

Isolation And Ultraviolet Ionisation Spectra of Alkali Lignin and Organosolv Lignin From Cassia Siamea

Koshankar Prakash T. and Ingle V. N.

ABSTRACT

Ionisation spectra of alkali lignin (CAL) and organosolv lignin (COSL) from Cassia Siamea have been analysed and attempt has been made to calculate the number of moles of phenolic hydroxyl group contents of both the preparation.

INTRODUCTION

The lignin is an essential component of woody stem and angiosperm in which their amount ranges from 20 to 40%¹ and it is well known that lignin exist as a polymeric cell wall constituents in almost all dry plants and to carbohydrate in natural polymer, lignin are second to carbohydrate in natural abundance. Lignin owing to its aromatic nature, absorbs strongly in ultraviolet range of the spectrum. Ultraviolet spectra of large number of lignin preparation and lignin model compounds have been determined by many investigators^{2,3,4}. The characteristic bands in the lignin spectrum are attributable to oxygen substituted benzene rings, and that the relatively high absorption in the 300 - 450 nm region suggest the presence of carbonyl groups or double bonds conjugated with the benzene ring⁵. The ultraviolet absorption spectrum definitely proved the aromatic nature of lignin⁶.

The hydroxyl groups - their differentiation and quantitative determination - have played an important role in recent lignin chemistry. There is no doubt that lignin contains phenolic and aliphatic hydroxyl groups and since some of them may be etherified and form either alkyl ether or heterocyclic rings, their quantitative determination may contribute to the elucidation of structure of lignin molecule.

Ultraviolet ionisation spectra of alkali lignin (CAL) and organosolv lignin (COSL) of Cassia siamea have been analysed and an attempt has been made to calculate the number of moles of phenolic hydroxyl group contents of the alkali lignin using the average λ max value of the sample and an average $\Delta \epsilon$ max (4100) value of conidendrin and eugenol as a reference compounds which has the following relation.⁷

$$\text{Mole of phenolic OH per gram} = \lambda \text{ max}/4100$$

EXPERIMENTS AND METHODS

PREPARATION OF SAMPLE

A log of fully grown (in the month of Sept.) Cassia siamea was selected and after removing its bark, it cut into chips of size 2 to 3 inches (50-75 mm) in length. These chips were dried in the oven at 105°C for 24h. These dried chips were then

Department of Chemistry
Nagpur University
Nagpur-440 010 (M.S.)

subjected to pulverizer to convert it into powder and then passed through 40-60 mesh sieves. The 40 -60 mesh fraction were used for analysis and oversize of 60 mesh was taken for isolation of alkali lignin(CAL) and organosolv lignin (COSL).

ISOLATION OF ALKALI LIGNIN⁹ (CAL)

The wood meal (350 g) was mixed with six litres of 5 % NaOH and the mixture was kept in digester at 100 (Pounds per square inch) for 2 h. After digesting, the contents were filtered through fine mesh. The residue was washed with little distilled water and filtrate was collected. The filtrate was, then, neutralised with conc. HCl when coagulated lignin was separated. The solution was warmed at 60-65°C to get solid lignin. The light brown color lignin was filtered and washed with water and dried. the yield was 11.4%. The crude lignin was purified by dioxane extraction. The purified sample was dried in vaccum over silica gel.

ISOLATION OF ORGANOSOLV LIGNIN⁹ (COSL)

The extractive free wood meal (350 g.) was mixed with ethanol and water (1:1) 6 litres and was kept in the digester at 100 psi for 2 h. After digestion, the contents were filtered through fine mesh. The residue was washed with ethanol and water (1:1) and the filtrate was collected. The filtrate was concentrated in vaccum and it was poured into three times their volume of water¹⁰. The precipitated lignin was filtered and dried. The yield was 5.7%. The crude lignin was purified and dried as usual.

U.V. IONISATION DIFFERENCE SPECTROSCOPY

Ultraviolet ionisation difference spectra of the isolated alkali lignin were recorded with U.V. spectrophotometre, Shimadzu, UV-240 following the procedure adopted by Goldschimid¹¹ with slight modification in choosing buffer capacity (Figure 1).

Isolated lignin [0.1006 g.] and organosolv lignin (0.1053 g.) were dissolved in a buffer [100 ml. pH 9.2] and 6 ml. of it was made up to 50 ml. with the same buffer solution. Another 6 ml. of the original solution was neutralised with 6 ml. 0.1 N H₂SO₄ and diluted to 50 ml with a buffer of pH 7. The difference spectra were measured as the absorbance of the alkaline solution relative to that of the neutralised solution in the reference cell. The difference spectra were plotted

in terms of absorbivity obtained by dividing the absorbance by the concentration of the diluted solution in gram per litre.

RESULTS AND DISCUSSION

Proximate analysis of the sample were carried out using the TAPPI standards.

Table 1 : Proximate analysis of dried wood powder of Cassia siamea.

