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A STUDY OF SOME VEGETABLE FIBRES BY X-RAY DIFFRACTION METHOD

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(Plates VA and VB)

ABSTRACT. X-ray photographs of several kinds of clean, delignified and fat free cellulosic fibres were taken and their tensile strengths measured. The fibres showing extensions of the spots along the Debye Scherrer rings indicating dishevelling of the fibre molecules were found to have tensile strengths generally smaller compared with those of other fibres. The fibres of Agava Sisalana Perrine (Sisal hemp) and Sansevieria Roxburgiana gave ring shaped photographs showing that the distribution of micelles in them was chaotic and at random. Diffraction patterns of these two kinds of fibres in a stretched condition showed that stretching partially orients the micelles of these fibres in a direction parallel to the length of the fibre.

INTRODUCTION

The method of X-ray investigation for the study of the internal structure of cellulose fibres was first applied by Polanyi (1922) and more thoroughly by Mark and Meyer (1939) and Herzog (1928) and his collaborators. As revealed by X-ray diffraction photographs the fibres are crystalline in the sense that they contain countless thin, invisible, submicroscopic crystallites, the atoms and molecules inside which are distributed in regular order. The properties of the fibres depend, to a great extent, on the size and arrangement of these minute crystals and also on the disposition of atoms and molecules within each crystal.

It is with a view to having an idea about the relationship between the internal structure and the physical properties, particularly the tensile strengths of various fibres that the present investigation was undertaken. The tensile strengths of the fibres under investigation were carefully determined and also their structures were investigated by the X-ray diffraction method.

Mark and Meyer from accurate measurements of the positions of the spots in X-ray photographs of ramie fibres definitely decided that the elementary unit of cellulose structure is monoclinic with four glucose units contained in a cell. They came to the conclusion that the space group is $C_2^2P2_1$. Andress (1929) calculating from known carbon to carbon and carbon to oxygen distances and from consideration of the chemical properties of cellulose, arrived at a structure which gave theoretical intensities of X-ray reflections in agreement with the observed intensities. X-ray investigation of jute fibres was first undertaken in India by Banerjee and Ray (1940) and later by Sircar, Saha and Rudra (1044) and by Sircar and Saha (1945). They found that the unit cell of jute fibre is identical with that of cellulose from other sources. In the present investigations we have taken in addition to jute fibres, some other vegetable fibres whose botanical names and Indian names (where possible) are given later in Table II. These fibres were kindly supplied to us by the Government Agricultural farm, Manipur, Dacca.

The raw fibres are composite in nature. They contain lignin, gummy and fatty substances whose presence give the fibres their peculiar characteristic colours. When they are removed and the X-ray photographs are taken, we get fairly clear photographs without indicating any change in the fundamental diffraction patterns of the fibres.

EXPERIMENTAL

The X-ray tube used throughout the investigation was of the Hadding-Sieghbahn type. The tube current was adjusted between 8 to 12 milliamperes at a voltage between 50 to 62 K. V.

The raw fibres were cleaned in a sohxlet apparatus with a mixture of alcohol and benzene about (1:1) which is very efficient for removing fats, waxes and resins. Lignin present in the fibres was removed by treating the fibres in a moist condition with the vapour of chlorine peroxide (ClO_2) in an atmosphere of CO_2. After removing the lignin the fibres were preserved in a bottle containing CO_2. For the photographs very thin bunches of fibres were taken to keep them straight and parallel.

IDENTIFICATION OF SPOTS

The photographs were taken with fairly high exposures, while using extremely thin bundles of fibres. The voltage applied to the X-ray tube was high so that the characteristic radiations of copper were considerably intensified compared to the white radiations. For these reasons a much larger number of spots could be measured than have been recorded by Meyer and Mark (1929). This number was still further increased by using a cylindrical camera which allowed a much wider range of angles to be studied. Since many of these spots have not been recorded by earlier workers it was considered worth while to identify them. In order to identify spots, the unit cell was assumed in each case to be monoclinic with the following dimensions for the unit monoclinic cell:

$$a=8.35\text{A},\ b=10.3\text{A},\ c=7.9\text{A and } \beta=84^\circ.$$

These values were accurately determined by Mark and Meyer. The glancing angles for the various planes were calculated from the monoclinic formula given below :—

$$\sin\theta_n=\frac{y}{2\sin\beta}\left(\frac{h^2}{a^2}+\frac{l^2}{c^2}-\frac{2hl}{ac}\cos\beta+\frac{k^2}{b^2}\sin^2\beta\right)^{\frac{1}{2}}$$

where θ_n is the glancing angle which was obtained from the geometry of the spot on the film ; β is the angle between the a and the c axes. h, k, l are the millerian indices of the plane giving rise to the spot in question. a, b, c are the axial lengths of the unit cell.

