

# Studies on infrared spectroscopy of thiolignins of some non-wood fibrous plants

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## ABSTRACT

The thiolignins of some non-wood fibrous plant, viz, *Hibiscus cannabinus*, *Hibiscus abdarirfa* and *cannabis sativa* were isolated by the acidification of the spent liquors of the kraft cooking carried out at different levels of sulphidity and temperatures. The isolated thiolignins were also analysed for their elemental composition and further subjected to alkaline nitrobenzene oxidation. The results of alkaline nitrobenzene oxidation products of these thiolignins revealed that these are composed of guaiacyl-, syringyl-, and p-hydroxy phenyl propane building units. The thiolignins isolated at 20% sulphidity level were further subjected to infrared spectroscopic studies. The infrared spectrums of these non-wood fibrous plants were compared with the infrared spectrum of *Eucalyptus grandis* (hard wood).

## INTRODUCTION

Although a great mass of literature is devoted to lignins (isolated from wood as spent Liquors) but the idea that the residual lignins associated with pulps may be different both, does not seem to have been pursued. Yet it appears reasonable that these lignins, having been exposed to pulping conditions, may represent an intermediate stage, changed in some way, but not sufficiently to become solubilized. The aim of the present investigations is to study the mechanism of various delignification processes of practical interest based on the information available together with the observation and conclusions of other workers in this field<sup>1-3</sup>. It is also of great interest to study the various changes, which may take place in the structure of lignin and polysacchrides and of the nature of the lignin-carbohydrate linkage, during pulping. Further the knowledge of chemistry of lignin will be of much use in formulating rational approaches to the development of new and improved delignification process.

Thorough investigation on thiolignin was carried out by Ahlm<sup>4</sup>. He isolated thiolignin from spruce under different cooking conditions and analysed for their elemental composition. Hagglund<sup>5</sup> put forward a hypothesis for the role of sulphidity in the sulphate digestion of softwood as well as hardwoods. As far as

Non-wood fibrous raw material are concerned, no systematic data are available. The present studies have been carried out on the properties of thiolignin isolated from *Hibiscus cannabinus*, *Hibiscus sabdariffa* and *Cannabis sativa*.

## EXPERIMENTAL METHODOLOGY

### RAW MATERIAL PREPARATION

For the present investigations, the desired non-wood fibrous plants were procured from nearby region and chopped by hand to cut chips of approximately 20mm in length and further screened and those passing through 12.7 mm screen but retained on 6.4mm screen were collected. The accepted chips were air dried under atmospheric conditions, the moisture content of the fresh (green) chips was 60% while that of air dried chips was 11%.

### PROXIMATE CHEMICAL ANALYSIS

The selected air dried material was disintegrated in the laboratory WEVERK disintegrator. The portion passing through 40 mesh sieve but retained on 60 mesh sieve was utilized for proximate chemical analysis. The proximate chemical analysis was carried out as per TAPPI standard methods and the results of proximate chemical analysis are reported in Table—I.

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Table—I: Proximate Chemical Analysis of *Hibiscus cannabinus*, *Hibiscus sabdariffa* and *Cannabis sativa*.

Sl. No.	Particulars	Plants		
		<i>H. cannabinus</i>	<i>H. sabdariffa</i>	<i>C. sativa</i>
1.	Cold Water solubles, %	4.56	5.81	3.94
2.	Hot Water solubles, %	6.42	8.24	7.46
3.	Alcohol-Benzene (1:2V/V) Solubles, %	4.28	3.88	3.56
4.	1% Sodium hydroxide solubles, %	28.50	25.80	24.00
5.	Holocellulose, %	71.80	71.40	73.80
6.	Hemicellulose, %	25.05	22.80	24.40
7.	Alpha Cellulose, %	46.75	48.60	49.40
8.	Beta Cellulose, %	10.24	9.56	10.60
9.	Gamma Cellulose, %	14.80	13.20	13.80
10.	Pentosan, %	17.30	18.45	16.40
11.	Lignin, %	18.50	19.20	18.25
12.	Ash, %	1.56	1.40	1.30
13.	Silica, %	0.35	0.28	0.25
14.	Acetyl content, %	2.62	2.24	3.12
15.	Methoxyl content, %	3.40	3.10	3.56

