

Studies on Ultraviolet Absorption Spectroscopy of Lignins Isolated From Non-Wood Fibrous Plants.

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ABSTRACT

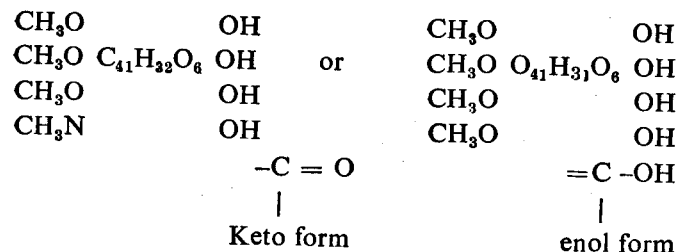
A study has been made on the absorption spectra of lignins isolated from *Sesbania sesban*, *Sesbania aculeata* and *Cajanus cajan* non-wood fibrous plants by ethanol, methanol, sulphuric acid, hydrochloric acid and spent liquor of sulphate cooking. All the lignins showed absorption band in the range of 280 to 283 m μ . The high absorption coefficient at 280 m μ was observed in methanol lignin and lignin isolated from spent liquor. The extinction coefficient were calculated. The absorption spectrum of lignins could be explained by the assumption that the lignin building unit contains two pyran rings. These oxygen rings would be responsible for the very persistent absorption band of lignin at 280–283 m μ . The carbonyl group be responsible for the absorption in the range of 300–350 m μ .

Introduction :

In contrast to the polysaccharides of the cell wall, which are transparent in visible and near-ultraviolet light, lignin owing to its aromatic nature, absorb strongly in the ultraviolet range of the spectrum. The absorption spectrophotometry refers to the measurement of the absorption or transmission of electro-magnetic radiation of a specified wavelength or frequency". The main problem in lignin spectroscopy, as well as in lignin chemistry in general, is the impossibility of dissolving atleast the main part of the very reactive material without simultaneously changing its structure in some unknown way. The another difficulty arises from the polydispersity of the soluble lignin derivatives.

Herzog and Hillmer^{1,3} have determined the spectra of liginosulphonic acids, alkali lignins, and methyl, and glycol lignins, and a number of simple organic compounds. They found a relationship between the plant source of the lignin and the wavelength of maximum absorption and a relationship between the intensity of absorption and the chemical nature of the derivatives. By a study of the spectra of simple aromatic compounds similar to those isolated as decomposition products of lignin, they discovered certain relations between, chemical structure and ultraviolet absorption spectra of this group of aromatic compounds. They concluded that the basic unit of lignin is a di or trihydroxyphenol, partly or wholly etherified, having a side chain of about three carbon atoms which contain no double bond or carbonyl group conjugated with the benzene ring.

In 1939 Brauns⁴ reported the isolation of native lignin and the preparation of several of its derivatives. A study of the chemical behavior of these lignins led to the conclusion that the native lignin building unit has the formula,



with a molecular weight of about 840.

This paper deals with the study on the ultraviolet absorption spectroscopy of different types of lignin isolated from non-wood fibrous plants viz. *Sesbania sesban*, *Sesbania aculeata* and *Cajanus cajan*.

Experimental

Preparation of Lignins :

The Klason and Willstatter lignins were isolated by Ritter et al⁵, Brook and Brauns⁶ methods. Thioglignin⁷ was produced by digestion of wood with sodium sulfide and sodium hydroxide. Ethanol lignin was isolated by method of Merewether⁸ and the methanol lignin was isolated similarly as ethanal lignin.

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Determination of Absorption Spectrum Curves :

Solutions of the carefully purified material to be used for absorption spectrum determination were prepared in concentration of .1 gm. per liter. The solvents used were a mixture of 90 parts by volume of purified dioxane and 10 parts of distilled water. In making the absorption spectrum determinations, a thin cell, giving thickness of about one mm was used for the 90% dioxane solutions. The thick cell was more convenient to work with and therefore was used whenever possible. Dioxane has a high ultraviolet absorption and had to be used in thin layers if it was to pass any considerable quantity of ultraviolet light and hence the thin cell was used.

