THE STRUCTURE OF JUTE

I. THE TWO-FOLD FUNCTION OF LIGNIN

by

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Not much systematic work has been done on the molecular structure of the bast fibres generally, although ramie has attained the status of a standard reference fibre in cellulose research. Such fibres as ramie and flax, however, are rather exceptional in that they are relatively pure cellulose; more usually the bast fibres contain high proportions of non-cellulosic inclusions, whose presence raises many important questions about the structure. In general it is safe to say that to a first approximation the structure of the crystalline fraction, as far as can be seen from the X-ray photographs, is much the same as in the purer cellulose fibres, and that therefore the non-cellulosic inclusions must exist, for the most part, in a non-crystalline condition. Some reservation with regard to the "hemicelluloses"—xylan and polyuronides—is, however, necessary in this connection, for their chain-molecules are sufficiently like those of cellulose to render plausible the suggestion[1] that they may in part be incorporated with the cellulose in a kind of mixed crystallization, without producing more than some slight distortion of the cellulose lattice. The other principal non-cellulosic constituent of the bast fibres, lignin, does not stand in any such close molecular relationship to cellulose, and its location is therefore almost certainly in the intercrystalline regions. It is the lignin in jute that we shall be chiefly concerned in this paper.

Raw jute

The X-ray photograph of raw jute is chiefly due to the crystalline cellulose in the fibre, and its main feature is that the reflections are more diffuse laterally than in ramie or cotton, so that, for example, the (101) and (10$\bar{1}$) reflections are not resolved even in photographs of moderate photographic density. Longitudinally, the reflections in jute are of comparable sharpness with those in ramie, and the intensities of the meridional reflections (OkO) are very much greater in jute than in ramie. Both ramie and jute photographs show an intense equatorial streak extending inwards from the (101) and (10$\bar{1}$) arcs and an even more intense equatorial small-angle scattering corresponding to spacings greater than 40 Å; these are rather more noticeable in jute. In the jute photograph there is also a darker background, and in particular a broad diffuse ring of mean spacing 4.2 Å which has been ascribed to lignin[2, 3].

In jute photographs of moderate density it is possible to see quite clearly two diffraction maxima in the equatorial streak; the spacings are 9.7 Å (X) and 14.6 Å (Y),

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and Y appears to be stronger and sharper than X. The first layer-line in both ramie and jute photographs tends to show as a continuous streak from the meridian to (011), and this effect is more pronounced in jute. Asterism is generally better seen in ramie, but at the position where one radial streak in ramie crosses the first layer-line (at a spacing of approximately 8.5 Å) there appears in jute a clearly defined reflection (Z), even though the corresponding asterism streak may be too weak to be seen. Careful examination of the photographs of a number of pure and impure celluloses have shown that reflections similar to X and Y are of frequent occurrence, but that the intensities are generally very much smaller in the purer samples, and they are best seen in the photographs of such materials as jute, sawdust and bamboo (for information about the last named fibre we are indebted to PRESTON AND SINGH[4]). R. R. MUKHERJEE, working in this laboratory, has recently shown that the intensity of Y, at least, is greatest in wet fibres, and that the reflection is absent from the photograph of fibres dried over phosphorus pentoxide; he has also succeeded in treating ramie fibres in such a way as to enhance the intensity of Y to a degree which makes it comparable with that in jute. Our own observations, made on jute under ordinary conditions of atmospheric humidity, suggested that X and Y were due in some way to the hemicellulose, since they become more diffuse when the jute is treated with alkali (boiling Na_2CO_3 or cold dilute caustic soda solutions), and though present in completely delignified jute (CROSS AND BEVAN cellulose) disappear when this is boiled in 7.5% caustic soda solution. The later results mentioned above, however, indicate that cellulose and water are both involved in the complex responsible for Y, and it is possible that the more frequent occurrence of the reflections in the "impure" fibres is due not so much to the presence in them of larger quantities of non-cellulosic materials as to the greater proportion of cellulose chains not taking part in the building of the crystallites and therefore available for forming a swelling compound with water. Since work on the subject of the new reflections is still proceeding, we shall defer any further consideration of this topic until this is completed.

