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**Note**

# On the ester linkage between lignin and 4-*O*-methyl-D-glucurono-D-xylan in jute fiber (*Corchorus capsularis*)

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It was reported[1] in our previous communication that the uronic acid side-chain residues on 4-*O*-methyl-D-glucurono-D-xylan in jute fiber are partially linked to the lignin component of the fiber by ester bonds. The degree of esterification (d.e.) was estimated to be 34% on the basis that the uronic acid content of D-xylan obtained from borohydride-treated jute fiber was found to be 34% less than that isolated from untreated fiber, and that a corresponding proportion of 4-*O*-methyl-D-glucose was introduced into the former xylan during the reductive treatment.

In a subsequent investigation[2] on the origin of the acidity in jute fiber, the pH–neutralization curves (n.c.) furnished by raw and demineralized fibers, each consisting of one inflection point only, were found to possess remarkable dissimilarity compared to that furnished by D-xylan isolated from the same fiber; the former curves resembling those of very weak acids, and the latter, those of weak acids. The n.c. furnished by cation-free, de-esterified jute fiber showed the presence of a mixture of weak and very weak acid in the fiber, the proportion of the latter acid (8.6 mmol/100 g) being quite comparable to the titratable acidity of demineralized fiber (9.0 mmol/100 g). In addition, both the raw and the demineralized fibers were capable of undergoing the diazo coupling-reaction with diazonium salts, each consuming ~12 mmol of the coupling reagent per 100 g of the respective fibers. The entire acidity in these fibers was thus attributed to phenolic groups of the lignin component, implying that the *in situ* d.e. in jute fiber is much greater than that reported earlier[1]. An attempt has therefore been made in this report to resolve the apparent ambiguity with the help of infrared spectroscopy.

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## EXPERIMENTAL

Extractive-free, pulverized jute fiber (grade $W_5$), prepared by the earlier method[1], was further powdered in batches in a vibratory ball-mill for exactly 2 min, using a steel ball. This powdered fiber was used in the present investigation. About 2 mg of fiber per 100 mg of potassium bromide were intimately mixed in a vibratory ball-mill, and a pellet was prepared from the mixture in the usual way for recording i.r. spectra of samples in a Perkin–Elmer Infrared Spectrophotometer, model 399B. All other methods were as described earlier[1].

## RESULTS AND DISCUSSION

It had been observed[1] that the *O*-acetyl groups associated with jute fiber in the form of ester linkages with the carbohydrate portion of the fiber could be completely reduced by three consecutive treatments of the fiber with M potassium borohydride. It was thus assumed that the lignin–carbohydrate ester bonds would also be completely reduced during these treatments. However, the i.r. spectrum of the fiber that had been treated 3 times with borohydride (*vide* Fig. 1) contained a broad absorption band at ~1730 $cm^{-1}$ due to C=O stretching vibrations of ester or free

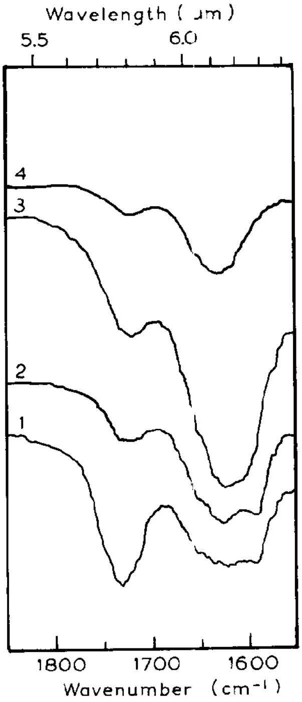

Fig. 1. Infrared spectral characteristics of 1, raw jute fiber; 2, fiber obtained by three successive, borohydride treatments of raw jute; 3, thrice borohydride-treated fiber after delignification; and 4, fiber obtained by two successive, borohydride treatments of the delignified fiber.

carboxylic acid groups or both. In order to accommodate the previous titration and coupling-reaction data[2], it might be reasonable to assume that the absorption band is due to unreduced lignin–carbohydrate ester bonds only. The intensity of this band relative to the adjacent aromatic band could not, however, be diminished further by treatment with borohydride, presumably due to inaccessibility of reaction sites to the reducing agent, on account of steric hindrance, hydrophobicity of lignin, and heterogeneity of the reaction medium.

The aforementioned, borohydride-treated fiber was delignified with sodium chlorite, and the water-soluble lignin fragments were washed out, in order to diminish these inhibitory factors, but the spectral characteristics of the delignified fiber did not change appreciably in the vicinity of 1730 $cm^{-1}$. This result also confirmed the earlier suggestion[1] that chlorite delignification does not affect the ester linkages. The intensity of the ester band furnished by the delignified fiber decreased considerably on two consecutive treatments with M borohydride, understandably so, because the originally unapproachable sites were rendered accessible on removal of the hindering lignin molecules. All attempts to diminish the ester band by further treatment with borohydride proved futile.

In order to estimate the extent to which the lignin–xylan ester bonds were reduced during these treatments, a crude D-xylan was isolated by alkaline extraction of the delignified and borohydride-treated fiber. Upon repeated precipitation of the contaminating hexoglycans in the resulting polysaccharide mixture with barium hydroxide, the supernatant liquor containing the barium complex afforded a pure D-xylan, that had 8.9 mol of 4-*O*-methylglucose per 100 xylosyl residues (estimated by g.l.c.). The former sugar must have been introduced into the polysaccharide as a consequence of reduction of a corresponding proportion of 4-*O*-methyl-D-glucuronic acid residues attached to the xylan backbone.

It may be noted, however, that the proportion of xylose escaped, along with D-xylo-oligouronic acids, during the preparation of the alditol acetate derivative for g.l.c. analysis was not accounted for in estimating the mole ratio of xylose to 4-*O*-methylglucose. The xylose not accounted for was assumed to be negligibly small compared to that appearing in the g.l.c. profile, because the uronic acid content of the purified D-xylan was small. The average number of uronic acid side-chains attached to the linear backbone of jute D-xylan has been variously reported[1–3] to be 15.9, 14.3, and 12.3 per 100 xylosyl residues, of which the last figure (arrived at by titrimetric estimation[2] of uronic acids) appears to be the most reliable. Consequently, by comparing the number of 4-*O*-methylglucose residues present in the reduced D-xylan with that of the uronic acid side-chains associated with the untreated D-xylan, it may be shown that only ~72% of the lignin–xylan ester linkages could be reduced during the aforementioned sequence of treatments.

Whether the failure to achieve complete reduction of the uronic acid residues is attributable to location of this portion of the D-xylan deep in the $S_3$ layers of the secondary wall, or to the protective action on these groups by residual lignin, could not be ascertained with certainty. It may be relevant to mention that the titration experiments with mesta fiber[4] also suggested that entire uronic acid side-chains on the D-xylan component of this fiber are ester bonded, and that a substantial part of these acidic sugars could not be reduced to the corresponding neutral sugar under the same conditions.

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