The spectras were measured with the the help of spectrophotometer (Perkin-Elmer model) within the wavelength range of 220 to 350 m u. The solvent cell is placed in a reference beam and the solution cell is placed in other beam. From the values for transmittance, thickness of the layer of solution through which the light passed, and concentration of the solution volues for $\log_{10} K$ were calculated according to the equation :

$$T = e^{-ck}$$

Where T = Transmittance of solution (as compared with solvent)

e = base of natural logarithms.

c = concentration of solute in grams per liter.

l = thickness of solution through which light passed in cm.

and k = absorption coefficient.

$$D = \log_{10} \left(\frac{I_0}{I_x} \right) = Ecx$$

Where D = Optical density, I_0 = intensity of incident light,

I_x = intensity of transmitted light at the thickness x of absorbing layer.

E = extinction coefficient per unit concentration.

c = concentration of absorbent (mg. per ml.)

x = thickness of the absorbing layer (mm.)

$\log_{10} k$ = plotted against wavelength gave the absorption curve of the solute. The graphare reported in fig. 1,2 and 3.

The value of absorption band with maxima and extinction coefficients for different lignins are calculated and tabulated in Table —I.

Results and Discussions :

The absorption spectra of almost all the lignins studied, Fig. 1 to 3 show an absorption band at about 280 m μ . This band persists in-spite of such alterations in the lignin molecule as are caused by methylation, acetylation, treatment with methanal, ethanol, acids, sodium hydroxide, or sodium hydrogen sulphide. This fact suggests that the band at about 280 m μ is due to some configuration of atoms in the lignin molecule which is not disturbed by ordinary substitution reactions and which, in its absorption of radiant energy, is not influenced by the state or action of other portions of molecule. Now the question arises, "what group or configuration of atoms is responsible for the