Delignification

Some clarification of the X-ray photograph usually accompanies the removal of lignin from highly lignified materials[5]. In jute we have observed a slight weakening of the background scattering and of the equatorial streak; but the most noticeable effect of delignification is that the diffuse ring at 4.2 Å appears to sharpen a little when the lignin content is reduced to some 2% whilst its intensity is reduced by further delignification. In some of our photographs the reflection seems to sharpen into a ring at 4.0 Å, but since this spacing nearly coincides witht the (002) of cellulose it is impossible to be sure that the observed effect is not due to angular dispersion of the cellulose crystallites. In these experiments delignification was carried out by treating the fibres in ClO_2 solutions (0.25 to 1.0%) for various times at 22.2° C, followed, after washing, by extraction in 2% sodium bisulphite solution at 90° C for 1 hour.

Powder photographs of lignin-free CROSS AND BEVAN cellulose[6] from jute were also cleaner in respect of the background than raw jute photographs, but by far the greatest improvement we have observed is the very pronounced change in clarity and cleanliness of the photograph brought about by boiling the CROSS AND BEVAN cellulose in 7.5% caustic soda solution. This treatment leaves the (101) and (10$\bar{1}$) reflections clearly resolved and reduces the intensity of the background, in each case to an extent which

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invites comparison with cotton cellulose, although even now the jute falls short of the perfection of the latter.

Mercerization

The main features of the X-ray photograph of mercerized raw jute are that the native-hydrate transformation never appears to proceed to completion*, and that the (101) hydrate spacing may have values very much greater than those observed in ramie or cotton. The reluctance of the last traces of the native cellulose to disappear from the photograph was established by examining jute after mercerization in caustic soda solutions of different concentrations at various temperatures. An attempt was made to estimate quantitatively the degree of modification by using the photometric method devised by SCHRAMEK[7]. This is based on measurements of the relative reflecting powers of the native and hydrate modifications in cellulose, and there is some doubt as to the validity of their application to jute; the results we give, therefore, must be considered with some reserve as to their accuracy, but they are adequate to establish the essential qualitative features of the phenomena. In Table I are shown the observed proportions of hydrate for jute mercerized without tension in caustic soda solutions of various concentrations at room temperature; in Table II the effect of temperature is shown for 20% and 30% caustic soda solutions. Measurements on jute fibres held taut during the

TABLE I

Concentration of caustic soda (%)	% hydrate
10	5
12	59
16	80
20	84
30	77

TABLE II

Temperature °C	% hydrate	
	20% NaOH	30% NaOH
0	74	84
25	83	77
40	85	88
80	84	91
100	81	86

treatment confirmed that in jute, as in the purer cellulose fibres, the effect of tension is to reduce the mercerizing action of the alkali, and that to an extent far greater in jute than in ramie, comparable figures for the proportions of hydrate being 5% and 75% respectively for jute and ramie treated with 20% caustic soda solution at 25° C.

It will be convenient to describe the behaviour with respect to the value of the (101) hydrate spacing in connection with the mercerization of delignified jute.

Mercerization of delignified jute

Removal of the bulk of the lignin from jute has little effect on the course of the native-hydrate transformation, as judged from the observed proportions of the two modifications present. The results are set out in Table III, and it will be clear from these that it is only when the delignification is nearing completion that the proportion of hydrate rises significantly above the value observed for raw jute.

* In this connection we may refer to a paper by SAHA (*Indian J. Physics*, 22 (1948) 141) in which he claims to have obtained complete mercerisation of raw jute under various conditions. We have not been able to confirm these findings in further experiments, the details of which will be published in due course. — H. J. W.

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The effect of delignification in the early stages is better shown by the results of experiments designed to test the effect of water adsorption on the value of the (101) spacing. That there are lattice changes accompanying water adsorption by mercerized cellulose has been established by HERMANS AND WEIDINGER[8], who report an increase from 7.3 Å to 7.7 Å in the (101) spacing of mercerized ramie when the fibres are conditioned at 65% R.H. after thorough drying. SIRKAR AND SAHA[9] have observed what appears to be an even greater effect in mercerized jute, their value at room humidity being 7.96 Å. We have investigated the phenomenon for raw jute and for jute delignified to various extents.

In mercerized raw jute, conditioned at 65% R.H. by *desorption* after washing free from alkali, that is, in fibres which have not been thoroughly dried after the alkali treatment, we obtain a spacing of 8.3 Å. This decreases as the fibres are dried further, reaching the value 7.4 Å for fibres dried over phosphorus pentoxide[14]. When the jute is now conditioned at 65% R.H. by *adsorption*, the spacing rises only to 7.7 Å, so that in this respect jute behaves like ordinary cellulose.

Similar measurements have been made for jute samples delignified to various degrees. At room humidity during the first drying the (101) spacing decreases with decreasing lignin content and reaches a minimum of 7.4 Å when the amount of lignin in the fibre has been reduced to about 2%, as may be seen from Table III. Beyond this stage the spacing rises again until it attains approximately the normal cellulose value when the lignin has been entirely removed.

