

Infrared Spectroscopic Studies On Lignins Of Some Non-Wood Fibrous Plants

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ABSTRACT

The Klason and Willstatter lignins of some non-wood fibrous plants viz. *Sesbania sesban*, *Sesbania aculeata* and *Cajanus Cajan* were isolated at 72% sulphuric acid and 42% hydrochloric acid concentration. The isolated lignins were also analysed for their elemental composition and further subjected to alkaline nitrobenzene oxidation. The results of alkaline nitrobenzene oxidation products of these lignins revealed that these are composed of guaiacyl-, syringyl- and p-hydroxyphenyl propane building units. These lignins were further subjected to infrared spectroscopic studies. The origin of various bands in the spectra of lignins was discussed and assignments are summarized.

Although a great mass of literature is devoted to lignin from wood and from spent liquors, the idea that the residual lignins associated with pulps may be different from 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 studies was to apply this information together with the observation and conclusions of other workers in this field,^(1,2) to study the mechanism of various delignification processes of practical interest, which may take place in the lignin and polysaccharides during the process of digestion and of the nature of the lignin-carbohydrate linkage in wood. 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.

The only practical methods for total isolation of wood lignin are treatment of wood with 12% sulphuric acid (Klason lignin) and 42% hydrochloric acid (Willstatter lignin). Infrared spectra have been reported for lignins isolated by these procedures from a wide variety of softwoods and hardwoods⁽³⁻⁶⁾ 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 Klason and Willstatter lignins

isolated from *Sesbania sesban*, *Sesbania aculeata* and *cajanus cajan*.

EXPERIMENTAL PROCEDURES :

RAW MATERIAL :

The *S. sesban*, *S. aculeata* and *C. Cajan* 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 (1:2 V/V). The extracted wood meal were washed with hot water and these preextracted wood meals were further utilized for the isolation of lignins.

ISOLATION OF LIGNINS :

The Klason and Willstatter lignins were isolated by Ritter et al⁷, Broak and Brauns⁸ methods.

ANALYSIS OF LIGNINS :

These Klason and Willstatter lignins were analysed for their C, H and methoxyl content. The methoxyl value of lignins were determined according to Viebock and Schwappah⁹ methods. The results of above analysis are reported in Table-1.

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ALKALINE NITROBENZENE OXIDATION :

The Klason and Willstatter lignins were subjected to alkaline nitrobenzene oxidation according to the method of Stone and Blundell¹⁰, and the result are reported in Table-II.

INFARED SPECTRUMS :

The infrared spectras of isolated lignin samples were recorded using Perkin-Elmer infracord spectrophotometer. Isolated lignin samples were examined

in clear pressed disc. containing 1.6 mg. of lignin in 100 mg of potassium bromide.

RESULTS AND DISCUSSION :

It is clear from the Table-I that the C, H and CH₃O—percentage of Klason and Willstatter lignins are almost same. The alkaline nitrobenzene oxidation of Klason and Willstatter lignins (Table-II) gives vanillin, syringaldehyde and p-hydroxybenzaldehyde as major products in varying

TABLE—1

Elementary Composition Of Lignins Isolated From *Sesbania sesban*, *Sesbania aculeata* and *Cajanus cajan*.

Sl. No.	Name of Plant species	Types of lignin	Carbon content [%]	Hydrogen content [%]	Methoxyl content [%]
1.	<i>Sesbania sesban</i>	Klason	61.4	5.5	14.8
2.	<i>Sesbania aculeata</i>	—do—	60.3	6.2	15.3
3.	<i>Cajanus cajan</i>	—do—	62.1	5.5	15.5
4.	<i>Sesbania sesban</i>	Willstatter	60.8	6.0	14.3
5.	<i>Sesbania aculeata</i>	—do—	61.0	5.7	15.4
6.	<i>Cajanus cajan</i>	—do—	61.6	6.1	15.0

TABLE—2

Alkaline nitrobenzene oxidation products of lignin isolated from *Sesbania sesban*, *Sesbania aculeata* and *Cajanus cajan*.