## PULPING STUDIES

All the cookings were done in a laboratory WEVERK cylindrical rotary electrical heated digester of 0.02 m<sup>3</sup> capacity, using a charge of 2.0 kg (o.d.) chips of each raw material by sulphate/kraft process, using a liquor to wood ratio of 4:1. The pulping studies were made 15% active alkali (as Na<sub>2</sub>O) with different sulphidity level (ranging from 0, 8, 15, 20 and 23%) using the following time schedule for digester heating :

Time from 30°C to 105°C	=	45 min.
Time from 105°C to 160°C	=	45 min.
Time at 160°C	=	120 min.

The detailed pulping conditions and results are reported in Tables-II and III.

## ISOLATION OF THIOLIGNINS

The kraft spent liquor were separated by filtration, and the thiolignins were precipitated by addition of a slight excess of hydrochloric acid. The precipitate was

allowed to settle, and the supernatant liquor was poured off. The precipitate was suspended in water, filtered, washed until neutral, and dried on a porous plate. The crude thiolignins were dissolved in anhydrous dioxane and concentrated under reduced pressure, with periodic addition of fresh dioxane until all traces of water had been removed. The dioxane solution was centrifuged to separate precipitated sulphur and carbohydrates, and the clear solution was diluted with dioxane to give a 10% solution. The thiolignins were isolated by adding the dioxane solution dropwise to vigorously stirred anhydrous ether. The precipitates were washed twice with ether and twice with petroleum ether and dried in a vacuum desiccator over sulphuric acid.

Similarly the thiolignins from these non-wood fibrous plants were isolated at different temperatures and different sulphidity levels and the results are reported in Tables-II and III.

## ALKALINE NITROBENZENE OXIDATION

The thiolignins isolated at 20 % sulphidity rep.e-

Table—II : Process conditions and characteristics of thiolignins isolated from *Hibiscus cannabinus*, *Hibiscus sabdariffa* and *Cannabis sativa*.

Active alkali (as Na<sub>2</sub>O) = 15%, Time from 30°C to 160°C = 90 minutes

Time at 160°C = 120 minutes and wood to liquor ratio = 1:4

Sl. No.	Name of Plant	Sulphidity (%)	Unbleached pulp yield (%)	Klason lignin in pulp (%)	Klason lignin in thio-lignin (%)	Methoxyl group (%)	Carbon (%)	Hydrogen (%)	Sulphur (%)	Molecular formula (at 20% sulphidity)
<b>1. <i>Hibiscus cannabinus</i></b>										
a.		0.0	55.2	8.02	75.7	15.1	61.80	5.80	0.00	
b.		8.0	54.4	7.42	76.0	14.8	61.04	5.75	1.48	
c.		15.0	53.0	5.10	76.4	14.4	60.52	5.68	1.75	
d.		20.0	52.4	4.81	75.5	14.2	59.68	5.65	2.08	
e.		23.0	52.2	4.62	74.7	13.9	58.98	5.61	2.15	C <sub>154</sub> H <sub>174</sub> S <sub>2</sub> O <sub>62</sub>
<b>2. <i>Hibiscus sabdariffa</i></b>										
a.		0.0	54.6	8.22	75.4	15.0	61.30	5.85	0.00	
b.		8.0	53.8	7.68	75.9	14.4	60.52	5.80	1.54	
c.		15.0	52.2	7.12	77.1	14.1	59.32	5.78	1.73	
d.		20.0	51.5	6.65	75.0	14.0	58.90	5.68	2.10	
e.		23.0	51.4	5.50	74.2	13.8	58.50	5.65	2.16	C <sub>154</sub> H <sub>174</sub> S <sub>2</sub> O <sub>64</sub>
<b>3. <i>Cannabis sativa</i></b>										
a.		0.0	59.5	8.36	75.6	15.4	60.98	5.70	0.00	
b.		8.0	58.1	7.82	76.9	15.2	60.56	5.62	1.55	
c.		15.0	56.9	7.34	77.8	15.0	59.00	5.48	1.77	
d.		20.0	56.2	5.23	77.3	14.5	58.65	5.40	2.12	
e.		23.0	56.0	4.95	76.5	14.1	58.22	5.34	2.20	C <sub>148</sub> H <sub>164</sub> S <sub>2</sub> O <sub>64</sub>

