

Spectroscopic studies on organosolv lignins isolated from *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis*

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ABSTRACT

The organosolv (ethanol & methanol) lignin of some non-wood fibrous plants viz. *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* were isolated at different hydrochloric acid concentration (0.4N-1.2N). The isolated organosolv lignins were also analysed for their elemental composition and further subjected to alkaline nitrobenzene oxidation. The results of alkaline nitrobenzene oxidation products of these organosolv lignins revealed that these are composed of guaiacyl-, syringyl- and p-hydroxy phenyl propane building units. The ethanol and methanol lignins isolated at 0.4N acid concentration were further subjected to infrared spectroscopic studies. The origin of various bands in the spectra of organosolv lignins is discussed and assignments are summarized in this communication.

INTRODUCTION

In the organosolv lignins (1,2), alcohols combine with lignin in the presence of mineral acids to form soluble alcohol lignins. Methyl-, ethyl-, isobutyl-, amyl-, benzyl alcohols, cyclohexanol and ethylene glycol have been employed, usually with hydrogen chloride as a catalyst. The aim of the present studies was to apply this information together with the observation and conclusion of other workers in this field (3,4) to study the mechanism of various delignification process of practical interest, which may take place in the lignin and polysaccharides during the process of solubilization, and of the nature of the lignin-carbohydrate linkage in fibrous raw material. Further the knowledge of the chemistry of lignin will be of much use in formulating rational approaches to the development of new and improved delignification processes.

Thorough investigation on organosolv lignins was carried out by Klason (5), Gruss (6), Friedrich and

Diwald (7). They isolated ethanol lignin from soft woods as well as hardwoods by using the different percentages of hydrochloric acid. As far as non-wood fibrous raw material are concerned no systematic data is available. The present studies have been carried out on the properties of organosolv lignins isolated from *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis*.

Experimental :

Raw Material :

The *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* stalks were procured and chopped by hand. The chips were then converted into wood meal (-40 + 60 mesh) in the laboratory disintegrator. The wood meals were extracted with a mixture of ethanol and benzene (1:2v/v). The extracted wood meal were

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washed with hot water, and further utilized for the isolation of organosolv lignins.

Isolation of Ethanol Lignin :

250 gms. of pre-extracted wood meal of *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* were taken separately in a 5 liter flask fitted with a reflux condenser. Ethyl alcohol (3 liters) containing hydrochloric acid to give a solution of required acid concentration (0.4N) was added to the flask. It was refluxed for 5 hours at 100°C. The insoluble residues were filtered off and washed with ethanol. The filtrate and washings were concentrated to about 1 liter, neutralized with sodium bicarbonate, filtered, and the filtrate was added dropwise to large quantities of distilled water. The crude ethanol lignins were filtered off, washed with water, and dried in a vacuum desiccator. The lignins were purified from acetone water mixture. In the similar fashion the ethanol lignins from these non-woody fibrous plants were isolated at different acid concentration. The results are tabulated in Table-I.

Isolation of Methanol Lignin :

26 gms of pre-extracted wood meals of *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* separately were heated in a 200 ml. Steel, "bombs" with 150 ml. absolute methanol containing hydrochloric acid (0.4N) at $150 \pm 1^\circ\text{C}$ for 40 hours with shaking. As the reaction was over, the bombs were cooled. The insoluble residues were filtered off and washed with methanol. The methanol filtrate was concentrated to about 20 ml. and further distilled water (400 ml) and sodium hydroxide solution (10 ml., 0.5N) were added, and the mixture was boiled for 1 hr. The pH was adjusted to 1.0 by the addition of hydrochloric acid (5N) and the precipitated lignin was filtered off, washed with distilled water, and dried in a vacuum desiccator. In the similar way methanol lignins from these non-wood fibrous plants were isolated at different acid concentration. The results are recorded in Table-II

Table—I
Yield and elementary composition of Ethanol lignin isolated from *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* wood meal at different Hydrochloric acid concentration {0.4 (15), 0.8, 1.2 N}

Sl. No.	Name of Plant species	Hydrochloric acid concentration in ethanol (N)	Yield of ethanol lignin (on O.D. wood meal basis) (%)	Methoxyl content (%)	Carbon content (%)	Hydrogen content (%)
<i>Adhatoda vasica</i>						
1.		0.4	9.14	17.12	59.00	6.02
2.		0.8	10.20	16.70	61.40	5.84
3.		1.2	10.90	16.50	62.12	5.68
<i>Ipomea carnea</i>						
1.		0.4	7.90	17.52	59.40	6.10
2.		0.8	8.94	16.60	61.68	5.80
3.		1.2	9.42	16.20	62.24	5.73
<i>Ricinus communis</i>						
1.		0.4	8.82	17.35	59.80	6.02
2.		0.8	10.02	16.98	61.62	5.74
3.		1.2	10.54	16.62	62.10	5.61