These measured glancing angles were then compared with those calculated from the formula for the various planes having the K index corresponding to the layer line in which the spot in question occurs and the other two indices could be thus found.

The results of identification of the spots in the X-ray diffraction photograph of delignified flax are given in Table I. Data for other fibres being quite similar are not reproduced.

TABLE I

Identification of the reflecting planes of lignin-free flax fibre.

Millerian indices.	Calculated θ_B for Cu K radiation.	Measured θ_B.	Estimated Intensity.
101	7° 18′	7° 13′	S
$\bar{1}01$	8° 6′	8° 12′	S
002	11° 18′	11° 24′	V S
201	11° 36′		
004	23° 6′	23° 12′	M W
$21\bar{2}$	17° 0′	17° 7′	M
311	17° 6′		
31	19° 24′	19° 16′	W
020	8° 36′	8° 40′	M W
120	10° 6′	10° 14′	M W
021	10° 18′		
221	14° 30′	14° 24′	M W
221	15° 24′	15° 28′	W
$1\bar{2}2$	15° 42′		
321	18° 48′	18° 51′	V W
322	20° 51′	20° 55′	V W
421	23° 44′	23° 50′	V W
130	14° 0′	14° 5′	M
131	14° 54′	15° 14′	M W
$1\bar{3}1$	15° 24′		
032	17° 18′	17° 15′	M S
232	21° 12′	21° 10′	M W
331	21° 16′		
040	17° 24′	17° 30′	M
141	19° 20′	19° 14′	W
042	20° 57′	20° 49′	M W

MEASUREMENT OF THE TENSILE STRENGTHS OF THE FIBRES

The tensile strengths of the fibres were determined with an apparatus shown in Fig. I. It consists of an ordinary balance in which the left pan has been replaced by two clips A and B. A is suspended from the left beam while B is attached to the balance pillar and can be moved up and down by rack and pinion arrangement. A and B lie in the same vertical line. A number of fibres of a particular sample were examined under a microscope and some two or three fairly uniform fibres were selected for determining the tensile strength. The diameter was measured with a travelling microscope at different parts of the fibre and the mean was taken. Readings were taken at some forty to fifty different points. Several readings were taken for the

diameter at each point after rolling the fibres sideways the mean giving the diameter at that point.

