

Studies on Pine Thiolignin and its Chlorination

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SUMMARY

Thiolignin prepared from pine was characterized for its elements, functional groups, ultraviolet and infrared spectra and molecular weight. The oxidation degradation products were evaluated by gas chromatographic technique. Thiolignin has $C_{9.21}H_{9.31}O_{1.43}S_{0.14}(OCH_3)_{0.89}(OH)_{1.17}(Ph-OH)_{0.40}$. The structural changes during pulping were studied by comparing thiolignin with milled wood lignin. It was observed that phenolic hydroxyl increases, whereas methoxyl contents decrease and the condensation reaction predominate over degradation.

Effect of time of chlorination on the elements, functional groups, ultraviolet and infrared spectra of the thiolignin were studied. Chlorination was observed to be very rapid, within a short period of 5 minutes, resulting in aromatic substitution, oxidation and demethylation.

INTRODUCTION

Sulphate pulping is most popular for more than three quarter of a century. To understand the changes in lignin structure that occurs during the cooking, it is essential to characterize the lignin before and after cooking.

Pulping process is followed by bleaching for whitening the pulp. Chlorine is an important bleaching agent. So it was decided to study the effect of time of chlorination on lignin.

To evaluate the mechanism of these reactions, it is essential to know the nature of the thiolignin as well as to know the effect of time of chlorination on changes in the structure of thiolignin.

EXPERIMENTAL

ISOLATION OF LIGNIN: Pine thiolignin was prepared by digestion of the pre-extracted wood dust (dust which had been extracted with ethanol benzene (1 : 2) and again extracted with acetone for 6 hours to free of lignins and stilbenes and then with low boiling petroleum ether for 6 hours to remove volatile oils) in 2.5 litre stainless steel auto-

clave under the following conditions :

Active alkali	—	20 %
Sulphidity	—	25 %
Initial temperature	—	50°C
Time to reach the maximum temperature	—	90 min.
Time to maximum temp.	—	90 min.

The dust was washed and the black liquor thus obtained was acidified to pH 9 with stirring and beating upto 80°C and again the pH was lowered to 3 using sulphuric acid. Lignin precipitate was washed with water and finally purified by the method of Brauns⁽¹⁾.

CHLORINATION OF LIGNIN : Chlorination of pine thiolignin was done in aqueous chlorine for different interval of time under the conditions :

Chlorine to lignin ratio	—	1 : 1
Consistency	—	0.4%
pH	—	2.0
Temperature	—	15°C
Time	—	5,30,60 min.

ANALYSES OF THIOLIGNIN AND CHLORINATED THIOLIGNIN : Lignin and the chlorinated lignin were analysed for its elements such as carbon, hydrogen, oxygen and sulphur. Sulphur was determined by Messinger's method⁽²⁾. Chloro-

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rine content was determined in chlorinated sample by the method adopted by Sarkar⁽³⁾.

Klason lignin⁽⁴⁾, acid soluble lignin⁽⁵⁾, methoxyl content⁽⁶⁾, total hydroxyls⁽⁷⁾, phenolic hydroxyl⁽⁸⁾ and molecular weight⁽⁹⁾ ⁽¹⁰⁾ were determined according to standard procedures.

Ultraviolet spectrum was taken by dissolving 25 mg lignin in 100 ml ethanol (Fig. 1), whereas

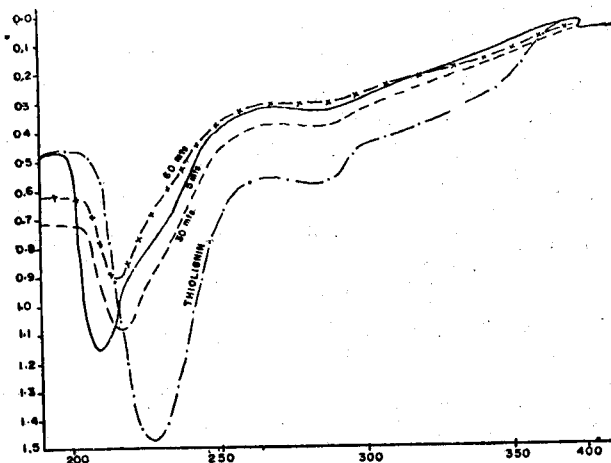


Fig. 1 ULTRA VIOLET SPECTRA OF THIOLIGNIN & CHLOROLIGNINS

Infrared spectrum was taken by KBr disc method (Fig. 2).