Sl. No.	Name of Plant Species	Types of lignin	Lignin Oxidation products [%]			Molar ratios	
			Vanillin [V]	Syringaldehyde [S]	p-hydroxybenaldehyde [H]	S/V	H/V
1.	<i>Sesbania sesban</i>	Klason	5.9	12.00	5.3	2.03 : 1	0.89 : 1
2.	<i>Sesbania aculeata</i>	—do—	6.2	12.20	5.8	1.96 : 1	0.93 : 1
3.	<i>Cajanus cajan</i>	—do—	6.0	12.30	5.0	2.65 : 1	0.83 : 1
4.	<i>Sesbania sesban</i>	Willstatter	5.6	11.62	5.1	2.03 : 1	0.91 : 1
5.	<i>Sesbania aculeata</i>	—do—	6.1	11.90	5.4	1.95 : 1	0.88 : 1
6.	<i>Cajanus cajan</i>	—do—	6.0	12.10	4.8	2.01 : 1	0.80 : 1

proportions indicating the presence of syringyl-, guaiacyl-, and p-hydroxyphenyl propane building units. The yields of syringaldehyde is higher as compared to that of vanillin. This suggests that these lignins contains more syringyl-repeating units than guaiacyl- repeating units. The syringaldehyde to vanillin (S/V) ratios and p-hydroxybenzaldehyde to vanillin (H/V) ratios remains practically the same. The S/V value may be roughly two times higher than the H/V values indicating the more efficient conversion of syringylpropane units to syringaldehyde in nitrobenzene oxidation.

The infrared spectra of Klason and Willstatter lignins (Fig. 1, 2) of *S. Sesban*, *S. aculeata* and *C. Cajan* were recorded in the range of 4000 to 600 cm^{-1} .

The spectra are generally more diffuse throughout the whole spectral range indicative of rearrangement and condensation during isolation. The band at 3700–3000 cm^{-1} is common to almost all types of lignins and is due to hydroxyl group O–H stretching frequencies both phenolic and alcoholic¹¹⁻¹², these frequencies indicates that they are strongly hydrogen bonded. The absorption bands at 2940 cm^{-1} and 2845 to 2835 cm^{-1} represents O–H stretching in methyl and methylene groups. The band at 1700–1715 cm^{-1} , is due to acetyl groups attached to the lignin.

The frequencies observed at 1605-1595 cm^{-1} , 1515-1505 cm^{-1} and 1460-1420 cm^{-1} can be assigned as skeletal band of guaiacyl and syringyl type compounds. The two bands at 1600 cm^{-1} and 1500 cm^{-1} and characteristic of aromatic compounds and are due to the C=C vibration of benzene ring. In soft woods lignins the intensity of 1600 cm^{-1} band is lower than that 1500 cm^{-1} band while in hardwood, the intensity of these two bands is approximately equal or the intensity of 1600 cm^{-1} band is greater than 1500 cm^{-1} bands. The band at 1430-1425 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 absorption bands at 1460 cm^{-1} is due to C–H bands including methoxyl groups. The band in the region of 1360-1350 cm^{-1} is due to the bending vibration of O–H bonds.

The origin of the band in the region 1300-1000 cm^{-1} is less clear. The band at 1265, 1220 and 1110

cm^{-1} are due to guaiacyl and 1325 and 1220 cm^{-1} due to syringyl derivatives are assignable to ring breathing with C–O stretching. guaiacylic band at 1160, 1120 and 1030 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 a band at 1270 cm^{-1} , this band is more intense than the 1230 cm^{-1} band, this band at 1030 cm^{-1} is having equal or greater intensity than the 1120–1135 cm^{-1} band in softwoods. The reverse is true for hardwood lignins.

The infrared absorption bands are also visible below 1000 cm^{-1} regions. The absorption band at 900 cm^{-1} and 830 cm^{-1} which vary in wavelength depending upon the electronegativity of the side chain. These bands are characteristic of syringyl compounds and are mostly found in tropical hardwoods lignins.

CONCLUSIONS :

1. The results of these investigations shows that the Klason and Willstatter lignin have nearly the same percentage of C, H and methoxyl group.
2. The alkaline nitrobenzene oxidation products of both the lignins indicates that it is composed of guaiacyl-, syringyl- and p-hydroxyphenyl propane units.
3. The lignins of *S. sesban*, *S. aculeata* and *C. cajan* contains both phenolic and aliphatic hydroxyl groups which appear to be strongly hydrogen bonded.
4. The presence of 1730–1700 cm^{-1} band show the presence of carbonyl group.
5. The absorption band at 1600 1500, 1460, 1425 and 1360 cm^{-1} further confirmed the presence of guaiacyl and syringyl groups. Greater intensity of 1600 cm^{-1} bands as compared to that of 1500 cm^{-1} supports the presence of p-hydroxyl phenyl propane units.
6. Absorption band at 830 cm^{-1} and 900 cm^{-1} is characteristics of hardwood lignins.
7. Greater intensity of 1120 cm^{-1} band than that of 1030 cm^{-1} band indicates that these lignins have similarities to hardwood lignin.

