# UV ionization difference spectra of milled wood lignin and dioxane acidolysis lignin of jute stick

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## ABSTRACT

Ultraviolet [UV] ionization difference spectra of milled wood lignins and dioxane acidolysis lignins of two varities of jute stick (*C. olitorius* and *C.capsularis)* were studied. For a particular lignin preparation, the spectra showed that the nature of the two varieties were almost same, whereas, those for the two lignin preparations were found to be different.

## Introduction

In neutral solution, the free and etherified phenols are nearly identical; in alkaline solution, on the other hand, ionization of the hydroxyl group shifts the absorption bands of the compounds with free phenolic groups towards longer wave lengths. Since the absorption of the non-ionizable units does not change when the solution is made alkaline, it can be eliminated by subtracting the spectrum of the neutral solution from that of the alkaline solution[1]. The resulting difference spectrum then represents essentially only the absorption of the ionizable phenolic units.By comparing the height of the difference maxima $\triangle$Ei of lignin preparation with those of the corresponding $\triangle$Ei maxima for appropriate model compounds,the free phenolic hydroxyl group content of the lignin preparations can be estimated.

Aulin-Erdtman et al have attempted to apply the $\triangle$E-method to the determination of phenolic groups in aspen milled wood lignin and aspen lignin sulphonates. However, in aspen(and poplar) lignins, the presence of syringyl and guaiacyl moieties in addition to p-hydroxy benzoate groups, renders the exact interpretation of the difference curves some what doubtful because the chromophoric system is much more complicated than in softwood lignins. Preliminary results for the aspen lignin suggested that 25-40% of the phenylpropane units carried unconjugated free phenolic hydroxyl groups. These appear to consist of approximately equal number of guaiacyl and syringylpropane units. In addition, the extended chromophores were interpreted to include unetherified p-coumaraldehyde groups and phenolic groups conjugated with $\alpha$-keto groups or possibly with biphenyl or ethylenic groups.

Milled wood lignin, which is obtained by a continuous mechanical subdivision of the lignocellulosic materials to progressively smaller particles does not cause significant chemical modifications. However, till today, milled wood lignin is the most commonly used lignin sample for studying its chemical nature[3].

Dioxane acidolysis lignin obtained by acidolysis of wood using dioxane-water (9 : 1 v/v) in presence of 0.2 N HCI, under nitrogen atmosphere after refluxing for 2 h is another commonly used lignin sample[4]. Acidolysis by dioxane-water (9 : 1v/v) in presence of 0.2 N HCI after 4h refluxing is known to produce w-hydroxyguaiacylacetone in softwoods, which gives Hibbert's Ketone-analogs as a secondary conversion products[4'16].

In this paper UV ionization difference spectra of milled wood lignins and dioxane acidolysis lignins of jute sticks of two varieties C. olitorius andC. capsularis

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have been analysed and compared.

## EXPERIMENTS AND METHODS

### Jute Sticks

Jute sticks of two verieties, C. capsularis (JRC 7447) andC. olitorius (JRO 524) were disintegrated in a wiley-mill. The disintegrated samples were difatted in a soxhlet using a mixture of benzene-ethanol (2:1 v/v), and then passed through 40 and 60 mesh sieves. The 40-60 mesh fractions were used for analysis of the chemical constituents of Jute stick samples and the 60mesh fractions for the isolation of milled wood lignin(MWL) and dioxane acidolysis lignin (DAL).

### Analysis of Jute Stick Samples

Tappi standard methods (indicated in the parenthesis for each estimation)[5] were used for the estimation of fat and wax (T 204 Os-76), ash content (T 211 om--85), organic nitrogen content (T 418 Om-85) and acid -insoluble lignin (T 222 Om-83). $\alpha$-Cellulose content was estimated by the modified method of chattopadhyay et al[6] using 1% sodium chlorite solution. Pentosans were estimated using Krober's tables following the procedure of Schorger.[7] Uronic acid was estimated by the method adopted by Nanji et al[8]. Acetyl content was estimated by hydrolysis with normal ethanolic potassium hydroxide[9].

### Isolation of milled wood lignins

Brownell's[10] procedure was followed for the preparation of milled wood lignin. Defatted jute stick of both the varieties JRO 524 and JRC 7447 (150-200 g, 60 mesh) was dry milled in a 4.5 litre porcelain pot of 24 cm dia at 60 r.p.m. for 500 h, the total mass of the milling bails was about 3 kg.

