidence of any change in the cellulose modification; the second resulted in a mixture of Cellulose I and II; and the last was effective in transforming the cellulose completely. These results are nearly enough the same as would be found for fibres mercerised without tension to show that only minor changes in the mercerisation process can have occurred.

It is also possible to obtain particulate degradation of regenerated fibres such as viscose and fortisan, but it was found that the concentrated acid technique was less successful with the rayons, and the best results were obtained by using the milder treatment of RANBY AND RIBI. Fortisan, boiled for 8 h in 2.5 *N* sulphuric acid gave, on washing, a colloidal solution of particles of a similar character to those from ramie and cotton (Fig. 5). Although the usual orientation effect in the X-ray photographs, and the tabular shape of the particles in the electron micrographs, were both observed, the particles were not so clearly-cut as to allow easy measurement of their dimensions, which were, however, of the same order, about 140 × 35 A, as in cotton and ramie. The particles from viscose were more irregular, and from cellulose acetate (Fig. 6) such particles as were obtained were ill-defined and obviously poorly organized.

Lignified fibres. The figures of Table I show that, of the varieties of fibre studied, ramie gives the largest particles, and jute cellulose the smallest. It is known that the X-ray photograph of jute is diffuse in comparison with that of ramie, and although the removal of non-cellulosic inclusions does something to improve matters in this respect, the perfection of the crystallinity of jute cellulose still falls below that of ramie or cotton. The tendency is also well-marked in the X-ray photographs of films of particles

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TABLE II

Fibre	*Half-width of 002*
Ramie	0.027 radians
Cotton	0.032
Jute cellulose	0.040

from the various sources, as is shown by the data of Table II, where the half-widths of the 002 reflections of ramie, cotton, and jute cellulose particles are given. It will be seen that the order of sharpness of the reflection is the same as the order of size of the particles (Table I). It is not unreasonable, therefore, to ascribe some, if not all, of the diffuseness in the X-ray photographs of jute cellulose to the small size of the crystallites.

A good deal of attention was paid to the problem of the hydrolytic breakdown of raw jute. It was found that treatments which were effective in causing the whole of a ramie or cotton sample to go into colloidal solution left jute fibres apparently unaffected. Thus, no particles were obtained from jute (950, 20, 48); but the fibres remaining after this treatment were found to be in the Cellulose II modification, which was a clear indication of the abnormal behaviour of jute, since in the "pure" celluloses particulation precedes the native-hydrate transformation. In fact, jute remained fibrous even after treatment in 1000 g/l sulphuric acid at 20° C, although this acid was strong enough to produce complete and almost instantaneous solution of ramie and cotton. Delignified jute, however, yields particles readily enough, and this at a lower acid concentration than ramie requires; and jute containing 0.5% by weight of lignin dissolves completely in 950 g/l acid.

By varying the conditions of treatment it was found possible to obtain a small yield of colloidal cellulose from raw jute; for example from jute (900, 24, 40), where a small fraction peptized on washing. The disintegration, however, was fibrillar rather than particulate; X-ray examination showed that the structure was still that of Cellulose I. It is, of course, possible that even here it is only the primary wall of the jute ultimates which are affected; the ready fibrillation which has been observed in the primary walls of other cellulose fibres would lend colour to such a suggestion. On the other hand, we have obtained quite striking fibrillation in jute by milder acid treatment (800, 20, 48) followed by pressure between glass plates of the washed fibres (Fig. 7). By this technique a fair proportion of the fibres could be brought to the colloidal condition, and it is unlikely that our observations were limited solely to the primary wall. Attempts to produce a corresponding fibrillation in ramie were comparatively unsuccessful, and Fig. 8 shows the best example which we have been able to obtain. There is no doubt, therefore, that fibrillation rather than particulation is the preferred mode of disintegration of jute, and that the reverse is true for ramie.

It is interesting to note in the present work a two-fold influence of the lignin in jute. In the first place it appears to be responsible for the fibrillar, as distinct from particulate, type of breakdown; and in the second place the transformation to Cellulose II occurs, in the acid treatments, more readily in jute than in the "pure" fibres. This latter effect may be compared with the effect of mercerising solutions of caustic soda, for jute begins to show the Cellulose I–II transformation at lower NaOH concentrations than does ramie[8]. This has been interpreted as implying that part of the lignin in jute is loosely bound into the less crystalline regions, and thus "opens" the structure to allow more easy penetration of the alkali. If this lignin is interfibrillar in location, it may also be responsible for the comparatively weak lateral consolidation of the fibrils which is established by the results of the disintegration experiments. On the other hand there is evidence[9] that part of the lignin in jute is more intimately associated with the cellulose crystallites; it is probable that this is responsible for the failure of the fibrils to break down into particles in the "normal" way.

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SUMMARY

Degradation of ramie and cotton fibres by sulphuric acid solutions of concentration near 950 g/l at temperatures up to 40° C leads to breakdown into elongated tabular particles of lateral dimensions about 30 A × 130 A and of widely varying lengths up to 2500 A. The particles are probably single crystallites of Cellulose I, and have their 101 crystallographic planes parallel to their largest faces. In the fibre the particles are arranged so that crystallographic orientation persists over relatively great distances. Similar results are obtained for the Cellulose II particles from mercerised fibres. Jute, containing a high proportion of lignin, tends to disintegrate in a fibrillar, as distinct from particulate, manner; but jute cellulose behaves more normally.

RÉSUMÉ

La dégradation de fibres de ramie et de coton par des solutions d'acide sulphurique de concentration voisine de 950 g/l à des températures allant jusqu'à 40° C donne naissance à des particules tabulaires dont les dimensions latérales sont d'environ 30 A × 130 A et dont la longueur varie beaucoup, atteignant parfois 2500 A. Ces particules sont probablement des crystallites simples de cellulose I, dont le plan crystallographique 101 est parallèle à la face la plus large. Dans la fibre les particules sont disposées de telle sorte que l'orientation crystallographique persiste sur des distances relativement grandes. L'on obtient des résultats semblables pour les particules de cellulose II de fibres mercérisées. La jute, qui contient une forte proportion de lignine, tend à se disintégrer en fibrilles plutôt qu'en particules; mais la cellulose de jute se comporte de façon plus normale.

ZUSAMMENFASSUNG

Der Abbau von Ramie- und Baumwollfasern mit Schwefelsäure-lösungen einer Konzentration nahe 950 g/l bei Temperaturen bis zu 40° führt zu einem Zusammenbruch in längliche tafelförmige Teilchen mit Seitendimensionen von ungefähr 30 A × 130 A und mit überaus variierenden Längen bis zu 2500 A. Diese Teilchen sind wahrscheinlich Cellulose I-Einkristalle mit der 101 kristallographischen Ebene parallel zur grössten Oberfläche. In den Fasern sind die Teilchen so angeordnet, dass die kristallographische Orientierung über relativ grosse Entfernungen besteht. Ähnliche Ergebnisse wurden für die Cellulose II-Teilchen aus mercerisierten Fasern erhalten. Jute, welche einen hohen Anteil Lignin enthält, neigt dazu sich in Fasern und nicht in Teilchen aufzulösen, während Jutecellulose sich normaler verhält.

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