The effect of complete drying has been investigated for jute containing 6% of lignin and also for CROSS AND BEVAN cellulose from jute. In both, the hydrate spacing of specimens dried over phosphorus pentoxide has the same value, 7.4 Å, as in the

TABLE III

Lignin (%)	% hydrate	(101) spacing (A)
0.0	100	7.6_7
0.3	91	7.5_5
2.0	85	7.4_0
6.0	81	7.4_5
9.0	83	7.6_0
11.0	86	7.8_5
Raw jute	84	8.3_0
Ramie	100	7.8_5

corresponding experiment with raw jute. It appears, therefore, that in the region where values near 7.4 Å are obtained spontaneously at room humidity during the first drying the effect of water in causing intra-crystallite lattice changes is practically eliminated, whilst the behaviour of CROSS AND BEVAN cellulose agrees closely with that of pure cellulose fibres.

DISCUSSION

The results set out in Table III make it clear that the removal of lignin from jute can be divided into two stages; during the first of these the larger part of the lignin comes away without leaving the jute any more susceptible to the mercerizing action of caustic soda solutions, whilst the second stage involves the removal of that lignin which is

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chiefly responsible for the non-completion of the native-hydrate transformation. The failure of jute containing more than a trace of lignin to mercerize completely must be ascribed to a depression of the swelling in caustic soda solutions, since it is generally accepted that successful mercerization is a consequence of a sufficiently high degree of swelling. One effect of the lignin in jute, therefore, is to reduce the swelling in caustic soda solutions, and it is the lignin which is most difficult to remove which is effective in this respect.

This, however, is not the only way in which the presence of lignin modifies the course of the mercerization process, for Table III shows also that there is an even more complicated relation between the lignin content and the value of the (101) hydrate spacing on first drying the fibres at room humidity after the alkali treatment. In particular, the spacing is exceptionally high in raw jute, and becomes smallest in the region where the proportion of the hydrate modification starts to increase. The course of the native-hydrate transformation is known to proceed through a series of recrystallizations from soda-cellulose through water-cellulose to the true cellulose II. These intracrystalline readjustments are characterized by changes in the (101) spacing, which in water-cellulose has the value 8.98 Å[10] and in cellulose II 7.3 Å increasing to 7.7 Å with adsorption of water[8]. It is not known whether the transition from water-cellulose to cellulose II is continuous in respect of the (101) spacing changes*, but we have observed, even in ramie, the hysteresis between the spacing assumed at room humidity during the first drying and that shown on conditioning by adsorption. The effect, however, is overwhelmingly greater in jute, so much so that the hypothesis of a continuous transition from water-cellulose to cellulose II becomes plausible; at any rate, we can describe the phenomenon in jute as a lag in the process of intracrystalline readjustment as the water is removed from the water-cellulose. Since the observed (101) spacing in mercerized jute depends on the lignin content we can ascribe this reluctance to assume the cellulose II configuration to the influence of the lignin, and in this respect it is the more easily removed lignin which is responsible. It is relevant in this connection to note that concurrently with the spacing changes noted in Table III we have observed corresponding changes in the sharpness of the (101) spacing, which improves as the value of the spacing decreases, so that there is some justification for describing the transition as a crystallization into the cellulose II form.

We are thus led, by consideration of the mercerization phenomena, to the idea that lignin can perform a double function in jute. In the first place it can hinder the swelling in the caustic soda solution, thus preventing the quantitative completion of the native-hydrate transformation, and in the second place it can, by its very presence, interfere with the packing together of the cellulose chains which is necessary for the development of perfect crystallinity. Although we have considered this latter effect as it appears in connection with the mercerization phenomena, it is possible that it might also be a contributary factor to the imperfect crystallinity of raw jute. For we know that lignin is distributed throughout the body of the jute cell (although the concentration is greater in the regions of the cell boundaries, at the middle lamella and near the lumen), so that part of the lignin can be thought of as existing as a kind of solid solution in the non-crystalline cellulose and hemicellulose. Since the latter must be assumed to form a continuum with the crystalline regions, any influence tending to

* Later results, for which we are indebted to R. R. MUKHERJEE, show that the spacing changes in jute are continuous.

