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X-RAY DIFFRACTION STUDY OF DYED MERCERISED AND INTENSIVELY DELIGNIFIED JUTE FIBRES

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(Plate VIII)

ABSTRACT. Effects of the organic dye-stuffs methylene blue and congo-red on the structure of (1) raw jute fibres, (2) jute fibres subjected to intensive delignification, and (3) jute fibres subjected to incomplete mercerisation have been studied by means of X-rays. In the case of intensive delignification it was found that the cellulose crystallites remain unaffected but their orientations parallel to the fibre axes become deranged considerably. This change does not take place on incomplete delignification. Thus it is concluded that a fraction of the lignin in jute cements the cellulose fibrils to parallelism in a jute fibre and gives strength to it. This part of the lignin is more difficult to remove. The dye-stuffs were found to produce no effect on either the structure or the orientations of the cellulose crystallites whether native or mercerised. No change could even be discerned in the case of the dishevelled crystallite structure of intensively delignified jute.

INTRODUCTION

X-ray diffraction study of cellulose fibres has attracted the attention of a large number of workers over more than a quarter of a century and this has contributed much to our knowledge regarding the crystalline structure of cellulose and its derivatives. The unit cell structure of cellulose proposed by Polanyi (1921) and later by Sponsler and Dore (1926) were orthorhombic. Later on Meyer and Mark (1929) worked out a monoclinic cell with four glucose units ($C_6H_{10}O_5$) per unit cell. A new type of monoclinic cell was later suggested by Sauter (1937). Gross and Clark (1935), however, concluded that a monoclinic cell with $a=8.35$ A, $b=10.3$ A, $c=7.95$ A and $\beta=84°$ is in best agreement with the experimental results. It has also been established that the cellulose fibre is a crystalline aggregate consisting of small crystal areas (crystallites) separated by the amorphous or intercrystalline areas. A crystalline area is built up by the repetition of the unit cell arrangement of the glucose units, mentioned above, in all directions. The cellulose fibres studied by X-rays are ramie, flax, hemp, jute, etc. X-ray diffraction photographs of jute fibres have been taken in recent years in India by Banerjee and Roy (1941) and the work has been followed by Sircar, Rudra and Saha (1944), who are carrying out an extensive X-ray investigation of jute fibres. Banerjee and Roy found that the crystalline structure of jute cellulose is indentical with that of ramie and other varieties of cellulose. They also observed that lignin and fat do not enter into chemical combination with cellulose in jute fibre. It has also been found that the partial delignifications that have been studied in these earlier communications have no effect on the sharpness of the X-ray diffraction spots showing that even the orientations of the crystalline parts of cellulose are unmodified. The effect of complete delignification has been studied by us and the results form a part of the present communication. The effect of dyeing cellulose fibre has not apparently received sufficient

attention of the X-ray diffraction workers. The purpose of the present investigation is also to study by the X-ray diffraction method the effect of dyeing raw, delignified and mercerised jute fibres by organic dye-stuffs.

EXPERIMENTAL

X-ray beam from a Hadding tube run at a voltage of about 40 K.V. and a tube current of 5 to 7 milliamps after collimation through a narrow circular slit was allowed to be incident on a bundle of parallel fibres about 1 mm. in diameter in a direction perpendicular to the fibre axis. The camera used was a cylindrical one of diameter 6 cm. The circular slit had a diameter of about .5 mm. and length 5 cm. In a cylindrical camera the diffracted rays in the equatorial plane fall normally on the film and the diffraction spots on the equatorial line are at equal distances from the centre of the camera thus minimising the intensity loss of the large angle spots that occur in a plate camera. This also produces a great increase in the range of observations in the equatorial plane.

