A Study of Chemical Structure of Soft and Hardwood and Wood Polymers by FTIR Spectroscopy

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ABSTRACT: Hard and softwood and wood constituent polymers (cellulose and lignin) were studied using Fourier transform infrared (FTIR) spectroscopy. The hollocellulose-to-lignin ratio was estimated for some of the timber species. The structural difference between Klason lignin isolated from softwood (*Pinus roxberghii* and *cupressus lusitanica*) and hard wood (*Acacia auriculaeformis* and *Eucalyptus tereticornis*) species was studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1969–1975, 1999

Key words: lignin; cellulose; FTIR spectroscopy; DRIFT; softwood; hardwood

INTRODUCTION

Wood is a naturally occurring polymeric composite composed of cellulose, hemicellulose, lignin, and extractives. It is most versatile and widely used structural material for indoor and outdoor applications. It has many attractive properties, has low density, low thermal expansion, renewable, and desirable mechanical strength, and it is aesthetically pleasing. All wood constituent polymers are responsible for most of the physical and chemical properties exhibited by wood and wood products. Because of its high degree of polymerization and crystallinity, cellulose is responsible for strength in wood fiber. Hemicellulose acts as a matrix for the cellulose and acts as a link between the fibrous cellulose and amorphous lignin. Lignin, a polyphenolic compound, acts as a cementing material for wood fibers. Though considerable work has been carried out on the vibrational analysis of wood and its constituents by infrared (IR) spectroscopy over the last two decades, knowledge of the molecular structure of wood constituents' polymers, their interaction in the polymer matrix is still not complete.

Infrared spectroscopy is a very useful tool for obtaining rapid information about the structure of wood constituents and chemical changes taking place in wood due to various treatments. Ever since the advent of the Fourier transform infrared (FTIR) spectrometer, this technique has been used for wood surface characterization, for estimating the lignin and carbohydrate contents in wood and lignoellulosics.[1–7] This has advantage over conventional chemical methods, which are time-consuming and also result in a concomitant degradation of natural polymers.

In this work, we have measured transmission and diffuse reflectance infrared (DRIFT) spectra from some of the softwood (gymnosperms) and hardwood (angiosperms) species to study the difference in their chemical structure and estimate the relative amount of lignin and cellulosic polymer in different wood species. The DRIFT technique has an advantage over other methods because it is a quick, easier, and nondestructive method, and the structure of the wood is maintained when spectra are measured directly from solid wood surfaces. The difference in the chemical structure of Klason lignin obtained from softwood and hardwood species was also studied. This work is part of a long-term project to study the structural changes that occur when wood is