Nitrobenzene oxidation was carried out by the micromethod of Stone and Blundell⁽¹¹⁾. Quantitative estimation of nitrobenzene degradation products was carried out by Gas chromatography in the following matter: Oxidation products were silylated using hexamethyl disilane and trimethyl chlorosilazane and trimethyl acetamide in pyridine. The silylated derivative was identified using Perkin Elmer Model 3920 Gas Chromatograph equipped with differential flame ionization detector under the following conditions—Column—Silicone SE 30, 5% on chromatosorb W DMCS (80–100 mesh), Carrier gas—nitrogen, gas flow rate—50 ml/min, column oven temperature—160°C (isothermal), injection—0.5 μ l sample solution.

Calibration of the chromatogram was done by preparing a reference solution containing p-hydroxybenzaldehyde, vanillin and syringaldehyde and then noting their relative time which was 4.0, 6.7 and 10.7 minutes (Fig. 3). Identification of peaks of nitrobenzene oxidation products were done by comparing their relative time. The peak area was measured using triangulation method.

The amount of the product was calculated, on the basis of quantity injected initially.

RESULTS AND DISCUSSION

In Tables I and II, the results of the yield analyses of thiolignin as well as milled wood lignin are recorded.

A perusal of Table I reveals that the yield is quite high in contrast to MWL, which is due to the high solubility of lignin in alkaline media. Total Klason lignin content is lesser than MWL indicating its contamination with non-lignin material. In contrast to Klason lignin, acid soluble is higher which may be due to the extraction of cell wall lignin by alkali.

Elemental analysis given in Table II shows sulphur in addition to carbon, hydrogen and oxygen. Methoxyl groups are decreased from 0.99 to 0.82/C₆ unit i.e. one methoxyl has been lost for every 6.6 phenylpropane unit.

Hydroxyl groups of thiolignin are somewhat similar to that of MWL (Table II). But the phenolic hydroxyls are higher showing that one phenolic hydroxyl has been increased for every nine phenylpropane unit. The increase in phenolic hydroxyls is compensated by the loss of alcoholic hydroxyls. It is evident from the data that almost half of the side chain alcoholic groups must have been lost.

Carbonyl content does not show remarkable difference. Thiolignin has molecular weight 4042 which is higher than MWL (3100). This can be explained by intramolecular dehydration and secondary reaction such as condensation. The increase phenolic hydroxyls should have activated the 5-position of aromatic ring, which condenses with β - or α -carbon atom of other unit. Since the molecular weight is high, number of phenylpropane units composing a lignin molecule is again higher than MWL due to condensation.

Ultraviolet spectra given in Fig. 1 shows 2 bands below 230 nm and at 284 nm. The absorption intensity above 300 nm is marked due to conjugated chromophores, may be stilbenes.

Infrared spectra (Fig. 2) shows several bands, indicating the presence of hydroxyl, methoxyl, alkyl-aryl ether bond and dialkyl ether bonds. Some of the differences between the infrared spectra of thiolignin and MWL is recorded in Table III and discussed briefly as under:

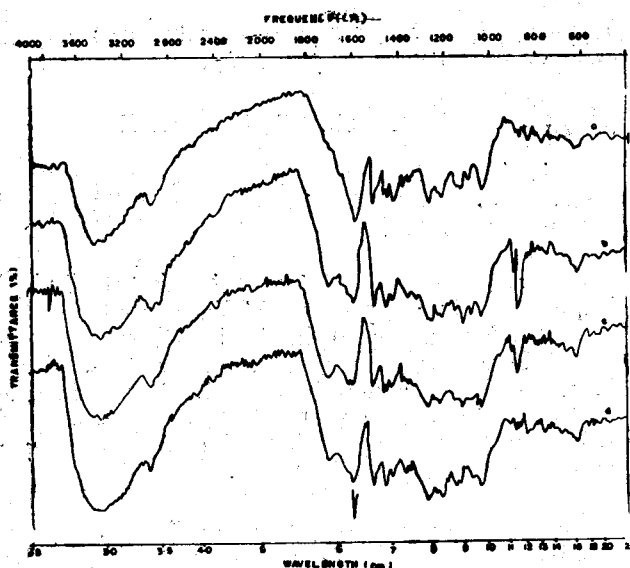


Fig. 2- INFRARED SPECTRA OF LIGNIN

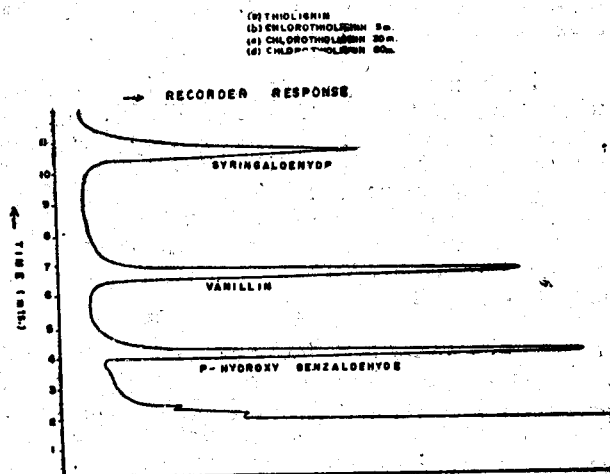


Fig. 3 GAS CHROMATOGRAM OF REFERENCE COMPOUNDS

The band at 1725 cm^{-1} is more intense at 1660 cm^{-1} is weaker than MWL. This may be ascribed as the loss of carbonyl groups and their replacement with carboxylic group. Two bands at 1500 cm^{-1} are due to aromatic stretching vibrations. The former band is stronger than in thiolignin-s and vice versa in MWL. This is because of the conjugated rings such as stilbens or carboxylic ions, in thiolignin.

In case of thiolignin the relative intensity of 1200 cm^{-1} band as compared to 1500 cm^{-1} is more intense than that in MWL as is seen in Table III. This is alleged to be an indication of increase in phenolic hydroxyls in thiolignin through ether cleavage and few from demethylation.

NITROBENZENE OXIDATION : The amount of aldehyde recovered from thiolignin as a result of nitrobenzene oxidation is given in Table IV. From the Table IV, it is seen that vanillin is the main oxidation product with minor amount of p-hydroxy-benzaldehyde. This suggests that pine thiolignin like other pine isolated lignin is composed of guaiacyl nucleus and few units of p-hydroxy-benzaldehyde units.

The estimation of vanillin yield is much lower than expected by theoretical values based on methoxyl content of lignin. Low yield of vanillin may be ascribed to condensation between units. From the results it is seen that the ratio of vanillin to p-hydroxybenzaldehyde is 17:1 whereas 10.8:1 in case of MWL. It can be explained as p-hydroxyl benzaldehyde units probably exists in lignin largely cordensed form and are therefore not converted to p-hydroxybenzaldehyde.

TABLE-I YIELD AND LIGNIN CONTENT OF PINE KRAFT LIGNIN & MILLED WOOD LIGNIN

	Thiolignin	Milled wood lignin
1. Yield %	21.04	3.05
2. Total Klason lignin	72.21	91.80
3. Acid-insoluble lignin	71.31	91.59
4. Acid-soluble lignin	0.90	0.21

TABLE-II REPRESENTATIVE COMPOSITION OF THIOLIGNIN AND MILLED WOOD LIGNIN.

	Thiolignin	Milled wood lignin
Carbon %	62.33	60.30
Hydrogen %	6.85	6.30
Oxygen %	28.56	33.40
Sulphur %	2.56	—
Methoxyl %	13.50	15.60
Total hydroxyl %	10.52	9.68
Phenolic hydroxyl %	3.58	1.55
Carbonyl/C ₉	0.18	0.17
C ₉ formulae	$\text{C}_9\text{H}_{9.31}\text{O}_{1.43}\text{S}_{0.14}$ (OCH ₃) _{0.82} (OH) _{1.17} (Ph-OH) _{0.40}	$\text{C}_9\text{H}_{8.39}\text{O}_{2.01}$ (OCH ₃) _{30.99} (OH) _{1.13} (Ph-OH) _{0.18}
Molecular weight	4042	3106
No. of unit/molecule	23	19

TABLE-III RESULTS FOR DETERMINATION OF IR-SPECTRA

(In IR Spectra the most convenient band for comparing the peaks is at 1500 cm⁻¹)

Frequency (cm ⁻¹)	Thiolignin	Milled wood lignin
1655/1500	0.11	0.32
1600/1500	1.76	1.25
1450/1500	0.35	0.57
1420/1500	0.47	0.43
1270/1500	0.53	0.71
1220/1500	0.53	0.46
1140/1500	0.35	0.71
1030/1500	0.88	0.92

TABLE-IV NITROBENZENE OXIDATION PRODUCTS OF THIOLIGNIN AND MWL

	Thiolignin	MWL
Vanillin, V %	13.97	23.8
p-hydroxybenzaldehyde, H %	0.82	2.2
Syringaldehyde V/H ratio	17:1	10.8:1

CHANGES IN LIGNIN MACROMOLECULE ON CHLORINATION :

In Table V, chlorinated derivatives of thiolignin is given. It is seen from Table V that almost 80% of the chlorine was consumed within 5 minutes, after that reaction speed was retarded. The yield of chlorolignin decreases as a result of prolonged treatment with chlorine. This may be due to water soluble reaction products resulting in loss of yield. This loss is prominent at 60 minutes.