Table—II

Yield and elementary composition of Ethanol lignin isolated from *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* wood meal at different Hydrochloric acid concentration [0.4 (15), 0.8, 1.2 N]

Sl. No.	Name of Plant species	Hydrochloric acid concentration in ethanol (N)	Yield of ethanol lignin (on O. D. wood meal basis) (%)	Methoxyl content (%)	Carbon content (%)	Hydrogen content (%)
<i>Adhatoda vasica</i>						
1.		0.4	5.52	20.80	60.85	5.80
2.		0.8	6.42	19.80	62.70	5.68
3.		1.2	7.00	19.10	63.42	5.58
<i>Ipomea carnea</i>						
1.		0.4	4.72	20.20	60.20	5.90
2.		0.8	6.18	18.90	61.40	5.78
3.		1.2	6.72	18.30	62.30	5.62
<i>Ricinus communis</i>						
1.		0.4	5.38	19.50	60.40	6.02
2.		0.8	6.10	18.70	62.30	5.74
3.		1.2	6.64	18.00	62.70	5.60

Table—III

Alkaline nitrobenzene oxidation products of Ethanol and Methanol lignin isolated from *Adhatoda vasica* (16), *Ipomea carnea* & *Ricinus communis* wood meal at 0.4 N Hydrochloric acid concentration.

Sl. No.	Name of Plant species	Types of lignin	Lignin oxidation Products			Molecular ratio	
			Vanillin (V)	Syringaldehyde (S)	p-hydroxy benzaldehyde (H)	S/V	H/V
1.	<i>Adhatoda vasica</i>	Ethanol	6.1	11.90	5.4	1.95 : 1	0.88 : 1
2.	<i>Ipomea carnea</i>	—do—	6.0	12.30	5.0	2.05 : 1	0.83 : 1
3.	<i>Ricinus communis</i>	—do—	5.7	11.30	5.4	1.98 : 1	0.95 : 1
1.	<i>Adhatoda vasica</i>	Methanol	6.9	12.48	5.3	2.10 : 1	0.89 : 1
2.	<i>Ipomea carnea</i>	—do—	6.0	12.25	5.9	2.04 : 1	0.98 : 1
3.	<i>Ricinus communis</i>	—do—	5.8	11.80	5.6	2.03 : 1	0.96 : 1

Alkaline Nitrobenzene Oxidation :

The organosolv lignins isolated at 0.4N hydrochloric acid concentration were further subjected to alkaline nitrobenzene oxidation according to the method of Stone and Blundell (8) and the result are reported in Table-III.

Analysis of Organosolv Lignins :

These organosolv lignins were analysed for their carbon, hydrogen and methoxyl content. The methoxyl value of lignins were determined according to Viebook and Schwappach method (9). The results of above analysis are reported in table-I and table-II.

Infrared Spectroscopic Studies :

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

Results and Discussion :

It is clear from the tables I and II that the organosolv lignins of *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* isolated by extraction of dust with increasing concentration of hydrochloric acid in alcohols shows that the percentage of carbon and yield of lignin increases whereas the percentage of hydrogen and methoxyl content decrease with increasing concentration of acid. The low yield of Ethanol and Methanol lignins indicated that almost 50% of the dissolved lignin remained in the aqueous alcoholic mother liquor. The values of methoxyl content of methanol lignins is higher than the ethanol lignins. Brauns (10) concluded that new methoxyl groups were introduced into the lignin building units in case of methanol lignins.

The alkaline nitrobenzene oxidation of ethanol lignins and methanol lignins (Table-III) gives vanillin, syringaldehyde and p-hydroxy behzaldehyde as major products in varying proportions indicating the presence of syringyl-, guaiacyl-, and p-hydroxy phenyl propane building units. The yields of syringaldehyde is higher as compared to that of vanillin. This suggests that these lignins contain more syringyl-repeating units than quaiacyl-repeating units. The yield of syringaldehyde

in methanol lignin is higher, it is due to the higher methoxyl value. The syringaldehyde to vanillin (S/V) ratios remain practically the same. The p-hydroxy benzaldehyde/vanillin (H/V) ratios also remains practically the same. But S/V values 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 organosolv lignins isolated at 0.4N acid concentration was taken for the spectroscopic studies. The spectrum of methanol lignins (Fig.1) and ethanol lignins (Fig. 2) of *Adhatoda vasica*, *Ipomea carnea* and *Ricinus communis* were recorded in the range of 4000 to 600 cm^{-1} .