Photographs of the following samples were taken :—

1. Untreated jute fibre
2. Untreated jute fibre dyed with methylene blue
3. Untreated jute fibre dyed with congo-red
4. Intensively delignified jute fibre
5. Jute fibre intensively delignified and dyed with methylene blue
6. Jute fibre mercerised with 25 % NaOH solution at a temperature between 25°C and 30°C for half an hour
7. Jute fibre mercerised as above and dyed with methylene blue
8. Jute fibre mercerised as above and dyed with congo-red

From the co-ordinates of the positions of the maxima in the spots on the different photographs their angular co-ordinates ϕ and μ were determined from the relations

$$\phi = \frac{x}{R} \quad \text{and} \quad \tan \mu = \frac{y}{R}$$

where x = half of the horizontal distance in the film between the two symmetrical spots on the same horizontal line at the two sides of the central spot.

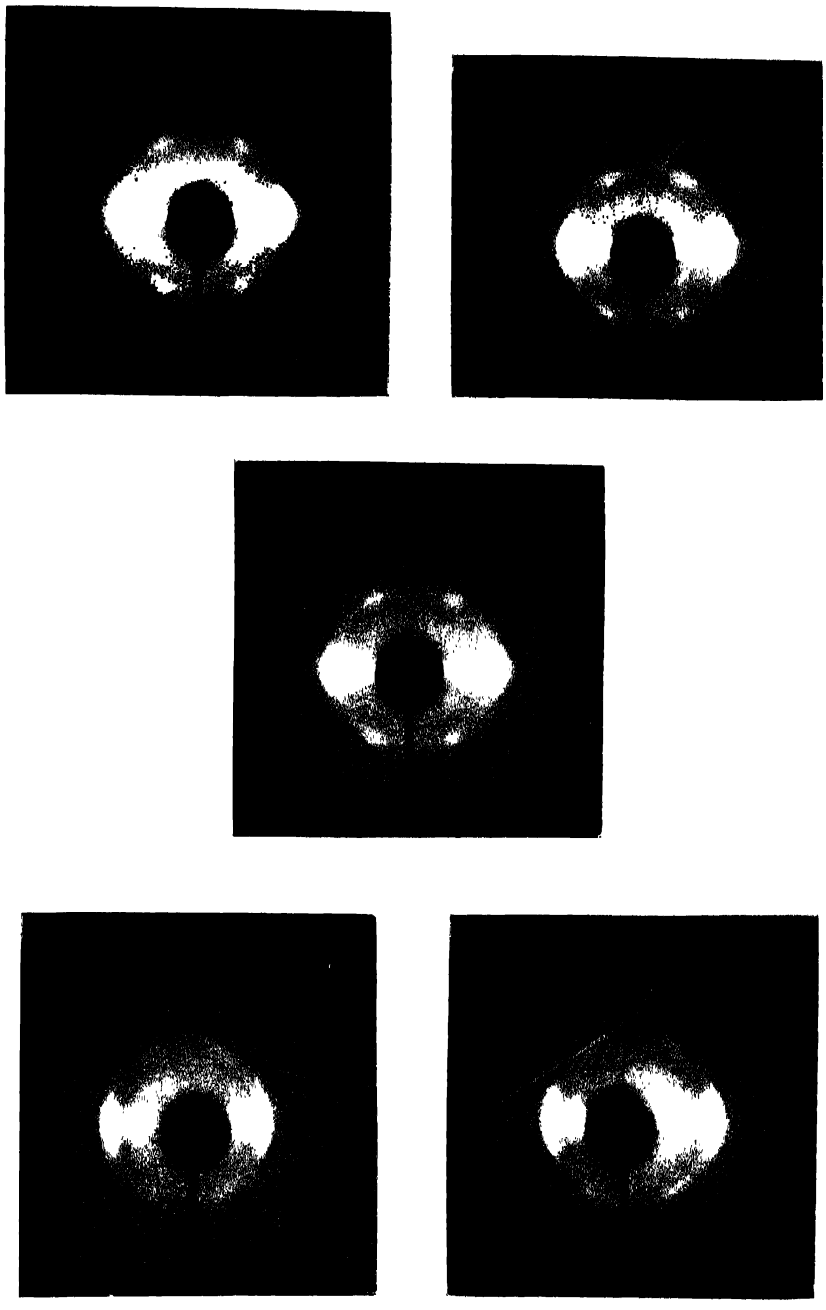
y = vertical distance in the film of the spots from the equatorial layer line