Elemental analysis shows the presence of carbon, hydrogen, oxygen, sulphur and chlorine. By comparing the elements to thiolignin (Table II) it is seen that carbon content considerably decreased. This loss may be explained as the electrophilic replacement of the side chain and also due to demethylation¹³.

Methoxyl content of thiolignin chlorinated for 5 min. is 7.31 indicating that demethylation is a very fast reaction and demethylation reaction after 5 minutes almost stops.

TABLE-V ANALYSIS OF CHLOROLIGNIN

Components	Chlorinated Period, min.		
	0	30	60
Chlorine consumed, % of lignin	80.20	98.86	98.93
Yield %	86.90	85.10	78.35
Carbon %	52.57	49.67	49.42
Hydrogen %	5.52	5.29	5.27
Oxygen %	29.23	30.78	31.21
Chlorine %	10.65	12.63	12.65
Sulphur %	2.03	1.73	1.43
Methoxyl %	7.31	7.26	7.24
Phenolic hydroxyl %	1.63	1.74	1.88
Aliphatic hydroxyl %	14.22	14.25	14.72
Carbonyl/C ₀ %	0.30	0.37	0.31

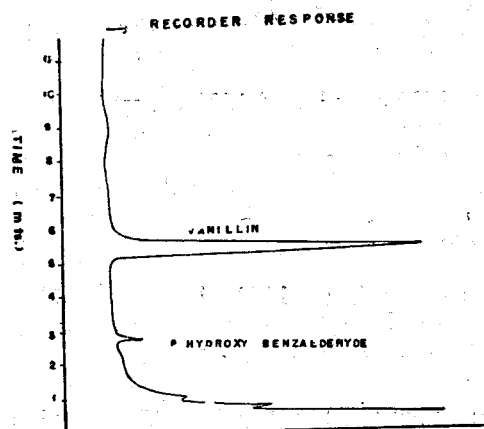


Fig. 4. GAS CHROMATOGRAM OF THIOLIGNIN OXIDATION PRODUCTS

Phenolic hydroxyls in chlorinated sample of lignin are decreased from 5.38 to 1.60%, but according to the reaction proposed by Hibbert¹³ for dealkylation, it is expected that both aliphatic and phenolic hydroxyls are liberated. This decrease in phenolic hydroxyls can be explained as the groups formed under these circumstances would be highly reactive and would be expected to react to form O-quinones. Gierer also supported to formation of O-quinones.

Carbonyl contents firstly increase upto 5 min., but on further chlorination; it starts decreasing.

ULTRAVIOLET SPECTRA : The UV spectra of chlorolignin are given in fig. 1. The ultraviolet spectra of chlorothiolignin was compared to untreated thiolignin. The spectral changes observed indicate that changes are due to instantaneous reactions taking place. Partial elimination of the

absorption maxima at 280 mm relative to maximum at 230 mm suggests the destruction of the aromatic nucleus. The absorption at 29 mm is due to the formation of chlorocompounds substituted at 6 position.

INFRARED SPECTRA : The infrared spectra was used to study the extent and nature of degradation of aromatic structure of lignin on chlorination. The IR spectra is given in Fig. 2.

A slight shifting of 3350 cm^{-1} band is due to the presence of chlorine atom in the molecule. The band at $1710-1620\text{ cm}^{-1}$ is consistent with carbonyl stretching in O-quinones in addition to β -keto and carboxyl groups. According to Mikaw, a very prominent band at 1710 cm^{-1} is assigned to carbonyl absorptions which have been shifted from the usual part of 1660 cm^{-1} through the influence of chlorine substitution.

Bands at 1600 cm^{-1} and 1520 cm^{-1} indicate the aromatic nature of chlorolignin. In all the chlorinated lignin 1510 cm^{-1} band is weaker than corresponding untreated lignin. It may be expected that carboxyl, carbonyl and/or O-quinone structure would be formed.

Absorption peak at 1470, 1435 and 1265 cm^{-1} is due to C—H bending vibration of methoxyl groups, is weaker than thiolignin, showing the loss of methoxyls.

The intensity of the band at 1220 cm^{-1} is less than thiolignin showing that phenolic hydroxyl decreases upto 5 minutes but increases with the chlorination period.

The usual bands at 870 and 820 cm^{-1} are characteristic of guaiacyl nucleus and progressively decreasing from a—d indicating some guaiacyl nucleus loss as the chlorination commences.

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