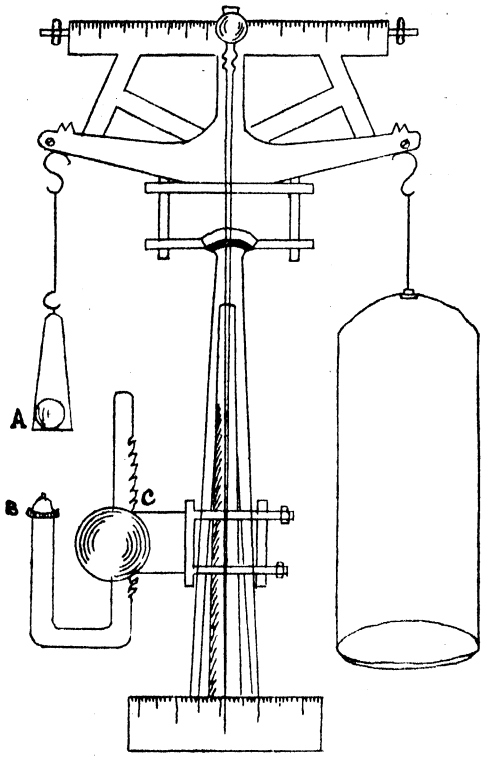


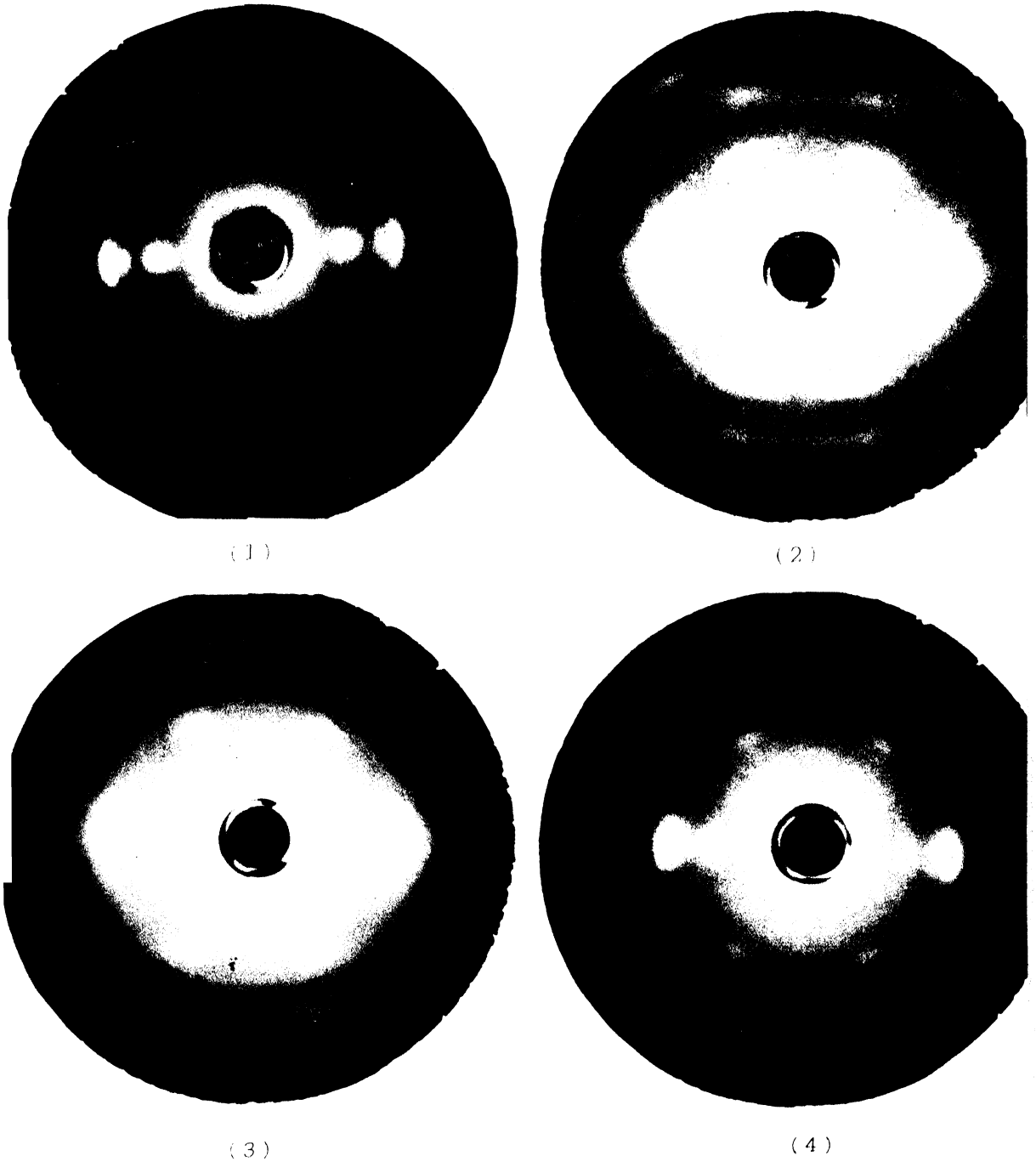
FIG. 1

Apparatus for measuring the tensile strength
A—upper clip B—lower clip
C—Rack-and-pinion arrangement