**Table—III : Elementry composition of thiolignins of Hibiscus cannabinus, Hibiscus sabdariffa and Cannabis Sativa isolated from spent kraft liquors (at 20% sulphidity) at different temperatures\***

Sl. No.	Name of the Plant	Temperature °C	Yield of lignin (%)	Klason lignin in thio-lignin, (%)	Methoxyl group (%)	Carbon (%)	Hydrogen (%)	Sulphur (%)	Molecular Formula (at 160°C)
<b>1. Hibiscus cannabinus</b>									
a.		120	3.56	79.0	16.6	61.24	5.90	1.88	
b.		130	4.32	78.2	16.2	61.12	5.85	1.95	
c.		140	5.98	77.3	15.8	60.43	5.79	1.98	
d.		150	6.35	76.2	15.0	60.12	5.71	2.02	
e.		160	6.75	75.5	14.2	59.68	5.65	2.08	$C_{151}H_{174}S_2O_{63}$
<b>2. Hibiscus sabdariffa</b>									
a.		120	3.48	78.6	16.7	61.11	5.98	1.90	
b.		130	3.92	78.0	16.1	60.89	5.86	1.98	
c.		140	6.25	77.2	15.5	60.15	5.78	2.03	
d.		150	6.88	76.3	14.6	59.22	5.72	2.06	
e.		160	7.32	75.0	14.0	58.90	5.68	2.10	$C_{152}H_{174}S_2O_{64}$
<b>3. Cannabis sativa</b>									
a.		120	3.60	79.7	16.5	60.17	5.89	1.93	
b.		130	4.20	79.1	16.0	60.00	5.78	2.00	
c.		140	6.25	78.6	15.4	59.79	5.61	2.05	
d.		150	6.45	78.0	14.8	59.48	5.55	2.09	
e.		160	7.22	77.3	14.5	58.65	5.40	2.12	$C_{148}H_{164}S_2O_{64}$

\*Pulping conditions are similar as mentioned in Table-II.

Table—IV : Alkaline Nitrobenzene Oxidation Products of Thiolignins Isolated from *Hibiscus cannabinus*, *Hibiscus sabdariffa* and *Cannabis sativa* at 20% sulphidity.

Sl.	Name of Plant	Lignin Oxidation Products (%)			Molecular Ratios	
		Vanillin (V)	Syring aldehyde (S)	P-hydroxy benzaldehyde (H)	S/V	H/V
1.	<i>Hibiscus cannabinus</i>	5.6	10.62	4.9	1.90:1	0.88:1
2.	<i>Hibiscus sabdariffa</i>	5.8	11.12	5.5	1.92:1	0.95:1
3.	<i>Cannabis sativa</i>	6.0	11.80	5.3	1.97:1	0.88:1

sent the major part of protolignin, were further subjected to alkaline nitrobenzene oxidation according to the method of Stone and Blundell<sup>6</sup>.

The Thiolignins were analysed for their C, H, S, methoxyl and Klason lignin content. The sulphur content was determined by the Messinger method<sup>7</sup>, and Klason lignin content was determined according to TAPPI standard method<sup>8</sup>. The methoxyl value of lignins were determined according to Viebock and Schwappach<sup>9,10</sup> methods. The results are reported in Table—IV.