The milled jute stick was extracted with acetone-water( 9:1 v/v, 600 ml) mixture for 48 h in a reciprocating shaker. The extract was filtered and the filtrate evaporated under vacuum until brown flakes appeared This solution was made alkaline with NaOH (0.1 N) and then acidified with HCI (6M) to pH 4. The precipitated lignin was collected by filtration, washed free of chloride and dried in vacuum, The crude milled wood lignin was purified by dissolving it in a small amount of distilled dioxane and precipitated with dry ether. The precipitate was repeatedly washed with dry ether and finally with petroleum ether (40-60°). The purified sample was dried in vacuum over $P_2O_5$ Yield of jute stick milled wood lignin of JRO 524 variety was 9.8% and that of JRC 7447 was 10.2%, as calculated on the basis of total Klason lignin contents of jute sticks[11].

### Isolation of dioxane acidolysis lignins

The procedure of Pepper et al[12,13,14] was followed for isolation of dioxane acidolysis lignin (DAL). Defatted jute stick (50g, 60 mesh) was refluxed with a mixture of dioxane-water (500 ml, 9:1 v/v) cantaining hydrochloric acid (0.2 N) under nitrogen atmosphere for 2h on a water bath. The reaction mixture was cooled, filtered and the residue washed with dioxane-water, (9:1 v/v) mixture. The combined filtrate and washings were concentrated under reduced pressure and the lignin precipitated from the resulting solution with excess of distilled water under stirring. The precipitate (crude dioxane acidolysis lignin) was collected on the filter, washed thoroughly with distilled water and dried in air. It was purified by redissolving it in distilled dioxane and precipitating with excess of dry ether and finally with petroleum ether (40-60°). The purified product DAL was dried in vacuum over $P_2O_5$. Yield of DAL from JRO 524 was 36.5% and that from JRC 7447, 33.3%, as calculated on the basis of total Klason lignin contents of defatted jute sticks[14].

### Ultraviolet ionization difference spectroscopy

Ultraviolet ionization difference spectra of isolated jute stick lignin samples were recorded with a UV-VIS spectrophotometer, Hitachi 139, following the procedure adopted by Goldschmidt [6], [15].

Isolated lignins (0.01g) were dissolved in a phosphate buffer (10 ml, pH 12). A portion of the lignin solution (2.0 ml) was diluted to 50 ml with the phosphate buffer (pH 12). Another portion of the lignin solution (2.0 ml) was neutralized with sulphuric acid (2.0ml, 0.1 N) and diluted to 50 ml with a boric acid buffer pH 6. The difference spectra were measured as the absorbance of the alkaline solution relative to that of the neutsralised solution in the reference cell. The difference spectra were plotted as absorptivity (litre/g-cm) obtained by dividing the absorbance readings (1 cm cell) by the concentration (g/litre) of the solution versus wave length.

## RESULTS AND DISCUSSION

**Table-1**

Chemical composition of jute stick samples

| Compositions % | Jute stick JRO 524 | Jute stick JRC 7447 |
|---|---|---|
| Fat and Wax | 1.6 | 1.19 |
| Ash content | 0.79 | 0.92 |
| Nitrogen | 0.18 | 0.16 |
| Protein | 1.12 | 1.0 |
| ∝Cellulose | 39.71 | 42.16 |
| Pentosans | 22.08 | 22 28 |
| Lignins | 23.59 | 23.8 |
| Uronic acid | 6.20 | 6.01 |
| Acetyl content | 4 82 | 4.50 |

The chemical composition of jute stick samples are given in Table-1 for comparison. The ultraviolet (uv) ionization difference spectra of MWL samples of the two varieties of jute sticks(JRO 524 and JRC 7447) are shown in Figure 1. The milled wood lignins (MWL) JRO524 and JRC 7447 varieties give difference maxima at 254-258 nm and 294 - 297 nm assigned to first primary and the secondary band, respectively due to ionization of phenolic hydroxyl group in alkaline solution, whereas, the maxima at 360 nm is ascribed to phenolic hydroxyl groups conjugated with ∝—carbonyl groups or possibly with biphenyl or ethylenic groups[2]. The peak maxima near 294 - 297 nm were used to determine the unconjugated phenolic hydroxyl content of the two lignin preparations according to Goldschimidt[15]. The unconjugated phenolic hydroxyl content of the *olitorius* variety was found to be slightly higher (0.16 Mole $OH/C_9$ unit ) than the *capsularis* variety (0 15 Mole/$C_9$ unit)[11,14]. Figure 1 shows that the difference maxima at 258 nm and 297 nm in the case of the *capsularis* variety have shifted to lower wave lengths 254 nm and 294 nm, respectively, as compared to the *olitorius* variety. The absorbance values of the two peaks in the *capsularis* variety have also reduced as compared to that of the *olitorius* variety.

