Structure of Native and Mercerized Celluloses

THE crystal unit-cells proposed by K. Meyer and H. Mark¹ and K. Meyer and L. Mish² for cellulose lattices I and II, and for which there seemed to be general agreement, have been discussed recently by M. K. Sen and S. C. Roy³. These authors have given a new interpretation to X-ray diagrams obtained from these fibres, based on the existence of a strong diffraction intensity corresponding to a reticular distance of the order of 14 Å. This interference result had hitherto not been observed for these substances. This new interpretation has been considered with certain reservations by G. O. Warwicker and H. J. Vellard⁴, who have pointed out the causes of errors already remarked upon by other investigators. H. J. Woods⁵, on the other hand, has observed a small-angle spot for jute very near that observed by Sen and Roy.

It seemed worth while to us to repeat this work on a group of textile fibres (ramie, viscose, linen, 'Fortisan', etc.) using experimental techniques beyond criticism.

X-ray diagrams were obtained with a diffraction camera which was designed especially for fibre studies⁶. In brief, the film is placed in a vacuum, the X-ray beam coming from a copper anticathode is monochromatized by reflexion from a curved quartz crystal, and the focalization is exact for all angles within the equatorial plane (Guinier⁷).

The diffraction diagrams may be obtained up to approximately 20 Å. Furthermore, the mounting of a double monochromator⁸ in a vacuum, making it possible to obtain diagrams at very small angles, permits us to record the diffusion from 200 Å. up to reticular distances corresponding to intense equatorial interferences of the cellulose fibres (101) and (101), or (101) for mercerized cellulose. Diagrams were obtained using samples that were dried as much as possible and then afterwards humidified.

In every case no reflexion corresponding to a reticular distance of 14 Å. could be observed. Only jute (an imperfectly delignified sample) gave an equatorial spot corresponding to 14 Å.; but its intensity was very weak (4 or 5 per cent of the intensity of (101) at the very most).

The perfect agreement of the results obtained by means of the use of two complementary methods indicated that, for the group of cellulose fibres, the interference observed by Sen and Roy could not be repeated. In the case of jute the purity of the cellulose must be challenged.

As a result it appears that the customary interpretation of fibre photographs will not have to be modified. On the other hand, we have succeeded in demonstrating that, under certain faulty experimental conditions, it is possible to observe aberrant reflexions. Thus by irradiating the fibres with a

beam from a tube having a chromium anode, we have observed the spots noted by Sen and Roy. Moreover, monochromatization of the beam caused these spots to disappear. This proves that in the case of substances which are as badly crystallized as the textile samples, one must give special attention to experimental techniques, and in particular to the composition of the X-ray beam used.

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Synthesis of Poly-S-Allylcysteine (Poly-Deoxo-Alliin)

WE wish to report briefly on the synthesis of poly-S-allylcysteine (IV) (poly-deoxo-alliin), from 1-S-allylcysteine (I), by the route indicated in the scheme:

1-S-Allylcysteine, prepared according to Stoll and Seebeck¹, yielded the appropriate N-carboxyanhydride (III), via the intermediary chloride (II), on passing phosgene for about two hours at 60° through a suspension in dry dioxane. The solution was evaporated *in vacuo* at 40° and the residue kept overnight in a vacuum desiccator over phosphorus pentoxide. The remaining crystalline mass (melting point about 50°) was recrystallized from dry ethylacetate - petroleum ether, and the pure N-carboxyanhydride (III) melted at 55° with resolidification at about 115°.

Polymerization of (III) was carried out either in solution or in bulk in high vacuum. Pyridine, dioxane (with the addition of a trace of water when working in the cold or dry if heating to about 100°), glacial acetic acid or ethanol was used as solvent. On heating in bulk in a high vacuum, actual polymerization took place only on raising the temperature considerably above the melting point of (III)—at about 150°; at temperatures of about 100–105°,