Note

Fiber structure of mannan triacetate

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Naturally occurring polysaccharides frequently occur partially acetylated. These acetyl groups allow unique solubility properties; for example, native (1→4)-β-D-mannan is water-insoluble but the mannan in *Tubera salep* contains acetyl groups, which eliminate crystallinity and allow solubility in water[1]. To understand more fully the conformational influence of the acetyl group on the polysaccharide backbone, we have recorded fiber X-ray diagrams for oriented, completely acetylated polysaccharides, which will provide conformational information for these peracetates.

Mannan triacetate[2] was dissolved in chloroform and the solution was dried to give a thin, transparent film. The film was hot-stretched at 210°. The fiber diagram (Fig. 1) was taken in a flat-film, vacuum camera. Strong reflections are found on the equator ($d = 9.73$ Å) and on the second layer-lines ($d = 5.0$ Å). The other reflections are more or less degenerated to layer-line streaks. Although the pattern is not of high quality, the orientation is adequate and the distribution of intensity is characteristic

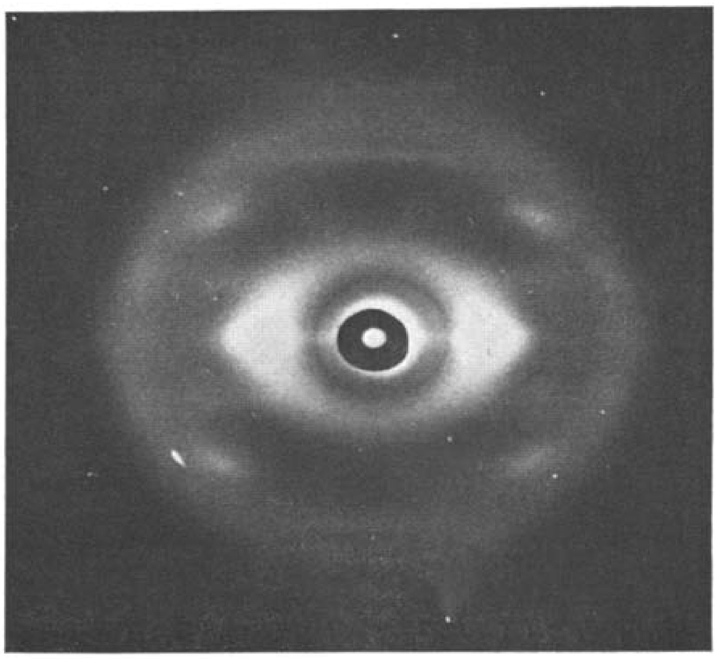

Fig. 1. X-Ray fiber diagram for oriented (1→4)-β-D-mannan triacetate. The fiber axis is vertical, the film-to-sample distance is 5 cm and CuK$_\alpha$ radiation was used

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of a helix. This is shown by the single, strong, equatorial reflection and the large area along the meridian where there is absence of diffracted intensity.

Based on layer-line measurements, the fiber repeat was found to be 15.24 Å. Meridional reflections are absent, except on the third layer-line, as was confirmed by appropriate "titled fiber" patterns. From conformational analytical data[3], based on minimum-energy considerations, for the unsubstituted mannan backbone it must be concluded that these data imply a threefold screw-axis along the chain. This is different from the original twofold screw-axis of unsubtituted mannan[4], with 10.27 Å and 10.2 Å fiber-repeats for mannan I and II, respectively. Very probably, the acetyl groups induce the threefold helix because of unfavorable contacts between substituents, either in the same or in neighboring chains. The influence of the acetyl groups on the chain conformation of D-mannan is just the opposite of that observed for the (1→4)-β-D-xylan and its diacetate: whereas the unsubstituted D-xylan has a threefold screw-axis[5], D-xylan diacetate has a twofold screw-axis[6]. Cellulose[7] and cellulose triacetate[8] both have twofold screw-axes; in amylose, a sixfold helix is the most likely[9], whereas amylose triacetate has a nonintegral helix[10] that is close to fivefold. Investigations are underway to study these phenomena by chain-conformational analysis from stereochemical criteria.

Clearly, if the non-bonded interactions between contiguous D-mannose residues are changed significantly by acetate substitution, as is suggested by the change in the X-ray fiber repeat, the solubility properties will be affected. This effect will be entropic, as new, coiled conformations will be favored compared with those that are most probable for the unsubstituted state. Previous thinking concerning the solubility of partial acetates of polysaccharides has tended to focus on disruption of crystallinity, caused by irregular substitution along the chain, as the only cause of increased solubility.

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