The maxima near 365 nm, although at almost the same wave length in both the samples under discussion, the absorbance value of the *olitorius* variety is lower than that in the case of the

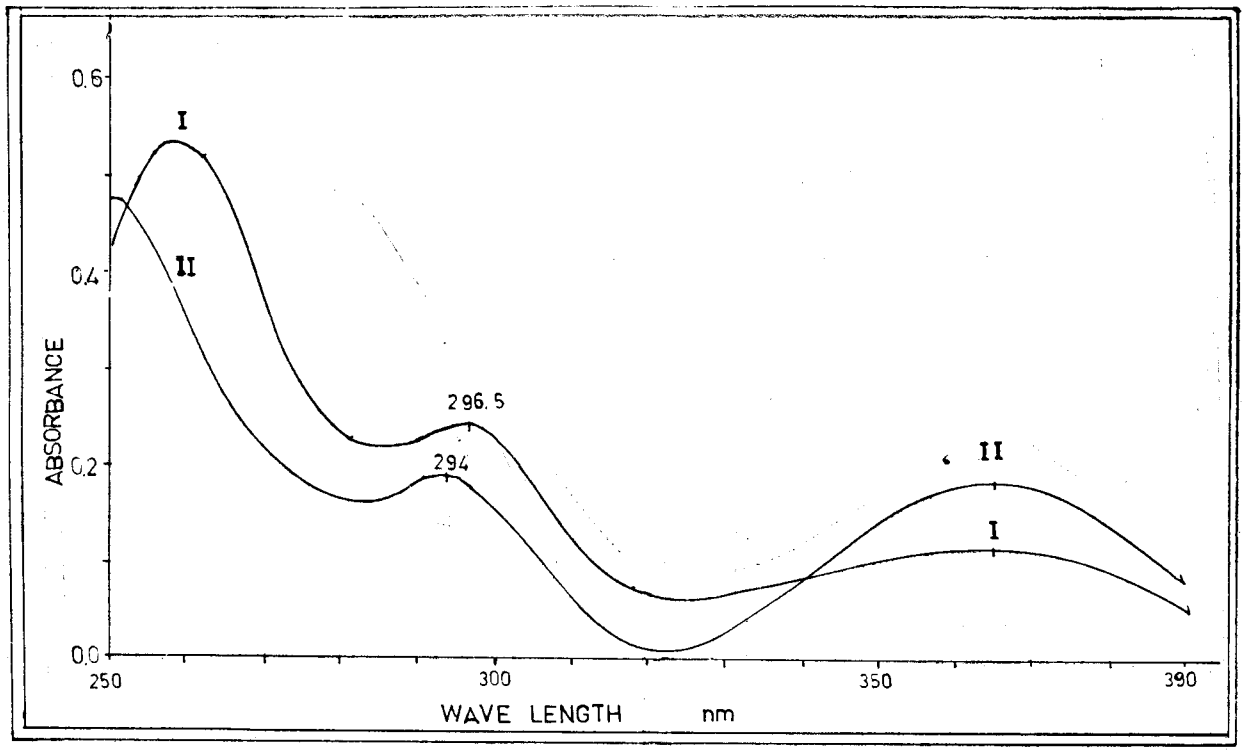


Fig.1 . UV ionization difference spectra of I - MWL JRO 524(c=0.0744 g/l) and II - MWL JRC 7447 (c=0.0752 g/l).

*capsularis* variety. The anomaly is difficult to explain, because of the complex chromophoric system of the hardwood lignins[4].

UV ionization difference spectra of dioxane acidolysis (DAL) samples of the two varieties are shown in Figure 2. The DAL samples, JRO 524 and JRC 7447 give difference maxima at 255 nm and 297 nm, ascribed to first primary band and the secondary band, respectively due to ionization of phenolic hydroxyl groups in alkaline solution, whereas, the maxima at 360 nm is assigned to phenolic hydroxyl groups conjugated with α-carbonyl groups or possibly with biphenyl or ethylenic groups[2]. The peak maxima near 297 nm were used to determine the unconjugated phenolic hydroxyl contents of the two lignin preparations[15]. The values of the unconjugated phenolic hydroxyl contents[4] of DAL JRO 524 and DAL JRC 7447 (0 06 Mole $OH/C_9$ unit and 0.08 Mole $OH/C_9$ unit, respectively)[14] are much smaller than the corresponding values of jute stick milled wood lignins. The reason may be ascribed to the formation of conjugated phenol substructures during the preparation of the DAL samples under the condition of acidolysis used in their isolation[14]. Higher absorbance maxima values of the DAL samples at 360 nm as compared to the corresponding values of the MWL samples are consistent with the above observation.