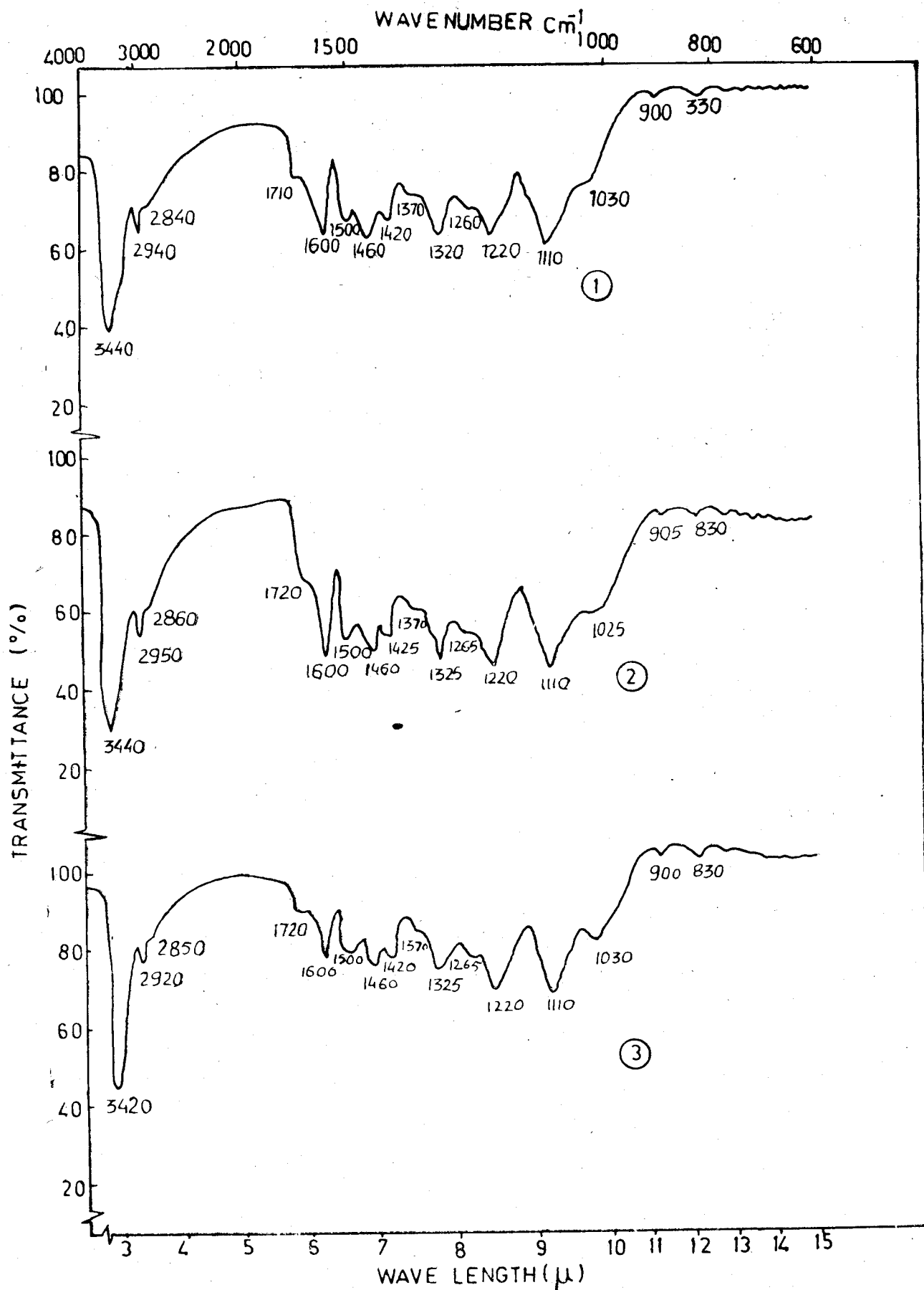


Fig 1 INFRARED ABSORPTION OF KLASON LIGNINS OF SESBANIA
 sesban ① SESBANIA aculeata ② CAJANUS cajan ③

