

Studies on the chemical nature of jute stick lignin for its commercial utilization

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ABSTRACT

Milled wood lignin (MWL) and dioxane acidolysis lignin (DAL) were isolated from jute stick of two varieties (*Corchorus capsularis* JRC 7447 and *Corchorus olitorius* JRO 524) and their chemical nature was studied by spectral and chemical methods. Various possibilities of commercial utilization of jute stick lignins have also been discussed.

INTRODUCTION

Next only to cellulose, lignin is the most abundant organic resource, produced annually in the form of huge agro residues in the agricultural sector of our country. Jute stick is a well known raw material for pulp and paper¹. 3-4 million tons of the raw material is obtained annually as an agricultural residue from jute cultivation.

While, the paper industry utilizes cellulosic fibre almost fully, hardly any serious attempt is made to isolate lignin from the spent liquor and convert it to valuable by products. As the knowledge of the chemical nature of jute stick lignin is a prerequisite for its commercial exploitation, the chemical nature of milled wood lignin and dioxane acidolysis lignin has been studied. The various possibilities of commercial exploitation of lignin and its by products have been discussed.

EXPERIMENTS AND METHODS

Jute stick of two varieties *Corchorus capsularis* (JRC 7447) and *Corchorus olitorius* (JRO 524) were disintegrated in a Wiley mill and defatted with benzene-ethanol (2:1, v/v) mixture. Defatted jute stick samples (60-mesh) were used to isolate milled wood lignins by adopting Brownell's dry ball milling method²

and dioxane acidolysis lignins by Pepper and Siddiqui's procedure³. Elemental analysis was carried out for carbon, hydrogen and oxygen. The methoxyl content was estimated by Zeisel's method⁴ and phenolic hydroxyl content by Delta Epsilon method of Goldschmid⁵. Carbohydrate contamination was estimated by hydrolysis according to the method of Jeffery et al⁶. The infrared (IR) spectra were determined by KBr pellet technique in Shimadzu IR 440 spectrophotometer.

RESULTS AND DISCUSSION

The results of the analytical composition of milled wood lignins (MWL) and dioxane acidolysis lignins (DAL) of the two varieties of jute stick (viz., JRC 7447 and JRO 524) are presented in Table I. As seen from the Table I the carbohydrate contents in the dioxane acidolysis lignin is negligible as compared to the milled wood lignins of jute stick, this is to be expected considering the acidolysis condition used in DAL samples. The carbon content of the *olitorius* variety JRO 524 is little higher than the *capsularis* variety JRC 7447 in both the lignin preparations. Similarly, the methoxyl content of the *olitorius* variety is little higher than that of the *capsularis* variety. The

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TABLE I
Characteristic of jute stick lignins-dioxane acidolysis and milled wood :-

	Dioxane JRO 524	acidolysis JRC 7447	Milled JRO 524	Wood JRC 7447
Approx. yield on total Klason lignin,%	36.5	33.3	9.8	10.2
Carbohydrate content, xylose,%	0.27	0.66	6.28	6.58
Elemental composition. %				
Carbon	61.51	60.2	59.5	56.9
Hydrogen	5.64	5.66	5.74	5.74
Oxygen	32.9	34.14	34.76	37.36
Methoxyl	20.5	19.7	18.3	17.5
Unconjugated Phenolic hydroxyl, mole OH/C ₉ unit Elemental formulae per C ₉ Unit	0.06	0.08	0.16	0.15
Carbon	6	9	9*	9*
Hydrogen	7.29	7.63	7.60	8.13
Oxygen	2.80	3.08	2.69	3.52
Methoxyl	1.33	1.30	1.28	1.27
C ₉ formula weight	202	206	203	212

* With carbohydrate corrections

high methoxyl to carbon ratio (Meo/C) is concurrence with other hardwood lignins. Based on the elemental composition the phenyl propane (C₉) units have been calculated as shown in Table I. The C₉ formulae show that the MWL samples of the two varieties of jute stick are almost the same and are similar to other hardwood lignins. The same observation was observed in the case of DAL preparations.

The IR spectra of the two varieties of jute stick lignins, MWL and DAL are shown in Figures 1 and 2, respectively. Figure 1 shows the band 1735 cm⁻¹, ascribed to acetyl group in carbohydrate contaminants in MWL. The 1690-cm⁻¹ band, attributed to C-O stretching in the α position to benzene ring⁷ gives small peaks in the MWL samples. The 1660-cm⁻¹ band also ascribed to the above reason, conjugated to p-hydroxy phenyl group or etherified p-hydroxy phenyl group⁷, shows quite prominent peaks in both the MWL samples.

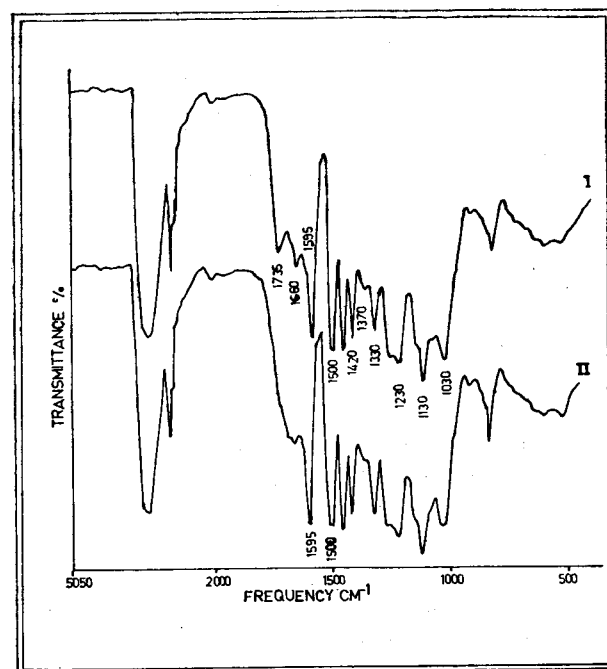


Fig.1 . IR spectra of I - MWL JRC 7447 and II - MWL JRO 524.