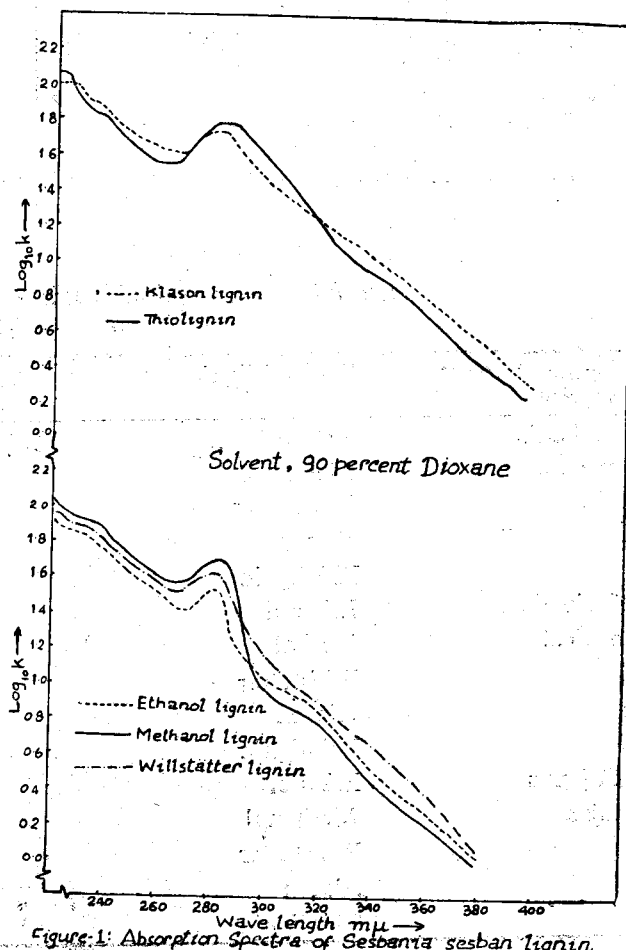


Figure 1: Absorption Spectra of Sesbania sesban lignin

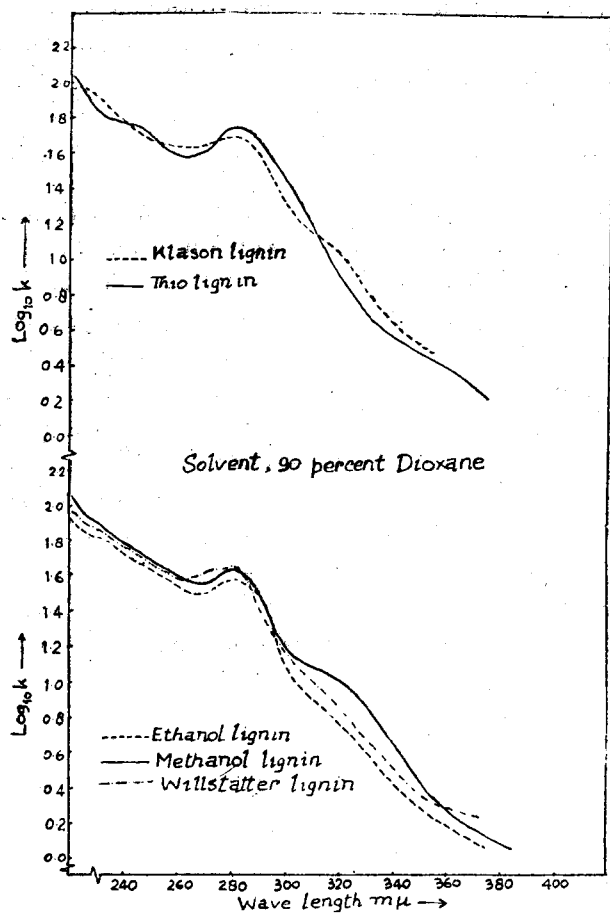


Figure-2 Absorption spectra of *Sesbania aculeata* lignins

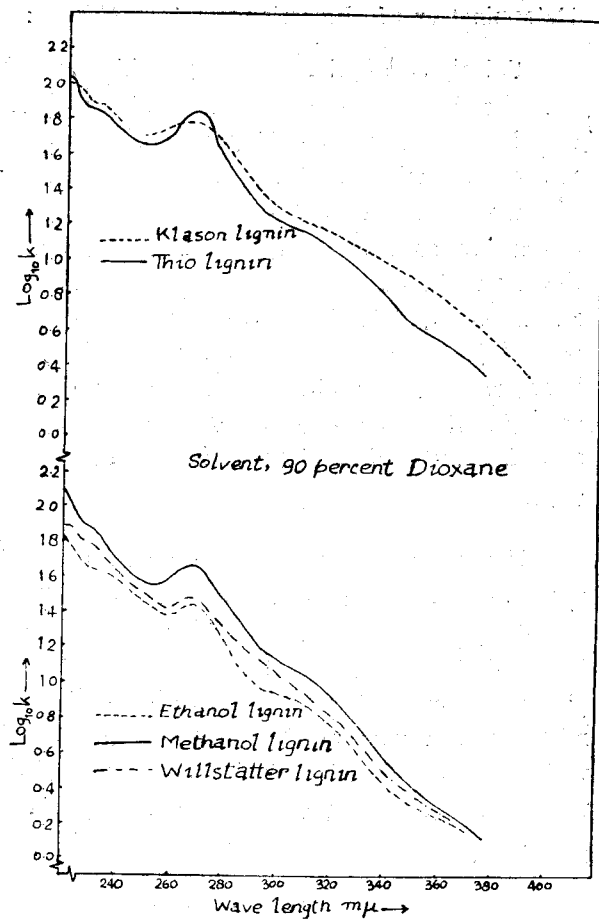


Figure-3 Absorption Spectra of *Cajanus cajan* lignins

TABLE-1
Ultraviolet absorption maxima and extinction coefficients of lignins isolated from non-wood fibrous plants.