After carefully clamping a single fibre at both the ends A and B, C was very slowly turned to stress the fibre just properly so that on releasing the pan, the pointer remained at the zero position. The weights were slowly and gradually increased, for it had been found that a fibre broke with a smaller weight when the latter was placed at once. It was also noticed that at a certain weight the fibre did not break as soon as the beam was raised but only after a few seconds. Even with all possible precautions, it was very difficult to get consistent results. Reproducible results could, however, be obtained after a large number of experiments. The tensile strength T expressed in Kgm per mm^2 was calculated from the equation

$$T=\frac{w}{\pi r^2}$$

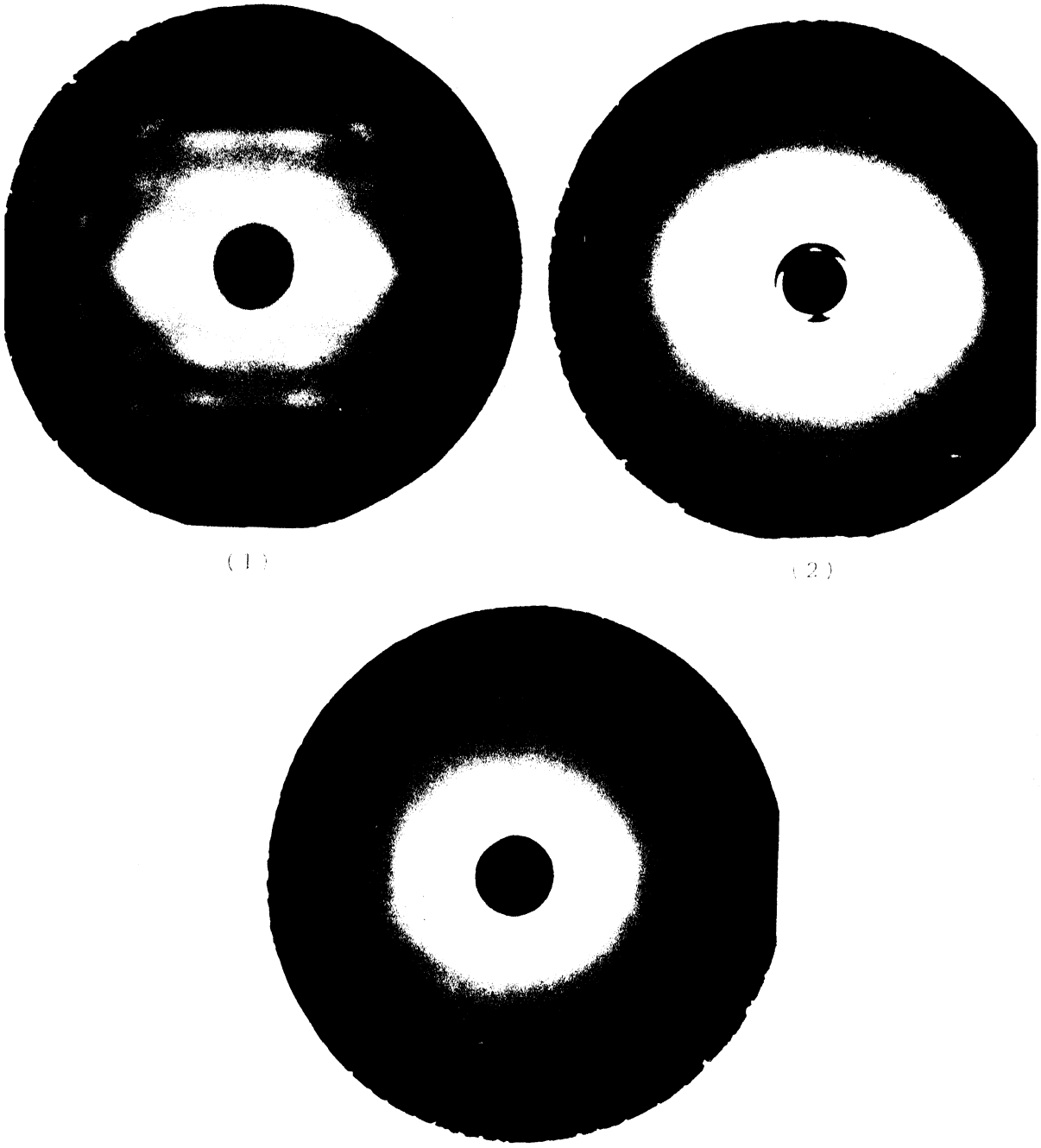
where w is the breaking weight expressed in Kgms and r is the mean radius of a single fibre in mm. The results are shown in Table II.



