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Spectroscopic Studies of Organosolv Lignin from Arecanut Husk

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The organosolv (ethanol) lignin of arecanut husk was isolated in 1 N concentrated HCl and studied by UV-visible and IR spectroscopic studies. The lignin showed maximum absorption in the range of 280–285 nm. The values of extinction coefficient were calculated.

INTRODUCTION

Most of the woody and non-woody fibrous materials contain, in addition to carbohydrates and extractives, an aromatic, amorphous, polymeric material called lignin[1–6]. It is characterised by a considerable content of methoxyl (—OCH_3) groups and by the presence of hydroxyl groups, part of which are phenolic in nature. The biological role of lignin in living plants is to form together with the cellulose and other carbohydrates of the cell walls, a tissue of excellent strength and durability. In the organosolv lignins[2,7], alcohols combine with the lignin in presence of mineral acids to form soluble alcohol lignins. These properties connected with the tendency to undergo secondary condensation reactions even as a result of relatively mild treatments have made structural studies on lignins exceedingly difficult and at present a detailed knowledge on lignin structure is lacking. Lignin owing to its aromatic nature absorbs strongly in the UV region of the spectrum. This spectrum is a plot of intensity of absorption[8] in terms of $\log_{10}$ k against the corresponding wavelength.

The aim of our present investigation is to study the lignin of arecanut husk, so that more light can be thrown on its structure together with the information available from the observation and conclusions of other workers in this field, to enable development of by-products from lignin and its uses as value-added products. The present studies have been carried out on the properties of organosolv (ethanol) lignin isolated from arecanut husk.

EXPERIMENTAL

The arecanut husk, after removing the endocarp, was disintegrated in the Laboratory Wiley Mill. The portion passing through 40 mesh sieve but retained on 60 mesh sieve was utilised for further process.

Isolation of ethanol lignin: The above prepared wood meal was pre-extracted with ethanol-benzene (1:2 v/v) mixture[9] in accordance with Technical Association of Pulp and Paper International (TAPPI) Standard T12 m–59. The extracted

meal was refluxed for 5 h at 100°C with absolute ethanol containing hydrochloric acid to get 1 N solution. The insoluble residue was filtered off and washed with ethanol. The filtrate and washings were collected together and concentrated. The concentrated solution was neutralised with $NaHCO_3$ and filtered. The filtrate was added dropwise to a large quantity of distilled water. The precipitated lignin was filtered, washed with water and finally with ether-water mixture.

Isolation of klason lignin: The klason lignin was also isolated from arecanut husk according to TAPPI standard testing method T222 os–74. Both the ethanol and klason lignin samples were dried in a vacuum desiccator.

UV-visible spectral studies: Solution of the purified ethanol lignin was prepared in concentration of 100 mg/L. The solvent used was a mixture of 90 parts by volume of 1,4-dioxane and 10 parts by volume of water. The spectral analyses were made with the help of spectrophotometer (Systronics make type–108) within the wavelength range of 250–350 nm. The transmittance values were taken at different wavelengthes which are recorded in Table-1. A graph of $\log_{10}$ k against the wavelength was plotted (Fig. 1).

TABLE-1
TRANSMITTANCY AND EXTINCTION COEFFICIENT VALUES OF ARECANUT HUSK LIGNIN

Wavelength nm	Transmittancy %	$\log_{10}$ k	log E
250	0.0	—	—
255	0.1	1.83	3.40
260	0.1	1.83	3.40
265	0.3	1.76	3.23
270	0.7	1.69	3.07
275	0.9	1.67	3.02
280	0.9	1.67	3.02
285	1.3	1.64	2.93
290	2.3	1.58	2.79
295	4.6	1.49	2.59
300	7.5	1.41	2.42
310	10.3	1.36	2.29
320	12.2	1.32	2.21
330	15.7	1.27	2.08
340	21.2	1.19	1.91