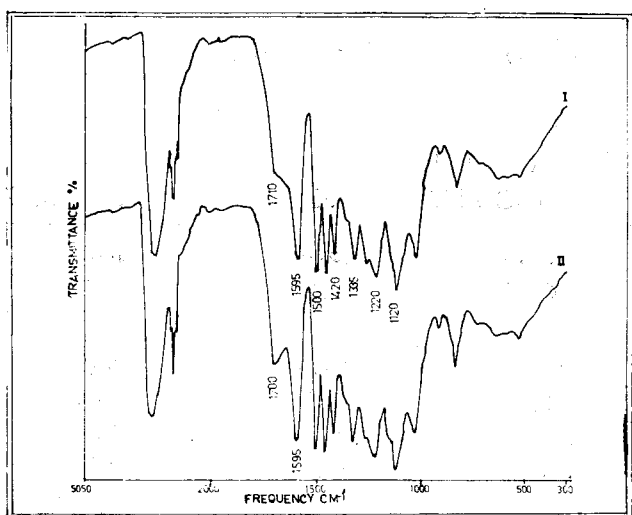


Fig. 2. IR spectra of I - DAL JRC 7447 and II - DAL JRO 524.

The bands attributed to aromatic skeleton ring vibrations are observed at 1595 and 1500 cm^{-1} as strong peaks. The band 1460- cm^{-1} ascribed to asymmetric C-H in-plane deformation is stronger than the 1420 cm^{-1} band, attributed to the same cause. The above observations are in concurrence with the results of hardwood lignins.

Hardwood lignins contain both guaiacyl as well as syringyl moieties. Guaiacyl moieties give absorption bands at 1270, 1160 and 1030 cm^{-1} , whereas the syringyl moieties give absorption bands at 1330, 1225 and 1130 cm^{-1} . The 1270- cm^{-1} bands ascribed to guaiacyl ring breathing with C-O stretching in both the MWL preparations are weak; similarly, shoulders at 1160 cm^{-1} attributed to aromatic C-H in-plane deformation are observed in both the MWL preparations. However, the 1030 cm^{-1} bands assigned to aromatic C-H in-plane, deformation, guaiacyl type, are sharp in both the varieties.

The peaks assigned to the syringyl moieties at 1330, 1225 and 1130 cm^{-1} give sharp absorption bands in conformity with the hardwood nature of jute stick lignins.

Figure 2 shows the sharp band at 1705 cm^{-1} in the case of the JRO 524 DAL sample, which appears as a shoulder in JRC 7447 DAL; both the peaks may be attributed to C-O stretching of carboxyl or nonconjugated ketone in both the preparations. The presence of the bands can be rationalized on the basis of acidic cleavage (during acidolysis of jute stick) of β -aryl

ethers and the subsequent rearrangement of guaiacyl/syringyl glycerol side chains and generation of the β -carbonyl groups. The absence of the 1690 and 1660 cm^{-1} bands in both the dioxane acidolysis lignin preparations as compared to those in milled wood lignins can be accounted for by the cleavage and loss of coniferaldehyde or sinapaldehyde end units in them.

The bands attributed to aromatic skeleton ring vibrations are again observed at 1595 and 1500 cm^{-1} as strong bands. The band 1460- cm^{-1} ascribed to asymmetric C-H in-plane deformation is stronger than attributed to the same cause. The above observations are in concurrence with the results of hardwood lignins.

Similar to MWL, DAL samples contain both guaiacyl as well as syringyl moieties. Guaiacyl moieties give absorption bands at 1270, 1160 and 1030 cm^{-1} , whereas the syringyl moieties give absorption bands at 1335, 1220 and 1120 cm^{-1} . The 1270 cm^{-1} band, ascribed to guaiacyl ring breathing with C-O stretching in both the DAL preparations are weak as compared to the corresponding bands in milled wood lignins of jute stick.

The peak, assigned to syringyl moieties at 1335, 1230 and 1120 cm^{-1} give sharp absorption peaks in conformity with the hardwood nature of jute stick lignin.

UTILIZATION OF JUTE STICK LIGNIN

Soda lignin isolated from jute stick pulping liquor was converted into resin by partial replacement of phenol in phenol-formaldehyde resin. Particle boards made from the resins showed that soda lignin isolated from jute stick can replace phenol upto a maximum of 50% in phenol-formaldehyde resin.

Lignosulphonates, which have attracted great deal of interest because of their diversified uses can also be prepared from jute stick. Fundamental studies on the colloidal properties of purified lignosulphonates demonstrated their specific value of emulsification, defloculation, chelation and adsorption uses. It can be used in oil well drilling mud, in cement and concrete additives, as dispersants, as emulsifiers and stabilizers, in electrolytic retining, as rubber additives, as binders and adhesives and as resin ingredients.

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