## Conclusion

UV ionization difference spectra of MWL of the two varieties of jute stick (C. olitorius and C. capsularis) are almost the same and show minor differences in the intensities and band positions of the maxima.

UV ionization difference spectra of DAL of the two varieties as mentioned above are almost the same and show minor differences in the intensities of the ionization difference maxima. The lower values of unconjugated phenolic hydroxyl contents of the DAL samples, calculated from the 297 nm maxima as compared to those of MWL samples' can be attributed to the formaion of conjugated phenol substructures during the preparation of the DAL samples under the condition of acidolysis used.

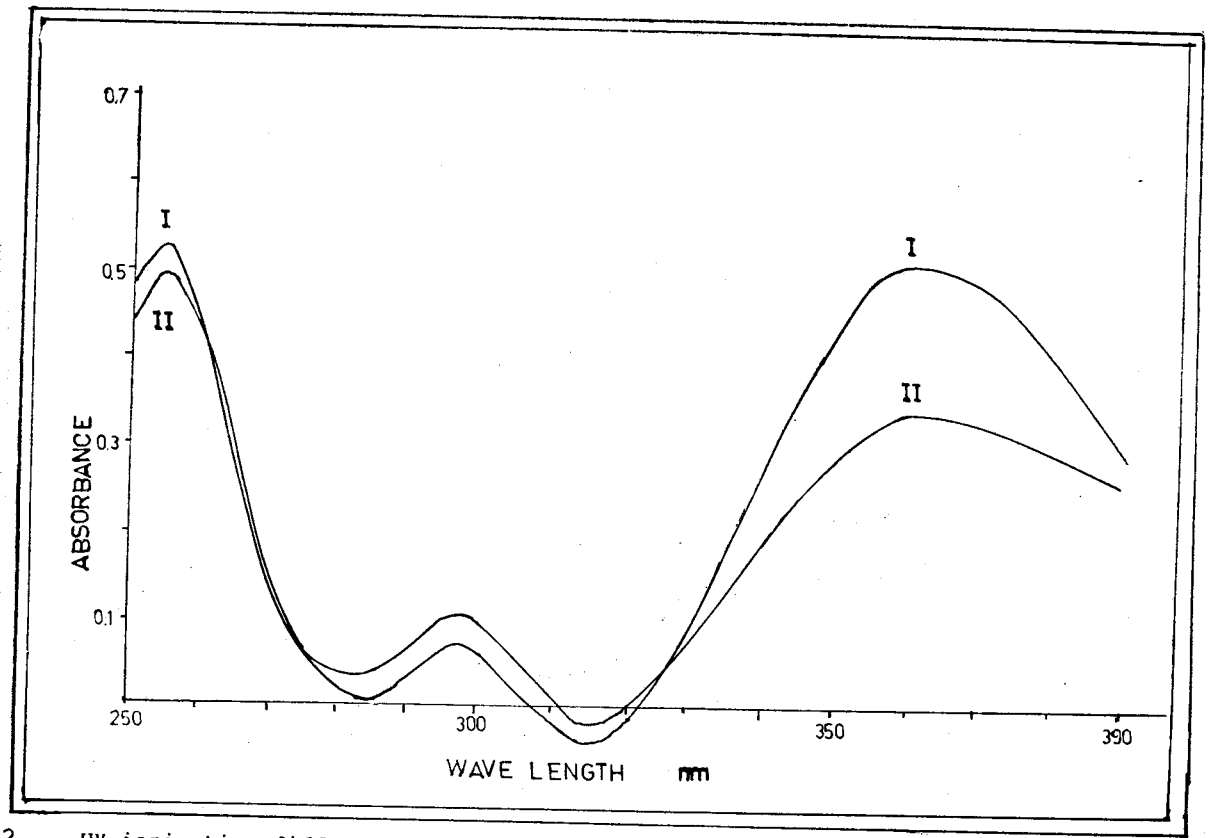


Fig. 2. UV ionization difference spectra of I - DAL JRO 524(c=0.0624 g/l) and II - DAL JRC 7447 (c=0.0672 g/l).

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