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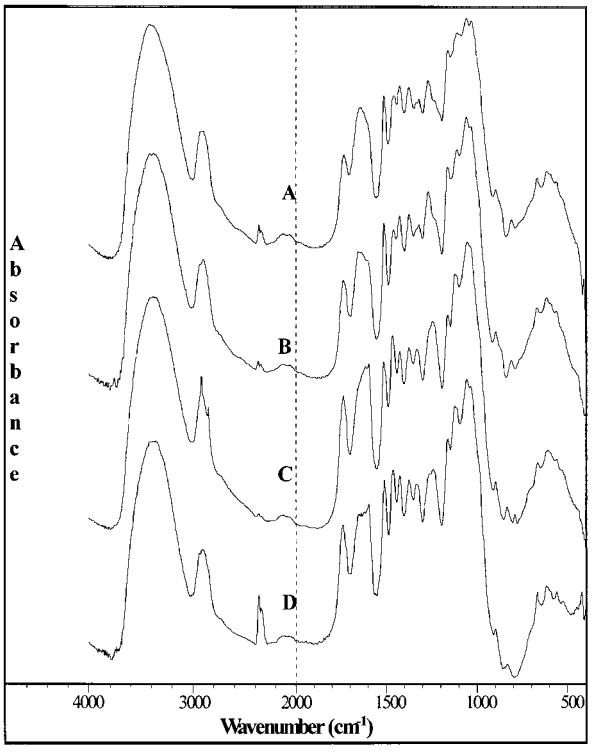
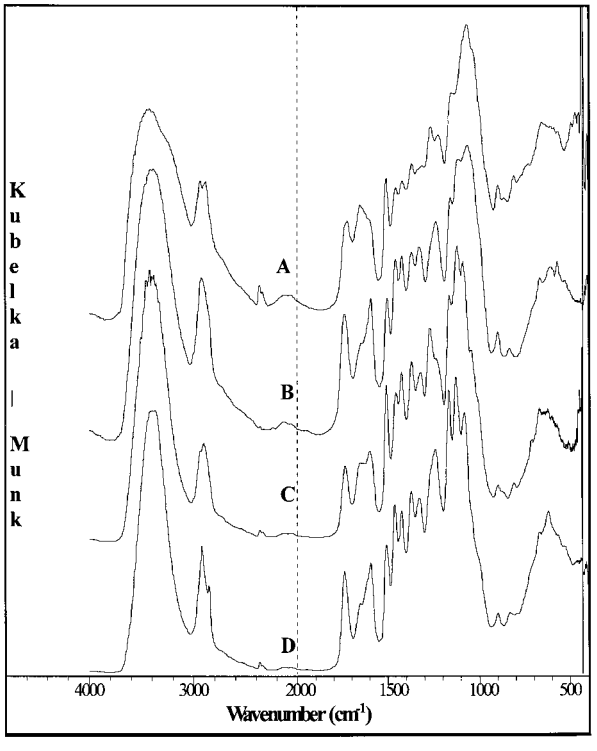


(a)



(b)

Figure 1 (a) Transmission spectra of softwood and hardwood (measured using the KBr pellet technique: (A) *Pinus roxburghii* (softwood); (B) *cupressus lusitanica* (softwood); (C) *Acacia auriculaeformis* (hardwood); and (D) *Eucalyptus tereticornis* (hardwood). (b) DRIFT spectra of soft and hardwood: (A) Softwood (*Pinus roxburghii*) and (B) hardwood (*Acacia auriculaeformis*). Curves (C) and (D) correspond to the DRIFT spectra measured directly from solid wood blocks of *Pinus roxburghii* and *Acacia auriculaeformis*, respectively.

treated with various chemical reagents and the changes in wood surfaces that occur when it is exposed to the varying environmental conditions.

EXPERIMENTAL

Klason lignin was isolated from hardwood (*Acacia auriculaeformis* and *Eucalyptus tereticornis*) and softwood (*Pinus roxberghii* and *cupressus lusitanica*) species according to the official test method T 222 om-83 of TAPPI (Technical Association of the Pulp and Paper Industry 1983).[8] Microcrystalline cellulose, used in this study, was obtained from S.d. fine-CHEM Ltd.

IR spectra of wood and its major constituents, cellulose and lignin, isolated from hard and softwood species, were measured by direct transmittance (using the KBr pellet technique) and the DRIFT method. DRIFT spectra were measured directly from wood surfaces, as well as from wood powder dispersed in KBr. Spectra were recorded using a Nicolet Impact 400 FTIR spectrometer equipped with a DTGS detector. All the spectra were taken at a spectral resolution of 8 cm^{-1} and an interferometer speed of 0.312 cm/s. Background spectra were collected using pure KBr. For DRIFT measurements, a Spectra Tech baseline diffuse reflectance accessory was used, and spectra were expressed in the values of Kubelka–Munk function, $F(R_\infty)$, defined by the following equation[9]:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{2.303ac}{s} \qquad (1)$$

where R_∞ is the ratio of the reflectance spectrum of an infinitely thick sample to that of a nonabsorbing reference, a is absorptivity, c is the concentration of the analyte, and s is the scattering coefficient. Peak due to CO_2 (at around 2360 cm^{-1}) was avoided in the analysis.

