Spectroscopic Studies of Lignins from Wheat Straw and Kai Grass

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Summary: Lignins were isolated from wheat straw and kai grass. Their IR, UV ^{1}H-NMR and Mass spectra were recorded to classify these compounds. The spectroscopic results indicate that these lignins are composed of guaiacyl-syringly unit and consequently the materials may be considered as the members of hardwood family.

Introduction

In view of the great role of lignin in life of plant and its importance in applied chemistry [1-5], we carried out spectroscopic studies of these compounds isolated from wheat straw (Triticum vulgare) and kai grass (Saccharum spotarum).

The word lignin originated from Latin word "Lignum" meaning wood. Basically, it consists of three units [4], Fig. 1, trans confieryl or guaiacyl **1** trans sinapyl or syringyl **2**, and trans -p-coumaryl alcohol **3**.

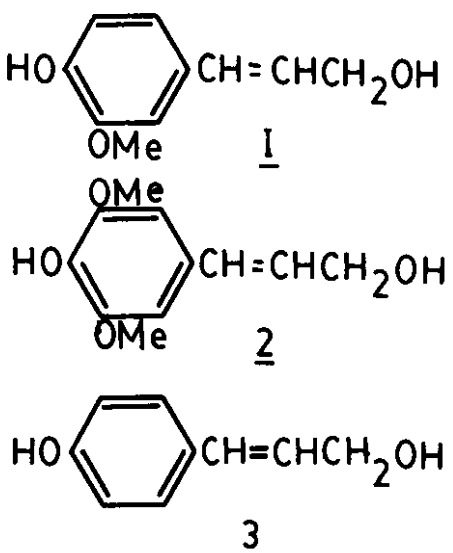

Fig.1: Lignin's Precursors, guaiacyl **1**, Syringyl **2** and trans -P- coumaryl alcohol **3**.

Freudenberg and Harkin[6] discussed the structure of spruce lignin in detail and proved that it contains twenty monomeric units. The majority of these were of the guaiacyl propane, two of these were assumed to be of the p-hydroxyl phenyl propane type and only one was of the syringyl propane type. The structure proposed by Freudenberg and co-workers has substantial merits in providing reasonable picture of the molecules architechure of lignins and a base for mapping the course of various chemicals.

The aim of the present investigation was to identify the lignins present in the raw materials being used in the paper industries of this country. For this purpose kai grass and wheat straw were selected and spectroscopic studies of isolated lignins from these materials were carried out.

Experimental

Wheat straw and kai grass were collected from Adamjee paper Mills Nowshera. Lignins were isolated from these materials by standard methods [7-9]. The samples were purified and dried under reduced pressure at room temperature.

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UV spectra were recorded on Shimadzu UV-200s and Pye-Unicam spectrophotometer with absolute alcohols as solvent. Pye-Unicam SP-3-100 was used for recording IR spectra of the lignins in nujol between KBr salt plates. ^{1}H-NMR spectra were obtained on Bruker A-100 and Varian EM-390 NMR spectrometers with DMSO as solvent and TMS as internal reference. Mass spectra were recorded on Varian Mass spectrometer 10125.

Results and Discussion

Lignins are the polymers built up through condensation of structural units of the similar types. Basically, these units are of phenyl propane moiety (C_6C_3), but they may be combined in a variety of ways.

The UV spectra of ligning preparations have been studied extensively by Herzog and Hillmer [10]. From the character of the Ultraviolet spectra of kai and wheat straw negative lignins it is deduced that lignins, contain a hydroxylated benzene nucleus. The most prominent absorption bands appear in the region of 200 nm and at 280-290 nm in Table I.These bands sare usually attributed to absorption by the oxygen substituted to aromatic ring [11]. Free and etherified hydroxyl group contribute significantly to the characteristic absorption maximum of lignins near 280 nm. Absorption at 300-350 nm is due to a carbonyl or ethylenic double bond in conjugation with the ring [12]. The absorption maxima at 274-276 nm and 280-287 nm are due to softwood and hardwood lignins respectively [13]. The UV spectra of the lignins obtained from kai grass and wheat straw have characteristic absorption at 280 nm which indicate that they are hardwood lignins [13].