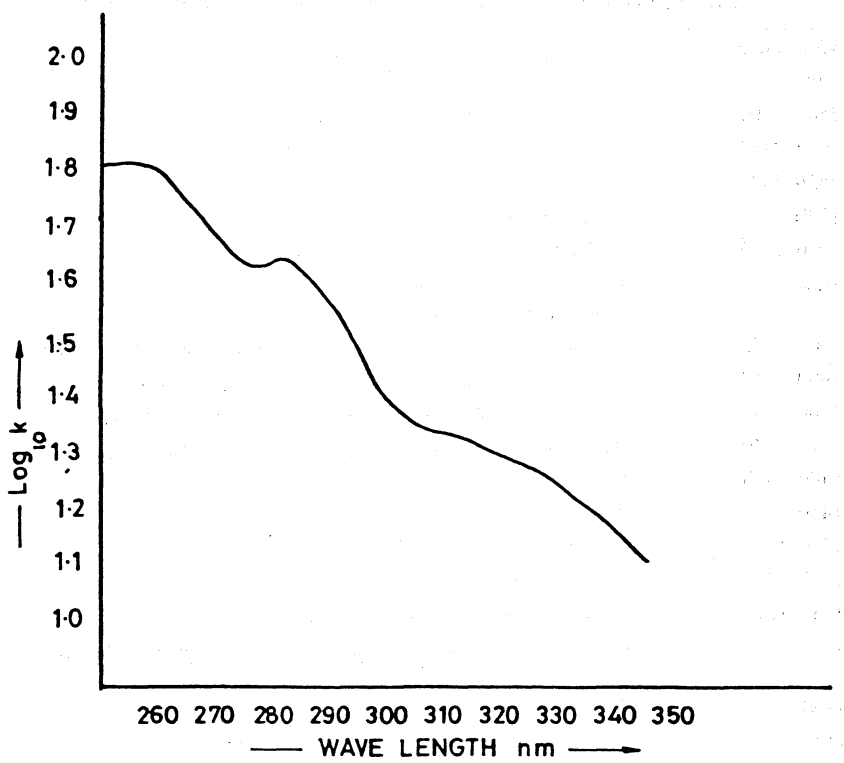

Fig. 1. UV-spectrum of ethanol lignin from arecanut husk

Infrared spectral studies: The infrared spectroscopic studies were carried out by examining the dried lignin samples (both klason and ethanol lignin samples) as mulls of Nujol using Perkin-Elmer (297) IR spectrophotometer. The spectra of both the lignin samples were recorded in the range of 4000–600 cm^{-1} and their comparative study has been done (Table-2).

RESULTS AND DISCUSSION

The UV absorption spectrum of organosolv (ethanol) lignin shows a characteristic absorption band at 280 nm. This may be due to some configuration of atoms or groups of atoms in the lignin molecule which is not disturbed by ordinary substitution reaction which can be supported by the fact that many lignin reactions do not involve the change in the basic structural chromophores responsible for ultraviolet absorption[10]. So it is clear that the band at 280 nm is only clearly defined and persistent band which the lignin spectrum shows. Hence we can say that the ethanol lignin of arecanut husk contains an oxygen substituted aromatic ring and is responsible for the characteristic absorption band of lignin at 280 nm[11].

TABLE-2
INFRARED ABSORPTION BANDS OF ARECANUT HUSK LIGNIN

Wave number (cm^{-1})	Structural assignments
3500–3300	Stretching vibrations of hydrogen bonded OH group
3075–2950	CH stretching vibrations
2850–2820	Methoxyl groups
1720	Acid or ester carbonyl groups
1720–1650	Carbonyl (C=O) stretching frequencies
1660	Ketone carbonyl α- to an aromatic ring (*p*-position etherified)
1605–1580	Aromatic stretching bands (typical of unconjugated guaiacyl nucleus)
1600–1510	General C=C skeletal vibrations in the aromatic ring
1560–1555	Vibrations of rings conjugated with an α- carbonyl group.
1515–1510	Aromatic stretching bands (typical unconjugated guaiacyl nucleus)
1480–1340	C—H deformation
1430	Aliphatic groupings
1380–1320	Bending vibrations of OH bonds
1275–1270	C—O stretching aromatic (methoxyl)
1240–1215	C—O stretching aromatic (phenyl)
1220	OH group vibration (C—O stretching made in phenolic hydroxyl groups)
1150	1,3,4-substituted aromatic ring
1140	Dialkyl ether linkages
1090–1075	Aliphatic ether linkages and secondary OH groups
1045	OH group vibrations
1035–1030	C—O deformation (methoxyl group)
970	C—H out-of-plane deformation in ethylenic double bonds
860	1,3,4-substituted aromatic ring (monohydrogen out-of-plane deformation)
830–825	Trisubstituted aromatic ring
815–810	1,3,4-substituted aromatic ring (two adjacent ring hydrogen out-of-plane deformation)

From the UV-spectrum it is deduced that lignin contains a hydroxylated benzene nucleus. The absorption in the 310–330 nm range is due to a carbonyl or ethylenic double bond in conjugation with the benzene ring.