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keep the chains apart and thereby restricting their freedom to fit together into a state of higher organization, even if limited in the first instance to the non-crystalline regions, must extend, by virtue of the structural continuity, into the crystallites themselves, which will therefore show less perfect crystallinity than would exist in the absence of the disturbing influence. Although we mention this possibility here, it must not be thought that we thereby deny the validity of the hypothesis put forward by ASTBURY, PRESTON AND NORMAN[1] that the imperfect crystallinity in jute and other fibres with high lignin and hemicellulose contents is largely due to the incorporation within the cellulose crystallites of some portion of the hemicelluloses in a state of mixed crystallization; we have, in fact, evidence, which we shall bring forward in a later paper, which offers strong support for this idea. We cannot, however, subscribe to NORMAN's later interpretation[11] of the original results, which implies that this mixed crystallization accounts for the whole of the hemicelluloses of the hexosan or pentosan types, whilst the polyuronide hemicelluloses and the lignin are incrustations existing in aggregations in the larger pores of the cellulose — cellulosan structure.

A further consequence of the presence of lignin in the non-crystalline regions of the fibre, where by steric hindrance it modifies the packing together of the cellulose chains, would be that in this respect the lignin would exert an influence in direct opposition to the anti-swelling tendency which we have had to postulate for the most tightly-held lignin. For the greater separation of the chains in the non-crystalline regions would lead to easier penetration of water or other swelling agents on account of the more open structure, and it might be possible on these lines to account for the fact that jute is much more hygroscopic than the purer cellulose fibres, although it has not been reported to show greater swelling in water. This idea would also fit in with the observations which we have made of the lattice changes consequent upon water adsorption by mercerized jute. We find that the value of the (101) spacing in perfectly dry fibres does not depend on the lignin content, and we can say that the intracrystalline readjustments which take place when both raw jute and completely delignified jute absorb water are practically eliminated, at least in the first part of the adsorption process, in jute containing a few per cent of lignin. At this stage in the delignification, therefore, only the anti-swelling influence of the residual lignin can be effective. In the last stages of delignification the lattice changes are again apparent in consequence of the removal of the final traces of lignin, which are chiefly responsible for the depression of the swelling.

It might, perhaps, be argued that the potentiality for increased swelling which results from the removal of the last few percent of lignin is due to some process of degradation of the cellulose itself as a consequence of the comparatively drastic treatment which the fibres have undergone. This argument must be rejected, however, since it does not account for the swelling behaviour of normal and moderately delignified jute in caustic soda solutions. To explain this it seems necessary to suppose that delignification must be regarded as removing some restrictive influence which prevents the full swelling of the cellulose-hemicellulose complex. It is tempting to speculate on other possibilities which are in conformity with this idea. We can imagine, for instance, that the highly lignified regions at the cell boundaries form a sort of envelope enclosing the bulk of the cell wall, and that this lowers the swelling by mechanical restriction[13]. If the distribution of lignin retains its essential non-uniformity during the course of the delignification it would be reasonable to suppose that the lower swelling would persist until a stage is reached where the removal of lignin from these highly lignified regions

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leaves them incapable of exerting their restrictive action. Some support for this hypothesis comes from the observation that the diffuse DEBEYE-SCHERRER ring at 4.2 Å on the X-ray photograph of jute, which has been attributed to lignin, persists until the lignin content is less than 2%; for we might expect the lignin which is sufficiently aggregated to give rise to an X-ray reflection, however diffuse, to be located in the most highly lignified regions of the fibre. Staining tests also indicate that the lignin near the lumen, at least, is rather difficult to remove. On the other hand LANGE[12] reports that in wood there is, during the early stages of delignification, a considerable removal of lignin from the middle lamella, although his published results do not exclude the possibility that the boundary concentrations should persist, in part at least, until the last stages.

The other possibility which we may consider is that the last lignin to be removed is combined in some way with the non-crystalline cellulose or hemicellulose chains which are located near the crystallites, forming, perhaps, bridges between them and thus reducing intercrystalline, and therefore intracrystalline, swelling. That this lignin should be the most difficult to remove would follow from the fact that it is so combined; and that there is some chemical combination between lignin and the hemicelluloses, at least, has been often conjectured.

It is clearly impossible to decide, on the evidence available, if either of these possibilities is correct. Further work, which it is hoped will clarify the position, is in progress, and will be reported on in a later paper in this series.

SUMMARY

1. There appear at relatively high intensity in the X-ray photograph of jute certain reflections not due to the accepted cellulose lattice, which are normally only seen with difficulty, if at all, in the purer cellulose fibres. In particular, one of these, an equatorial reflection of spacing 14.7 Å, occurs not only in jute but in a wide range of other plant fibres; its intensity is strongly dependent on the water content of the fibres, which suggests that it is due to some sort of swelling compound between water and either cellulose or hemicellulose chains which is sufficiently regular, laterally at least, to give rise to X-ray reflections.