#### INFRARED SPECTROSCOPIC STUDIES

The infrared spectrums of the isolated lignin samples were recorded by using a Perkin - Elmer infracord spectrophotometer. The isolated lignin samples were examined in clear pressed discs containing 1.6mg of lignin in 100 mg of Potassium bromide.

#### RESULTS AND DISCUSSION

The results of proximate chemical analysis clearly indicated that these non-wood fibrous plants have moderate quantities of solubles thereby creating lesser pitch troubles with improved homogenities in the paper sheet. These plants have low lignins and high alpha cellulose content, thereby require less cooking chemicals with shorter cooking cycle to give comparatively higher pulp yields.

#### INFLUENCE OF SULPHIDITY

It is clear from Table—II, that the alkaline pulping of these non-wood fibrous materials in presence of sodium Sulphide introduced sulphur into the lignin molecule. Higher concentration of sodium sulphide resulted in an increase in amount of sulphur in the isolated lignins. The Klason lignin contents of the

isolated thiolignins remained practically the same while the Klason lignin content of pulp decreased continuously. It has also been observed that the maximum amount of lignin was delignified from the original raw material at a level of 20% sulphidity. The methoxyl content of all the isolated thiolignins are in indirect proportion with the sulphidity i.e. as the sulphidity increased, the amount of methoxyl content in thiolignin decreased.

The thiolignins are formed as a result of treating wood with sodium hydrogen sulphide.<sup>11</sup> The lignin combines with approximately 8% sulphur and only a small part of it desolves<sup>12</sup>. When the treatment is done at some-what higher temperature, the thiolignin melts and flows out into the lumina of tracheid cells. The thiolignin then reacted with sodium hydroxide at cooking temperature, loses the greater part of its sulphur, forming a product very similar to kraft lignins, with a sulphur content of 2-3%. The reported sulphur contents of kraft lignins vary generally from 1.5-3%. Consequently, it appears probable that in the formation of thiolignins, kraft delignification is arrested at its early stage.

During the kraft process, the overall consumption of sulphide has been claimed to be one-fifth to one-half of the charged sulphide, depending on the sulphidity of the cooking liquor<sup>13</sup>. The lost sulphur is mainly found as residual sulphur present in elemental form in the sulphate lignin. The existence of lignin-sulphur bonds in kraft lignins has been eloquently defended by Enkvist<sup>14</sup>. The molecular weight of *H. cannabinus*, *H. sabdariffa* and *C. Sativa* were found to be 3050, 3100 and 3000 respectively. Based on elemental composition and molecular weight determinations, the molecular formulas were also calculated for thiolignins of these plants, as reported in Table—II and III.

## INFLUENCE OF TEMPERATURE

The results of Table—III, indicated that as the temperature increased, the lignin recovery from the spent liquor increased but the carbon content decreased continuously while on the other hand the hydrogen content remained practically constant. The sulphur content in the isolated thiolignins increased with an increase in temperature and remained almost the same beyond 140°C. The methoxyl content of the isolated thiolignins remained practically the same.

The alkaline nitrobenzene oxidation of thiolignins (Table—IV) produced vanillin, Syringaldehyde and p-hydroxybenzaldehyde as a major products, in varying proportions, indicating the presence of syringyl-guaiacyl—and p-hydroxy phenyl propane building units. The yield of syringaldehyde is higher as compared to that of vanillin, suggesting that these lignins, contain more syringyl-repeating units than guaiacyl-repeating units. The higher yield of syringaldehyde in thiolignin is due to the higher methoxyl value. The syringaldehyde to vanillin (S/V) ratio remained practically the same. The p-hydroxy-benzaldehyde to vanillin (H/V) ratio also remained practically the same. The S/V ratio may be roughly two times higher than the H/V values, indicating the more efficient conversion of syringyl propane units to syringaldehyde in nitrobenzene oxidation.