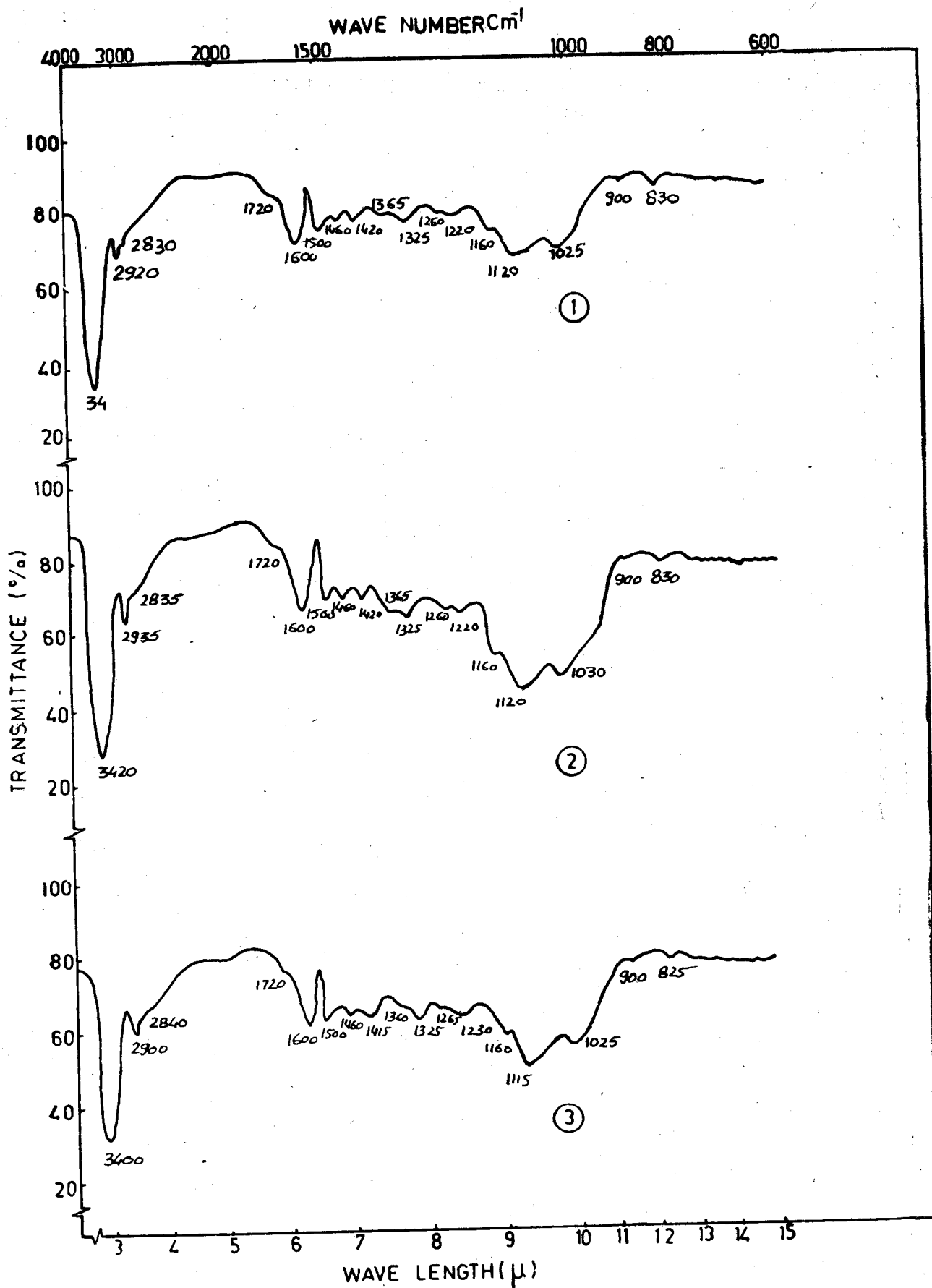


Fig. 2. INFRARED ABSORPTION SPECTRUM OF WILLSTATTER LIGNINS OF
 SESBANIA sesban ① SESBANIA aculeata ② CAJANUS cajan ③

From the above conclusion, it is concluded that these lignin of *S. sesban*, *S. aculeata* and *C. cajan* have somewhat similarity to hardwood lignins, rather than softwood lignins.

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