R = radius of the camera

The relation $\cos\phi \cos\mu = \cos 2\theta_n$, then gives the angle of diffraction. The indices of the planes giving rise to the X-ray diffraction spots were determined by comparing the observed Bragg angles of reflection, with those calculated from the formula,

$$\sin \theta_n = \frac{\lambda}{2} \sqrt{\left(\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl}{ac}\cos\beta\right) \Big/ \sin^2 \beta + \frac{k^2}{b^2}}$$

where θ_n = Bragg angle of reflection for the plane (hkl) and a, b, c, are the axial lengths along the three axes; β = angle between a and c axes; and λ = wavelength of the characteristic radiation used. The values of a, b, c and β were



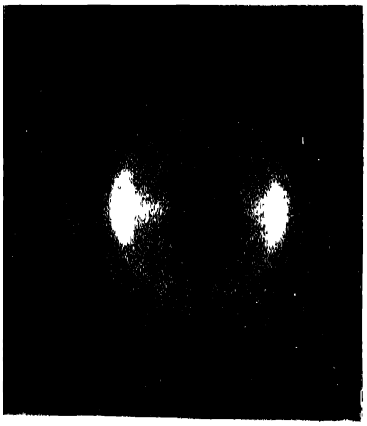
(a) — Raw Jute.

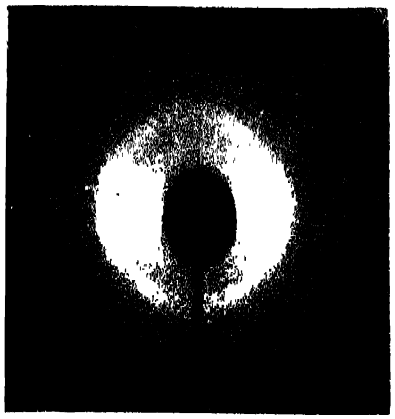
(b) — Raw Jute dyed methylene blue.

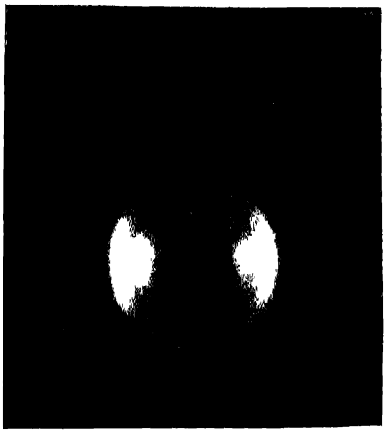
(c) -- Raw Jute dyed congo red.

(d) — Raw Jute delignified and dyed blue.

(e) -- Raw Jute delignified.







(a) Mercerised Jute

(b) — Raw Jute Mercerised and dyed blue.

(c) — Raw Jute Mercerised and dyed red.

taken to be those given by Meyer and Mark for (1929) the unit cell structure of cellulose. The indexing was facilitated by the knowledge of the order of the layer line to which a spot belongs. For this uniquely determines the index k of the planes giving rise to the spots. The Bragg angles of reflection for the different reflecting planes observed in the photographs of the different samples of jute and the calculated Bragg angles for the corresponding planes are given in the following tables.

TABLE I

Indices of the reflection planes	θ_n observed in the present investigation			θ_n Calculated
	Raw jute	Raw jute dyed blue	Raw jute dyed red	
101	7° 30′	7° 35′	7° 39′	7° 18′
101				8° 6′
120	10° 10′	10° 12′	10° 10′	10° 6′
021				10° 18′
002	11° 5′	11° 3′	11° 4′	11° 18′
311	17° 20′	17° 17′	17° 17′	17° 6′
212				17° 0′
032	17° 11′	17° 17′	17° 21′	17° 18′
004	23° 1′	23° 8′	23° 1′	23° 6′