Name of Plant species	Type of lignin	Solvent	Maximum mμ	Extinction coefficient LogE
Sesbania sesban	Ethanol	90% dioxane	280.5	3.18
	Methanol	"	283	3.23
	Willstätter	"	282.5	3.21
	Klason	"	282	3.24
	Thiolignin	"	284	3.25
Sesbania aculeata	Ethanol	"	281	3.20
	Methol	"	282	3.21
	Willstätter	"	280	3.21
	Klason	"	282	3.23
	Thiolignin	"	283.5	3.25
Cajanus cajan	Ethanol	"	280.5	3.15
	Methanol	"	283	3.22
	Willstätter	"	282	3.17
	Klason	"	282.3	3.25
	Thiolignin	"	282.5	3.26

lignin absorption band at $280\text{ m}\mu$?" It is the only clearly defined and persistent band which the lignin spectra show. It is not affected by ordinary substitutions in the lignin molecule and has been shown to persist in lignins separated from wood by alcohols,^{9, 10} alkaline pulping agents.⁹ Lignin contains an oxygen ring and the oxygen ring is responsible for the characteristic absorption band of lignin at $280\text{ m}\mu$, and the oxygen ring is unaffected by substitutions in the lignin molecules and is relatively insensitive to ordinary chemical agents. Some values listed in Table—I. are low, while some are high.

These high values could be due to either some change in the structure of the molecules which enable that group responsible for the absorption band at $280\text{ m}\mu$ to absorb more strongly or the presence of a substituent which also had a relatively high absorption coefficient at $280\text{ m}\mu$. methanol lignin, willstatler lignin Klason lignin and thioglignin show the high value of maximum. The low value in the case of ethanol lignin is due to the exthoxyl group being split off with the methoxyl in the analysis. The high value for thioglignin and in fact, the high k value at $280\text{ m}\mu$ for thioglignin are possible due to changes in the lignin molecule brought about by the alkaline cooking conditions. A possible explanation would be that, under the strong acid conditions in the cooking process, water is split off from the lignin molecule, giving rise to double bonds in conjugation with the benzene rings. In any case, it is evident that atleast the isolated lignin derivatives contain some kind of larger chromophores^{11, 12} than optically insulated benzene, rings, though the proportion of these large chromophores must be small, since the absorption coefficient at about $320\text{ m}\mu$ is relatively low. Hence the double bonds conjugated with the benzene rings were excluded in the lignin. Thus, with the exceptions just noted, it appears that the absorption coefficients at $280\text{ m}\mu$ of the lignins studied are directly proportional to their native lignin contents.

All the spectrum nearly shows a decrease from $220\text{ m}\mu$ to a shallow minimum near $260\text{ m}\mu$, with a pronounced shoulder near $230\text{ m}\mu$ and a characteristic absorption maximum of lignin near $280\text{ m}\mu$. Herzog and Hillmer¹⁻³ showed that the absorption curves of hard-

wood lignins, however, differed from those of softwood lignins in the position of the maximum absorption band, of the hardwood lignins occurring at shorter wavelength and in the intensity of absorption in the near-red. Oguri and Takei¹³ found that bamboo lignins resembles with hardwood lignins shows (absorption maxima at $281\text{-}283\text{ m}\mu$) isolated by means of alcohol, Hydrochloric acid and sulfuric acid. The spectrum of *Sesbania besban*, *Sesbania aculeata* and *Cajanus cajan* show an absorption maxima in the range of ($280\text{-}283\text{ m}\mu$) hence the lignin of these non wood fibrous plant resembles with hardwood lignin rather than soft wood lignins.

Conclusion :

To sum up, an evaluation of the experimental evidence regarding the ultraviolet absorption spectrum of lignin leads to the following conclusions that the reaction of lignin with methyl alcohol of alkaline pulping agents increases its absorption coefficient. The two characteristic bands in the lignin spectrum at 200 to $230\text{ m}\mu$ and 280 to $285\text{ m}\mu$ are specifically attributable to the oxygen-substituted benzene nucleus in lignin.

The high absorption in the 300 to $350\text{ m}\mu$ range suggests the presence of a "masked maximum" and indicates the presence of other chromophoric groups in lignin viz. carbonyl groups of double bonds conjugated with the benzene rings. The absorption maxima showed that the nature of lignin of these plants resembles with hardwood lignin.

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