2. Both the diffuseness of the cellulose reflections, and to some extent the background scattering, in the X-ray photograph of jute are associated with the presence of lignin and the hemicelluloses. Removal of both types of inclusion can increase the degree of perfection of the crystallinity of the cellulose to a level approaching, but not reaching, that of cotton. Removal of either type alone has relatively little effect.

3. The presence of lignin can a) act as a swelling depressant, and so impose a limitation of the intra-crystalline swelling necessary for the transformation into the hydrate modification; and b) by its presence between the cellulose and hemicellulose chains hinder any tendency on their part to assume a state of higher organization. Thus the extent of mercerization of jute in caustic soda solutions, the intra-crystalline swelling of the hydrate modification, and the sharpness of the reflections in the hydrate photograph all depend on the lignin content.

RÉSUMÉ

1. Des photographies faites avec des rayons X montrent dans le jute certaines réflexions qui ne sont pas dues aux réseaux connus de la cellulose, et qui ne sont visibles qu'avec beaucoup de difficulté, ou même ne sont pas visibles du tout dans les fibres de cellulose pure. En particulier, l'une de ces réflexions, équatoriale, correspondant à un espace de 14.7 Å, se rencontre non seulement dans le jute, mais chez une série d'autres fibres végétales; son intensité dépend dans une large mesure de la teneur en eau des fibres, ce qui conduit à penser qu'elle est due à un système résultant de l'imbibition par l'eau soit de cellulose, soit d'hémicellulose, dont l'arrangement est suffisamment régulier pour donner naissance à des réflexions des rayons X.

2. Le degré de diffusion de réflexion de la cellulose, et le flou du fond de la photographie du jute par les rayons X, sont dûs à la présence de lignine et des hémicelluloses. L'élimination de ces deux types de substances permet d'accroître la purification de la cristalinité de la cellulose, jusqu'à l'approche de celle du coton. L'élimination d'un des types seulement n'a guère de résultats.

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3. La présence de lignine peut: a) agir comme un inhibiteur du gonflement et ainsi limiter le gonflement intracristallin nécessaire pour la transformation en l'hydrate; b) par sa présence entre les chaînes de cellulose et d'hémicellulose, les empêcher de prendre un état d'organisation plus élevé. Ainsi, le degré de mercerisation du jute dans une solution de soude caustique, le gonflement intracristallin de l'hydrate et la netteté des réflexions obtenues par photographie de l'hydrate, tout ceci dépend de la teneur en lignine.

ZUSAMMENFASSUNG

1. Photographische Aufnahmen von Jute mit Röntgenstrahlen zeigen gewisse Reflexionen, welche nicht von dem bekannten Zellulosegitter stammen und die in reinen Zellulosefasern nur schwer oder garnicht sichtbar sind. Insbesondere eine äquatoriale Reflexion, welche einem Abstand von 14.7 Å entspricht, tritt nicht nur bei Jute auf, sondern auch bei anderen Pflanzenfasern; ihre Intensität hängt stark vom Wassergehalt der Fasern ab, was darauf schliessen lässt, dass sie von einer durch Quellung der Zellulose- oder Hemizelluloseketten entstandenen Verbindung herrührt, deren Anordnung, zumindest lateral, genügend regelmässig ist, um Reflexionen der Röntgenstrahlen zu bewirken.

2. Die unscharfen Reflexionen und der verschwommene Hintergrund der Röntgenstrahlenaufnahmen von Jute rühren vom Lignin und den Hemizellulosen her. Entfernt man diese beiden Arten von Einschlüssen, so kann man die Zellulose nahezu so rein und kristallin erhalten, wie sie in der Baumwolle vorliegt. Entfernt man nur die eine oder andere Art, so ist das Ergenis gering.

3. Das Lignin kann entweder: a) die Quellung hemmen und so die zur Bildung des Hydrates nötige intra-kristalline Quellung eindämmen, oder b) durch seine Lage zwischen den Zellulose- und Hemizelluloseketten, deren etwaige Neigung in einen Zustand höherer Organisierung überzugehen, hindern.

Die Merzerisierung der Jute in Natronlange, die intra-kristalline Quellung des Hydrates sowie die Schärfe der Reflexionen in photographischen Aufnahmen des Hydrates hängen also alle vom Ligningehalt ab.

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