

X-ray diffraction studies on the xyloglucan from tamarind (*Tamarindus indica*) seed

Iain E.P. Taylor and Edward D.T. Atkins

Department of Botany, University of British Columbia, Vancouver, BC V6T 2B1, Canada and H.H. Wills Physics Laboratory, University of Bristol, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, England

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Oriented samples of the xyloglucan polysaccharide from tamarind seed were examined using X-ray diffraction. Periodicities indexing on a spacing of 2.06 nm were observed along the chain direction. This value is twice that reported for cellulose and is commensurate with four β -1,4-linked glucose residues. Flat, ribbon-like two-fold helical models for the β -1,4-linked polyglucose backbone, with two possible schemes for decoration with xylose and galactose side groups, are proposed.

Xyloglucan X-ray diffraction Tamarind seed Polysaccharide Conformation

1. INTRODUCTION

Thickened cell walls in *Tamarindus indica* (tamarind) cotyledons contain amyloid [1]. This is a water-soluble xyloglucan [2] with a backbone of β -1,4 linked D-glucose. Xylose residues are attached to 60–75% of the glucoses by α -1,6 linkages and galactose residues are attached to 25–30% of the xyloses by β -1,2 linkages [1,3]. A similar xyloglucan has been reported from other plant cell wall preparations [4,5], but isolation requires extraction with concentrated alkali [6].

It is widely believed [4,7] that, in vivo, this xyloglucan forms a strong, hydrogen bond association with cellulose. The formation of such an association must depend upon the presence in the xyloglucan of molecular surface(s) that are compatible with cellulose. This first report of X-ray diffraction results shows that tamarind xyloglucan contains such domains of structure.

2. MATERIALS AND METHODS

Seeds of *Tamarindus indica* were obtained from tamarind pulp purchased from the local market.

Xyloglucan was prepared by the method of Kooiman [1]. The sugar composition was deter-

mined by gas-liquid chromatography of alditol acetates [8] after hydrolysis in 2 N trifluoroacetic acid or 72% H_2SO_4 . An oriented preparation was obtained by dissolving the xyloglucan in warm water (10 mg/ml) and preparing a film which was extended in a stress field at 100% relative humidity at 75°C for 48 h.

2.1. X-ray diffraction

X-ray diffraction patterns were taken using a fine focus Elliott rotating anode generator with pinhole collimation and a fully enclosed flat plate camera. Nickel filtered CuK radiation was used. Helium was passed through the camera to reduce air scatter of the X-rays since exposure times were of the order of 24 h. The relative humidity inside the camera was also maintained with saturated salt solutions by bubbling the incoming helium through one solution and placing another within the camera. Photographs of specimens taken with the samples in a number of orientations about the stretch direction were all similar indicating that the samples had cylindrical symmetry. Calibration of the photographs was achieved by dusting them with finely powdered calcite which has a prominent (111) diffraction ring with characteristic spacing 0.3035 nm.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern (fig.1) from the xyloglucan exhibits layer lines which index on a lattice spacing of 2.06 nm, twice that observed for cellulose. A straightforward and reasonable interpretation, in light of our extensive knowledge of cellulosic geometries and shapes (e.g., [9-11]) is outlined as follows.

The basic polyglucose backbone exists as a two-fold helix, similar to cellulose and is therefore likely, in the first instance, to be compatible with it at the molecular level. Two-fold helices of 1,4 diequatorially linked polysaccharides generate flat, ribbon-like structures. The overall periodicity, or pitch, of such a helix is 1.03 nm, with an axial advance per glucose unit of $1.03/2 = 0.515$ nm. Superimposed on this backbone, and decorating it, is a substitution pattern of xylose residues which can attach to the hydroxymethyl groups in position 6 of the glucose residues. Further secondary substitution of galactose residues can occur onto the xylose units. The observed periodicity of 2.06 nm, which represents a periodicity along the polysaccharide chain, argues for a chemical repeating sequence commensurate with four 1,4

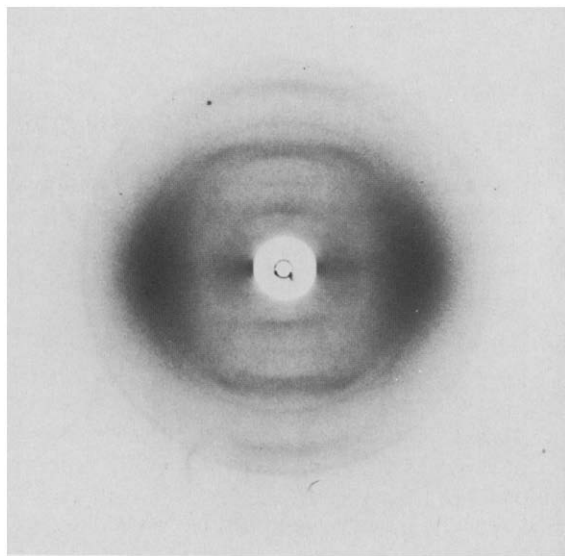


Fig.1. X-ray fibre diffraction pattern of xyloglucan. The sample was stretched in the vertical direction and rings are for calibration purposes.

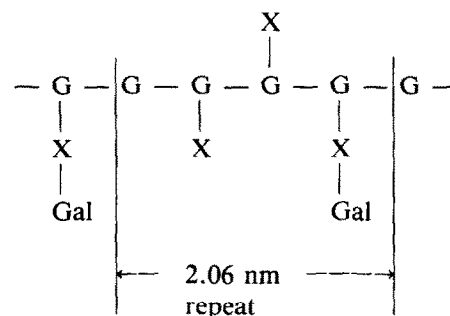
Table 1

Spacings and intensities of diffraction signals observed along the meridional direction (fibre direction)

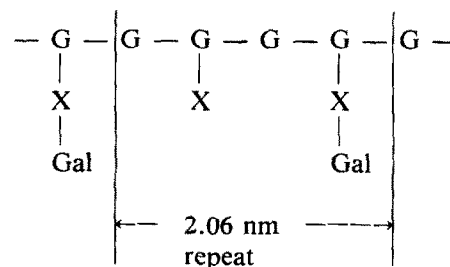
Spacing (nm)	Observed intensity
1.03 ± 0.01	strong
0.68 ± 0.01	medium
0.51 ± 0.01	strong
0.34 ± 0.01	medium-weak
0.25 ± 0.01	strong

diequatorially linked glucose units along the polysaccharide backbone.

This result agrees with independent composition determinations showing that glucose (G), xylose (X) and galactose (Gal) occurred in the molar ratios of 4:3:1. We could suggest a model:



Ideally the model requires that all substituents emanate from the same side of the backbone. If there is some uneven distribution of the substituents, with some domains having all glucose residues substituted with xylose and the regions of crystallization having molar ratios of 4:2:1, one side of the molecule could be unsubstituted and free to order with similar segments or with cellulosic material thus:



Four diffraction signals at spacings of 2.02, 0.823, 0.589 and 0.44 nm are observed on the equator. These do not correspond with either cellulose I [9] or cellulose II [10], nor would we expect them to a priori, since the substitution of the backbone will alter the chain packing substantially. The spacing at 2.02 nm, in particular, indicates a unit cell dimension some 2–3-times larger than cellulose and is presumably caused by the xylose/galactose appendages.

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