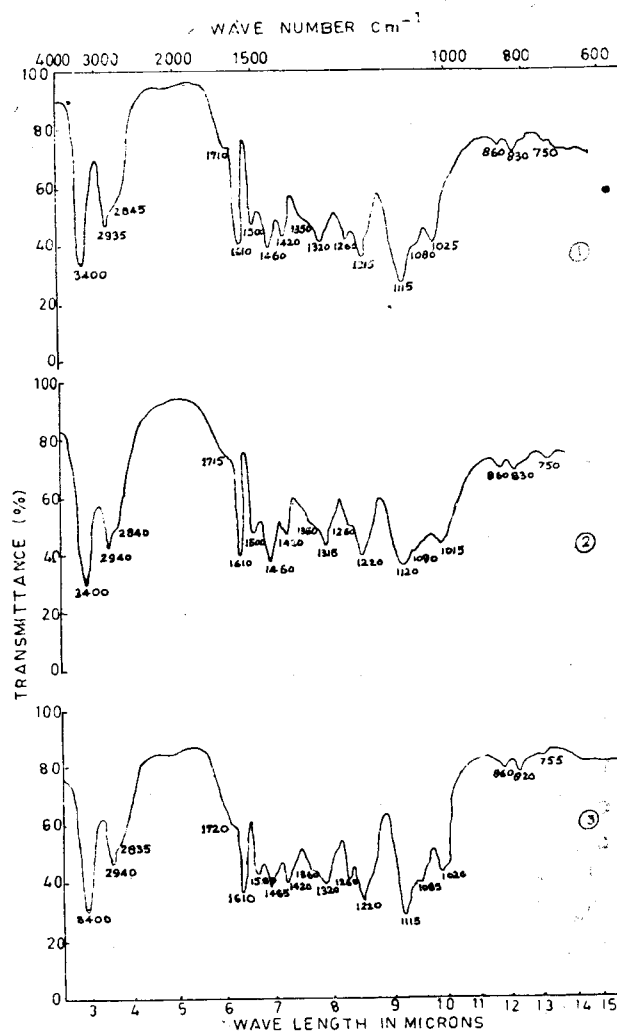


Fig.-1. INFRARED ABSORPTION SPECTRUM OF METHANOL LIGNIN OF (1) *Adhatoda vasica* (2) *Ipomea carnea* (3) *Ricinus com*

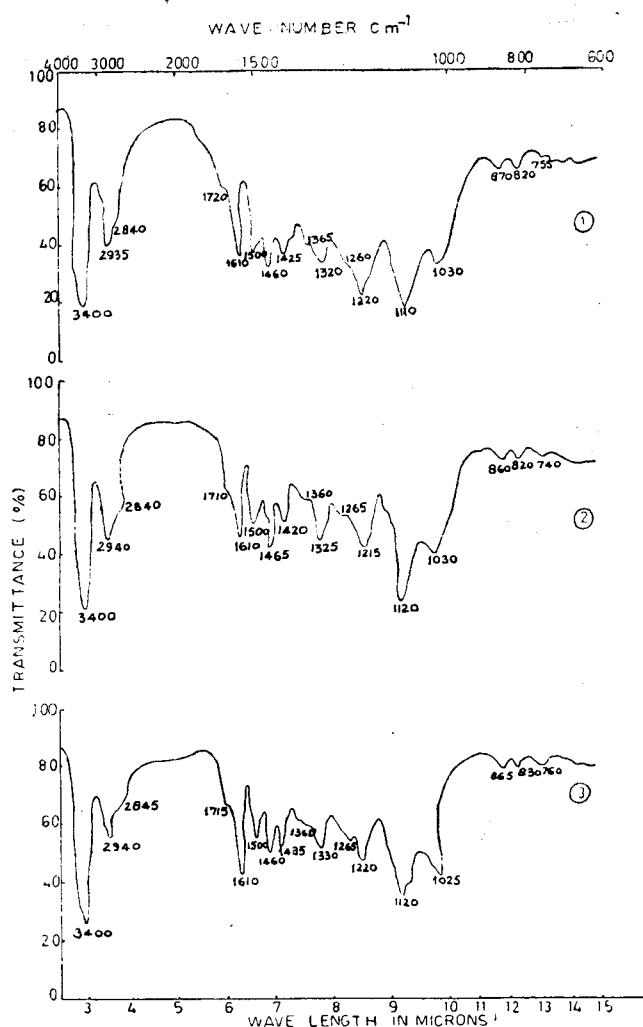


Fig. - 2 - INFRARED ABSORPTION SPECTRUM OF ETHANOL LIGNIN OF (1) *Adhatoda vasica* (2) *Ipomea carnea* (3) *Ricinus communis*