The thiolignin isolated at 20% sulphidity was taken for the spectroscopic studies. The spectrum of thiolignin of *H. cannabinus*, *H. sabdariffa* and *C. sativa* were recorded in the range of 4000 to 600 $\text{cm}^{-1}$  and compared with I R spectrum of thiolignin of *Eucalyptus grandis*<sup>15</sup>.

The band at 3400  $\text{cm}^{-1}$  is common to almost all type of lignins and it is due to hydroxyl groups, i. e. O-H stretching frequencies, both phenolic and alcoholic<sup>16,18</sup> and this band is broadened due to hydrogen bonding. The absorption bands from 3100 to 2800 $\text{cm}^{-1}$  represents various types of C-H bonds. The shoulder at 2850-2860  $\text{cm}^{-1}$  is assignable to methoxyl groups<sup>17</sup>. In thiolignin there is no band at 1700-1660  $\text{cm}^{-1}$  region which can represent the carboxyl group. Thus principle change occurred in C-O region of thiolignins. Similar findings have been reported by Marton<sup>19</sup> in the case of Pine milled wood lignins and kraft lignin. The frequencies observed at 1605-1595  $\text{cm}^{-1}$ , 1515-1505  $\text{cm}^{-1}$

and 1460-1420  $\text{cm}^{-1}$  can be assigned to the skeleton band of guaiacyl and syringyl type compounds. The two bands at 1600  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$  are characteristics for aromatic compounds and they are due to the C=C vibration of the benzene ring. In soft wood lignin, the intensity of the 1600  $\text{cm}^{-1}$  band is lower than that of 1500  $\text{cm}^{-1}$  band. The absorption bands at 1430—1420  $\text{cm}^{-1}$  are considered to be ring stretching modes, strongly coupled by C-H in plane deformation. The intensity of the band depends on the nature of ring