The absorption maximum showed that the nature of lignin of arecanut husk is similar to hardwood lignins which absorb at 280 nm or slightly higher. So the arecanut husk lignin, which resembles hardwood lignin, is seen to contain more number of syringyl building units and hence the oxidative degradation of the lignin[12–15] containing mainly syringyl building units yields vanillin in small quantities and major amount of syringaldehyde, which find wide applications. The concluding remarks of UV are further confirmed by IR studies.

The infrared spectrum of ethanol lignin as well as klason lignin of arecanut husk contain many absorption bands, indicating stretching and deformation of

structural groups. Comparison of spectra with the previous studies in this field permits many assignments but the structure of lignin cannot be deduced with certainty from spectral evidence alone. There is no single lignin which is of uniform composition regardless of source *i.e.* its nature varies from species to species.

Here in the spectra, both the samples show band at 3500–3300 cm^{-1} and is due to hydroxyl groups, *i.e.* O—H stretching frequencies, both phenolic and alcoholic[16] and the band is broadened due to hydrogen bonding, indicating that they are strongly hydrogen bonded. The absorption band at 3025–2850 cm^{-1} represents various types of C–H bonds. The band at 2850–2820 cm^{-1} is assignable to methoxyl groups[17]. The intensive bands of the carbonyl groups appear in the range of 1720–1650 cm^{-1} indicating the presence of this functional group in lignin structure. The interfering groups with carbonyl bands like acetyl groups and uronil ester groups of polysaccharide residues absorb at 1760–1720 cm^{-1}.

The frequencies observed at 1650 cm^{-1}, 1500 cm^{-1} and 1480–1430 cm^{-1} can be assigned as skeletal band of guaiacyl and syringyl type compounds. The two bands at 1650 cm^{-1} and 1500 cm^{-1} are characteristic of aromatic compounds and are due to the C=C vibration of benzene ring. The absorption bands at 1480–1340 cm^{-1} are considered to be ring stretching modes strongly coupled by C—H in-plane deformation. The intensity of the band is sensitive to the nature of ring substituents. The band at 1480 cm^{-1} is due to C—H bonds including methoxyl groups. The band in the region of 1380–1320 cm^{-1} is due to the bending vibration of O—H bonds.

The typical guaiacyl band is located at about 1270 cm^{-1}. The bands in the region of 1400–1000 cm^{-1} are caused by the combination and overlapping of C—O stretching bands and by several deformations. The bands at 1275–1270 cm^{-1}, 1220–1215 cm^{-1} and 1120–1110 cm^{-1} are due to guaiacyl and at 1325–1320 cm^{-1} due to syringyl derivatives are assignable to ring breathing with C—O stretching. Guaiacyl bands at 1120–1110 cm^{-1} and 1045–1040 cm^{-1} are assigned to aromatic C—H in-plane deformation.

The infrared absorption bands are also visible below 1000 cm^{-1} regions. A strong absorption band at 830 cm^{-1} with a weaker band at 860 cm^{-1} are characteristic of syringyl compounds and are mostly found in tropical hardwood lignins. Similar observations have been made by Agarwal *et al.*[18] for the species like *Adhatoda vasica*, *Ipomea carnea* and *Ricinus communis*.

Both the acid (klason) and ethanol (organosolv) lignins of arecanut husk contain phenolic as well as aliphatic hydroxyl groups which appear to be strongly hydrogen bonded. The presence of 1720 cm^{-1} band shows the presence of carbonyl group. Greater intensity of 1650 cm^{-1} band as compared to that of 1555 cm^{-1} supports the presence of *p*-hydroxy phenyl propane units. The intensity of the band at 1275 cm^{-1} is higher than that of the band at 1220 cm^{-1} indicates that it is a hardwood lignin. And also a greater intensity of 1175–1170 cm^{-1} band than that of 1090–1080 cm^{-1} band indicates that these lignins have similar characteristics with hardwood lignins.

From all these conclusions we can infer that the organosolv lignin as well as the klason lignin of arecanut husk almost resembles hardwood lignins and offers

great potential for development of a host of organosolv lignin based, value-added, industrially useful products.

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