(1) (2)

(3) (4)

1. X-ray diffraction pattern of delignified Ramie
2. X-ray diffraction pattern of delignified Flax
3. X-ray diffraction pattern of delignified Hibiscus Esculantus
4. X-ray diffraction pattern of delignified Malachra Capitala



(1) (2)

(3)

1. X-ray diffraction pattern of delignified Crotalania Juncea (Sunn hemp)
2. X-ray diffraction pattern of delignified Agane Sisalana (Tisol hemph) (unstretched)
3. X-ray diffraction pattern of stretched Agane Sisalana

Table II.

Tensile strengths of the different fibres

Botanical names	Indian Names	Mean radius of fibres	Mean tensile strength
Boehmeria Nivea Hook & Arm (Plate I) (Ramie)	Rhea	·01855	24. 24
Hibiscus Abelmosehns (Musk Mallow)	Kasturi	.02500	35. 10
Rinum Usitatissimum (Flax) (Plate II)	Tisi	.02953	38. 82
Hibiscus Esculantus (Plate III)	Dhenras	.02940	22. 66
Malachra Capitata (Plate IV)		.02753	21. 16
Hibiscus Sabdariffa Var-altissima	Chukoir	.04359	10. 71
C. Capsularis	Pat	.02476	22. 97
Sida Rhombifolia (Berella)	Berela	.02042	17. 02
Crotalaria Juncea (Sun hemp) (Plate V)	Sonn	03797	18. 68
Agava Sisalana Perrine (Sisal hemp) (Plate VI & VII)		.05779	9. 51
Sansevieria Roxburghiana Schult	Gorachakra Murba	.04083	14. 68

DISCUSSION

A large number of different types of vegetable fibres were examined. The diffraction patterns of the different fibres show that the fundamental constituent is in each case cellulose.

X-ray diffraction patterns of these fibres are not similar in the strictest sense of the term. Though many of the photographs resemble as regards their pattern and position of spot yet the character, shape and size etc. of these spots are quite different in different pictures. In some of the photographs the spots are more discreet and better resolutions are obtained. This shows that crystallities in the corresponding fibres are more regularly arranged in a direction parallel to the length of the fibres.

There are other pictures where the spots are remarkably long. These spots always take the form of an arc of a circle with the central spot on the film as their centre of curvature. This indicates that the micellels or the crystallites in the corresponding fibres are much more irregularly distributed in the fibre and they are not strictly parallel to each other or to the fibre axis.

Again there are two particular varieties of fibres namely, Agava Sisalana Perrine (Sisal hemp) and Sansevieria Roxburghiana which have almost got no discreet reflected spots except two intense spots in the central layer and these two are very much elongated and bent in the form of an arc of a circle making an angle of about 60° at the centre. These photographs also show

two or three complete circular rings of almost uniform blackness, corresponding to the rings obtained in a powder photograph.

A special X-ray diffraction pattern of one of these two fibres, (Sisal hemp) was taken with the fibre stretched to a great extent. The difference between the stretched and unstretched fibre photographs is that the rings in the stretched one show more pronounced intensity maxima along the rings. Thus it may be said that the distribution of the micelles in these two fibres are almost a chaos, even in the direction of the long axis of the fibres. The stretching of the fibres partially orients the micelles towards more or less parallelism to the length of the fibre.

The tensile strengths of fibres play an important part in their industrial application. Hence the tensile strengths of all the fibres were measured with care to see if any relation could be derived between the tensile strengths and the X-ray diffraction patterns of the fibres specially with regard to the character of the spots, their sizes and shapes and also the tendencies towards formation of rings. On examining the data it is found that the two fibres characterised by rings in the X-ray diffraction patterns have tensile strengths generally smaller compared with those of other fibres. On further examination of the data it is found that the mean radii of these two fibres (as measured for determining the tensile strength) are greater than those of the others. Thus it seems that the more random and chaotic are the micelles in them the less are their tensile strength.

ACKNOWLEDGMENT

The investigations were carried out at the Physics Laboratory of the Dacca University at the suggestion and under the guidance of Prof. S. N. Bose to whom our heartfelt thanks are due. Our sincere thanks are also due to Prof. K. Banerjee for his advice at the time of writing out the paper.

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