TABLE II

Indices of the reflection planes	θ_n observed in the present investigation		θ_n Calculated
	Delignified jute	Jute delignified and dyed with methylene blue	
101	7° 49′	7° 46′	7° 18′
101			8° 6′
120	10° 11′	10° 16′	10° 6′
021			10° 18′
002	11° 22′	11° 18′	11° 18′
032	17° 18′	17° 18′	17° 18′
311	17° 20′	17° 21′	17° 6′
212			17° 0′
004	22° 56′	22° 53′	23° 6′

TABLE III

Indices of the reflection planes	θ_u observed			θ_u Calculated
	Mercerised jute fibre	Jute mercerised and dyed blue	Jute mercerised and dyed red	
$10\bar{1}$ mercerised	5° 55′	5° 58′	5° 48′	6° 3′
$10\bar{1}$ native	8° 1′	8° 5′	7° 53′	7° 18′
$10\bar{1}$,,				8° 6′
002 mercerised				11° 0′
101 ,,	11° 1′	10° 59′	10° 54′	10° 3′
002 native				11° 18′

EFFECT OF COMPLETE DELIGNIFICATION OF JUTE

From the tables it is observed that the values of θ_u observed for the corresponding diffraction spots in the photographs of raw jute and perfectly delignified jute are within the limits of experimental error, in conformity with the earlier results of comparatively milder delignification. But in the case of completely delignified jute (Plate VIIIA*a*) there is an important difference namely that the spots are no longer as sharp as those of raw jute (Plate VIIIA*a*). They retain their sharpness along the radial directions but extend along the directions of Debye Scherrer rings so as to form arcs. This shows that the crystallites of retain their cellulose size but deteriorate as regards their alignment along the fibre axis. A part of the lignin thus helps to keep the cellulose crystallites in regular orientation. This part of the lignin is more difficult to remove while at the same time it does not produce any alteration in the cellulose lattice. From the above results we are led to the conclusion that in jute a bundle of elementary cellulose fibres are cemented together by a small amount of lignin to form a fibre in which the crystallites of cellulose are parallel. This fibre is again imbedded into an excess of lignin which is comparatively easier to remove. The removal of this excess of lignin does not produce appreciable change in the nature of X-ray diffraction spots or the strength of the fibres. The removal of the more resistant part of the lignin, however, produces a dishevelling of the fibres producing an extension of the X-ray spots as well as weakening of fibre strength.

ACTION OF ORGANIC DYESTUFFS ON JUTE FIBRES

X-ray photographs of raw jute fibres dyed with congo-red (Plate VIIIA*b*) as well as with methylene blue (Plate VIIIA*c*) and also delignified jute fibres dyed with methylene blue (Plate VIIIA*c*) have been found to be exactly identical with those of the corresponding undyed fibres as shown by the positions of the maxima (Tables I and II) and diffuseness of the spots. The dyestuffs do not give rise to any

powder lines indicating that they enter the fibres in the amorphous state. This shows that not only the dyestuffs do not enter into the fibre crystallites but they are also unable to affect in any way the nature of the cementing of the cellulose fibrils by lignin, far to speak of any chemical combination with cellulose. It is of special interest that in perfectly delignified cellulose also dyeing does not produce any change in the extension of the diffraction spots. So the dyestuffs do not have any cementing action like lignin which would have produced an ordering of the crystallites and consequent shortening of the extensions of the spots.

X-ray photographs of jute fibres mercerised with 25% NaOH solution for half an hour at a temperature lying between 25 -30°C were taken (Plate VIIIBa). They showed the superposed patterns of both native and mercerised cellulose indicating that the fibres were partially mercerised. X-ray photographs of these mercerised fibres after dyeing with methylene blue (Plate VIIIB*b*) and with congo-red (Plate VIIIB*c*) were also taken. The patterns were quite identical with those of the fibres previous to dyeing as seen from the measurements of the positions of the maxima (Table III) as well as from the diffuseness of the spots except for an extension along the direction of the Debye Scherrer rings. This proves that even for mercerised cellulose the dyestuff has neither any effect on the crystalline structure of the mercerised cellulose nor on its aggregation, but a deterioration of alignment of the crystallites of both native and mercerised cellulose along the fibre axis takes place.

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