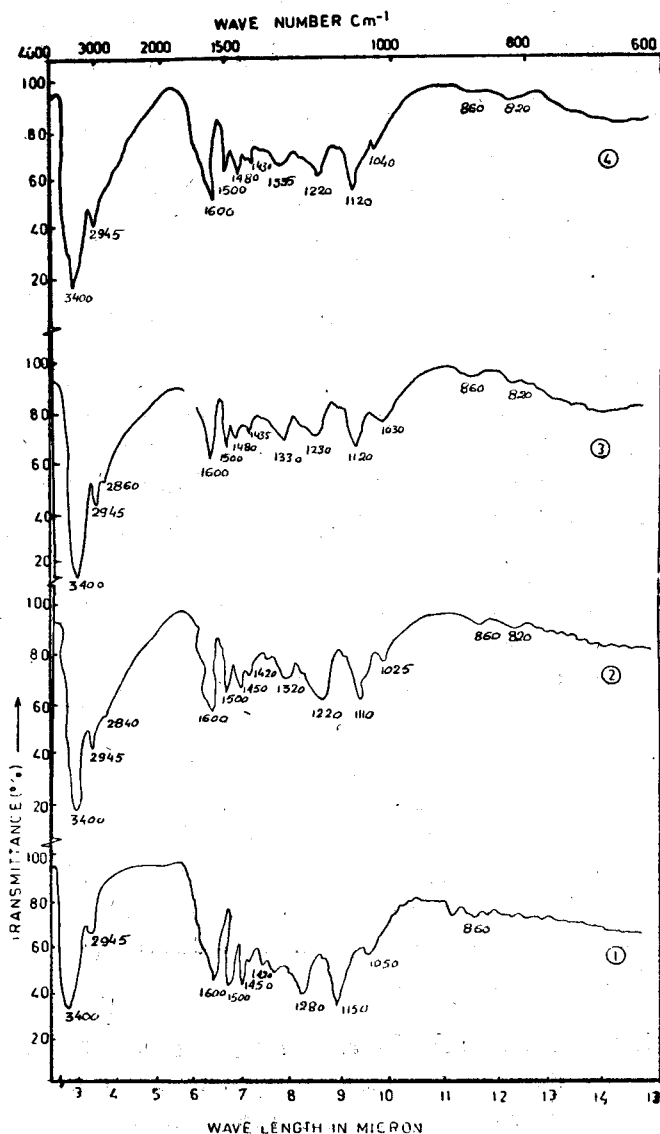


Fig. 1 : Infrared Absorption Spectrum of Thiolignins of *Eucalyptus grandis* (1) (at 25% sulphidity) *Cannabissativa* (2) *Hibiscus Cannabinus* (3) and *Hibiscus sabdariffa* (4) at 20% Sulphidity.

substituents. The band at  $1460\text{cm}^{-1}$  is due to C—H bonds including methoxyl groups. The band in the region of  $1390\text{-}1380\text{ cm}^{-1}$  is due to the bending vibration of O—H bonds. The band at  $1270$ ,  $1220$  and  $1120\text{ cm}^{-1}$  are due to guaiacyl and  $1330$  and  $1220\text{ cm}^{-1}$  due to syringyl-derivatives, being assignable to ring breathing with C—O stretching, while the guaiacyl bands at  $1120$  and  $1030\text{ cm}^{-1}$  are assigned to aromatic C—H in plane deformation. A general method to distinguish hardwood lignins from softwood lignins is based on the presence of bands at  $1270\text{ cm}^{-1}$  and  $1230\text{ cm}^{-1}$ , but intensity of the band at  $1270\text{ cm}^{-1}$  is higher than that of the band at  $1230\text{ cm}^{-1}$ . The band at  $1030\text{ cm}^{-1}$  is having equal or greater intensity than the  $1135\text{-}1120\text{cm}^{-1}$  band in softwood. The reverse is true for hardwood lignins. The band at  $1160\text{ cm}^{-1}$  is assignable to both the mode. The weak band in the region  $860\text{-}850\text{ cm}^{-1}$  and  $830\text{-}820\text{ cm}^{-1}$  are also visible, being characteristics of syringyl- compounds.

## CONCLUSIONS

The results of these investigations showed that, as the sulphidity increased, the amount of sulphur content increased in the isolated thioglignins. The sulphur content in the thioglignins increased with an increase in temperature and remains practically same beyond the temperature  $140^\circ\text{C}$ .

The results of alkaline nitrobenzene oxidation products of thioglignin indicated that it is composed of guaiacyl-, syringyl- and p-hydroxyphenyl propane units.

Thioglignin of *H. cannabinus*, *H. sabdariffa* and *C. sativa* contained both phenolic and aliphatic hydroxyl groups which appears to be strongly hydrogen bonded. The absence of  $1700\text{-}1660\text{ cm}^{-1}$  band in IR spectra of the lignin isolated from all these non-wood fibrous plants as well as *eucalyptus grand* is indicated the absence of C=O region.

The presence of guaiacyl-, and syringyl-, groups is further confirmed by the absorption bands at  $1600$ ,  $1500$ ,  $1460$ ,  $1420$  and  $1370\text{ cm}^{-1}$ . Greater intensity of  $1600\text{ cm}^{-1}$  bands as compared to that of  $1500\text{ cm}^{-1}$  supported the presence of p-hydroxyphenyl propane units. The absorption band at  $835\text{ cm}^{-1}$  accompanied

by weak band at  $860\text{ cm}^{-1}$  is characteristic of syringyl-units generally found in hardwoods. A greater intensity of  $1130\text{ cm}^{-1}$  band than that of  $1030\text{ cm}^{-1}$  band indicated that these lignins have similar characteristics with hardwood lignins

All these observations lead us to the conclusion that the lignin of *H. cannabinus*, *H. sabdariffa* and *C. sativa* showed almost similar characteristics with hardwood lignins, rather than softwood lignin.

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