The IR spectral bands corresponding to OH group appear to be involved

Table-1: UV maxima of Isolated Lignins

Compound	Concentration (g/100 ml)	Wavelength λ max(nm)	Absorbance
Wheat Straw	4.0×10^{-3}	220	0.80
Native Lignin	280	0.59	
Kai Native	4.0×10^{-3}	220	0.80
Lignin		280	0.58

Table-II: Infrared Absorption Bands of Native Lignins

Wheat Straw Native Lignin	Kai Native Lignin	Band Origin
3400 cm^{-1}	3350 cm^{-1}	OH Stretching
2925	2940	CH Stretching of methyl or methylene group
2850	2750	Same
1720	1700	C-O Stretching
1600	1595	Aromatic Skeletal Vibration.
1505	1500	Same
1440	1420	Same
1325	1320	Syringyl ring breathing with CO stretching.
1280	1260	Guaiacyl ring breathing with CO
1220	1221	Same
1155	1161	Aromatic CH in-plane deformation guaiacyl type
1120	1120	Aromatic CH in plane deformation syringyl type.
1015	1020	Aromatic CH in-plane deformation guaiacyl type.
840	830	Aromatic C-H out of plane bending.

in hydrogen bonding in the lignin macromolecules and it is difficult to differentiate between the aliphatic and phenolic OH absorption because they overlap each other. The CO frequency lies between 1750-1725 cm^{-1} in Table II. This has similar range as compared to the lignins reported by Sarkanen [14].

The aromatic skeletal vibrations in wheat straw and kai native lignins show absorption at 1600-1595, and 1440-1420 cm^{-1} which are comparable to guaiacyl and syringyl type model compounds [15,16] (1605-1595, 1515-1505, 1450-1420 cm^{-1}). This is another evidence of the presence of guaiacyl and syringyl units in the materials in question.

Table-III: Chemical shifts of Protons in δ (ppm)

Source of Lignin	Methoxy Protons	Aromatic Protons	Aliphatic Protons	High Shielded Aliphatic Protons
Wheat Straw native lignin	3.60	6.70	4.25 4.80	2.25
Kai native lignin	3.45	6.75	3.10 3.70	2.50

Table-IV: Relative Intensities of Prominent Peaks of Mass Spectra of Lignin in Methanol

m/z	Wheat Straw (% intensity) native Lignin	Kai (% intensity) native Lignin
64	100	4
95	30	32
97	14	100
114	12	18
120	14	44
124	6	26
137	16	18
151	20	22
154	12	12
168	10	12
180	12	14
194	10	10

In hardwood lignins and unconjugated syringyl model compounds the bands at 1600 and 1510 cm^{-1} have either equal intensity or the first one is stronger than the second. A similar pattern is observed in wheat straw and kai native lignins i.e. the peaks in the region 1600-1595 cm^{-1} are much stronger than those in 1505-1500 cm^{-1}. It appears from this observation that syringyl units are dominating the material under investigation.

This view is supported by ^{1}H-NMR spectra of these compounds. The strong methoxy peaks at 3.45 ppm and 3.60 ppm reflect the presence of additional methoxyl groups in the syringyl type units [17]. In addition to this aromatic protons of hardwood lignins normally show broad signals at 6.8 ppm [17] which is comparable to the peaks (6.70 ppm and 6.75 ppm) obtained in this study. The chemical shift range 2.25-4.80 ppm is for aliphatic protons in Table-III. These all chemical shifts resemble to those model compounds which form the units of guaiacyl-syringyl type lignins. The variation in distribution of aliphatic protons in lignins from different sources can be easily visualised from the ^{1}H-NMR spectra.

Mass spectrometry is a universal method for detection and identification of the compounds alongwith the aid of IR, UV and NMR techniques. It is difficult to obtained any major information about lignin's structure from it's mass spectra. However, in case of these lignins the parahydroxyl benzoic, guaiacylic, and syringylic acid moities giving rise to three discrete series of phenolic signals are observed (Table IV) which resemble to the signals reported elsewhere [19].

It may be concluded from this study that the guaiacyl-syringyl type of lignins are present in kai grass and wheat straw and these materials belong to the hardwood family where syringyl unit 2 Fig. 1 seems to be the major component.

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