The band at 3700-300 cm^{-1} is common to almost all types of lignins and is due to hydroxyl groups O-H stretching frequencies both phenolic and alcoholic (11-13), these frequencies indicates that they are strongly hydrogen bonded. The intensity of this band is more in ethanol lignin than methanol lignin. The absorption bands at 3100 to 2800 cm^{-1} represents various types of C-H bonds. The shoulder at 2845-2835 cm^{-1} is assignable to methoxyl groups (14) and the band at 1720-1710 cm^{-1} is due to acetyl groups attached to the lignin and these bands appear especially in monocotyledons (14).

The frequencies observed at 1610 cm^{-1} , 1500 cm^{-1} and 1465-1420 cm^{-1} can be assigned as skeletal band of guaiacyl and syringyl type compounds. The two bands at

1610 cm^{-1} and 1500 cm^{-1} are characteristic of aromatic compounds and are due to the C=C vibration of benzene ring. In softwoods lignins the intensity of the 1610 cm^{-1} band is lower than that of 1500 cm^{-1} band. The absorption bands at 1435-1420 cm^{-1} are considered to be ring stretching modes strongly coupled by C-H in plane deformation. The intensity of the band is sensitive to the nature of ring substituents. The band at 1465-1460 cm^{-1} is due to C-H bonds including methoxyl groups. The band in the region of 1365-1350 cm^{-1} is due to the bending vibration of O-H bonds.

Although the bands are appeared at 1330-1315 cm^{-1} , 1220-1215 cm^{-1} , 1120-1110 cm^{-1} , 1085 cm^{-1} and 1030-1015 cm^{-1} in the IR spectrum, but the origin of these bands are less clear (There may be slight error due to shift in calibration). The band at 1265-1260, 1220-1215 and 1120-1110 cm^{-1} are due to guaiacyl and 1330-1315 and 1220-1215 cm^{-1} due to syringyl derivatives are assignable to ring breathing with C-O stretching, Guaiacyl band at 1120-1110 and 1030-1015 cm^{-1} are assigned to aromatic C-H in plane deformation. A general method to distinguish hardwood lignins from softwood lignins is, the presence of band at 1265-1260 cm^{-1} and at 1220-1215 cm^{-1} , but the intensity of band at 1265-1260 cm^{-1} , is more than the intensity of band at 1220-1215 cm^{-1} . The band at 1030 cm^{-1} is having equal or greater intensity than the 1120-1115 cm^{-1} band in softwood. The reverse is true for hardwood lignins. A band at 1090-1080 cm^{-1} is also visible in IR spectrum of methanol lignin. It is probably due to the symmetric stretching analog of either the band at 1260 cm^{-1} or that at 1220-1215 cm^{-1} .

The infrared absorption bands are also visible below 1000 cm^{-1} regions. A strong absorption band at 830-820 cm^{-1} with a weaker band at 870-860 cm^{-1} are characteristic of Syringyl compounds and are mostly found in tropical hardwoods lignins.

Conclusions :

1. The results of these investigations shows that as the acid concentration in alcohols increases the yield and carbon content also increases while the hydrogen and methoxyl content decreases.
2. The alkaline nitrobenzene oxidation products of organosolv lignins indicates that it is composed of guaiacyl, syringyl- and p-hydroxy phenyl propane units.

3. The organosolv lignins of *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* contain both phenolic and aliphatic hydroxyl groups which appear to be strongly hydrogen bonded.
4. The presence of 1720-1710 cm^{-1} band show the presence of carbonyl group.
5. The absorption band at 1610, 1500, 1465-1460, 1435-1420 and 1365-1350 cm^{-1} further confirmed the presence of guaiacyl and syringyl groups. Greater intensity of 1610 cm^{-1} bands as compared to that of 1500 cm^{-1} supports the presence of p-hydroxyphenyl propane units.
6. Absorption band at 830-820 cm^{-1} accompanied by a weak band at 870-860 cm^{-1} is characteristic of hardwood lignins.
7. Greater intensity of 1120-1110 cm^{-1} band than that of 1030-1015 cm^{-1} band indicates that these lignins have similarities to hardwood lignin.

From the above conclusion, it is concluded that the lignin of *Adhatoda vasica*, *Ipomea carnea* & *Ricinus communis* have some what similarity to hardwood lignins, rather than soft wood lignins.

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