Contents	Percentage
Water extraction	12.5
Ethanol extraction	4
Benzene extraction	2.14
Ethyl acetate extraction	2.62
Dioxane extraction	0.44
Ethanol- Benzene[1:2] extraction	4.87
Lignin	39.54
Moisture	4.77
Ash content	3.06
Cold water solubility	3.2
Hot water solubility	7.44
1 % NaOH solubility	22.54

The alkali lignin gives difference maxima at 220 nm and 260 nm while organosolv lignin renders maxima at 210 and near 260 nm assigned to first primary and secondary band respectively due to ionisation of phenolic hydroxyl groups in alkaline solution; where as maxima 360 nm is ascribed to phenolic hydroxyl groups conjugated with carbonyl groups or possibly with biphenyl or ethelinic groups. The resulting spectra with a linear shoulder near 270 nm and a maximum at 350 nm clearly indicate the formation of - carbonyl group during ethanolysis. The peak maxima at 220 and 210 nm were used to determine unconjugated phenolic hydroxyl contents of alkali lignin and organosolv lignin. The moles of unconjugated phenolic hydroxyl contents of CAL and COSL per gram was found to be 0.0536 and 0.0512

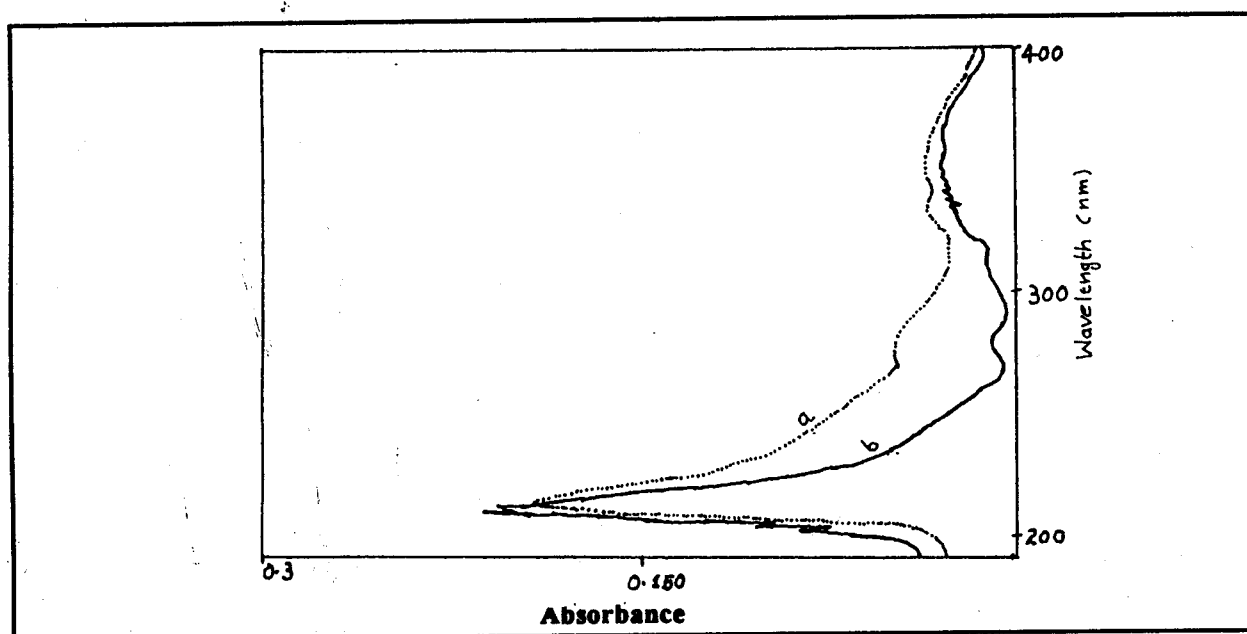


Fig. 1 : a) U.V. Ionisation Spectra of Cassia Alkali lignin (c=0.028 g/L)
 b) U.V. Ionisation Spectra of Cassia organsolv lignin (c=0.0872 g/L)

respectively.

CONCLUSION

UV ionisation spectra of CAL and COSL are almost the same and show only lower value of absorbance in COSL than that in the case of CAL. This anomaly may be due to the complex chromophoric system of the lignins. The relatively high absorption in the 300-450 nm region suggesting the presence of carbonyl groups or double bonds conjugated with benzene ring⁵. It also supports the aromatic nature of lignin.

REFERENCES

1. Bruno Jigersons, *Natural organic macromolecules*, 1962 p. 128.
2. R.F. Pattersons and H. Hibbert, *J. Am. Chem. Soc.*, 65, 1852 (1943)
3. *Ibid*, 65, 1869 (1943)
4. G. Aulin-Erdtman, *Svensk Papperstidn.*, 47, 91 (1944)
5. E.J. Jones, Jr. *Tappi.*, 32, 311, (1944)
6. G. Aulin-Erdtman, *Tappi*, 32, 160 (1949)
7. Braun and Braun., *the chemistry of lignin*, Academic press, 1960 p. 248.
8. B.L. Browing, *Methods of wood chemistry*, p. 742.
9. *Ibid*, p. 730
10. Braun and Braun. *The chemistry of lignin*, supplement volume, 1960 p. 88
11. Goldschimid., *Anal. chem.*, 26, 1421 (1954)