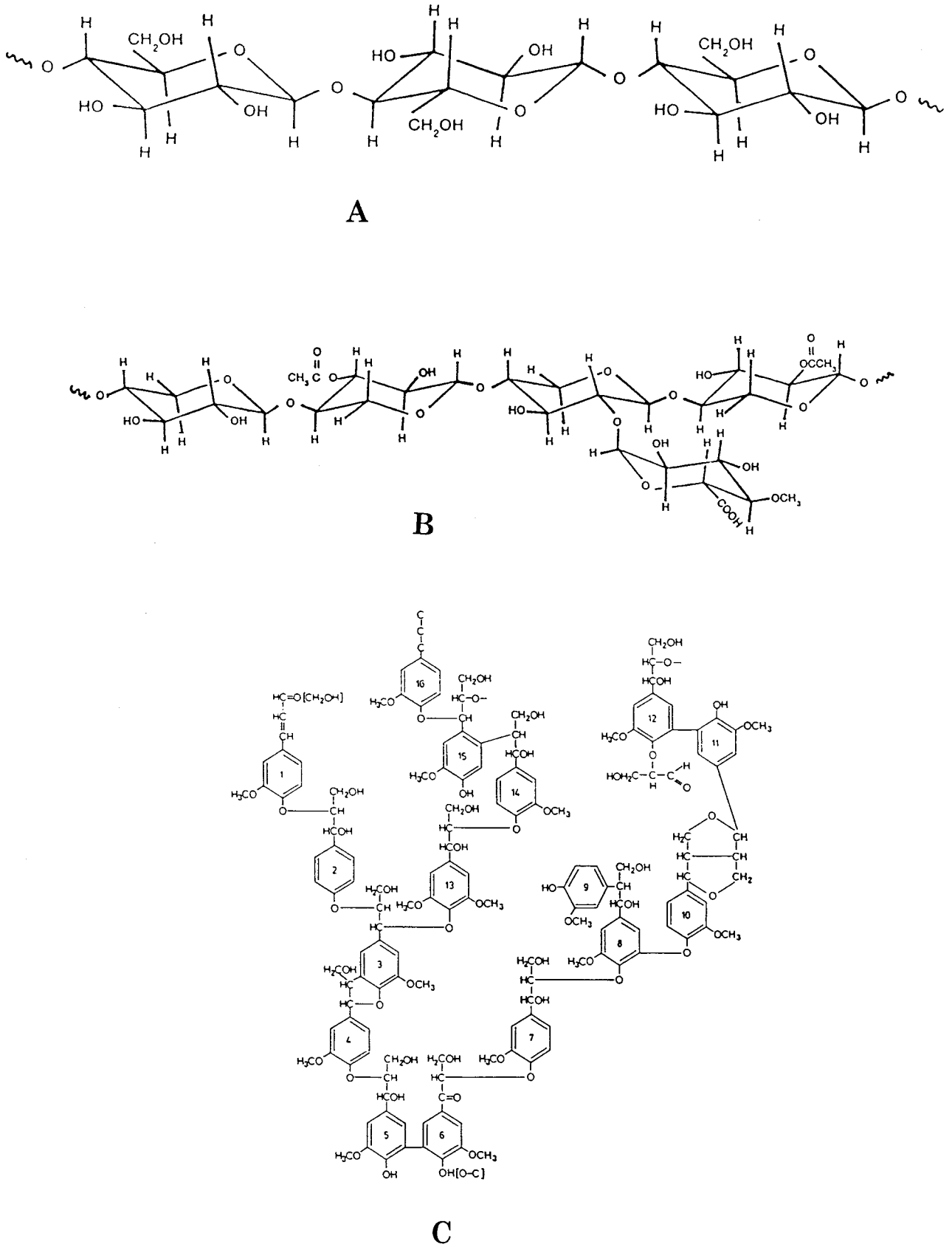


Figure 2 Schematic diagram of a representative section of the molecular structure of (A) cellulose, (B) hemicellulose, and (C) softwood lignin (Adler).[13]

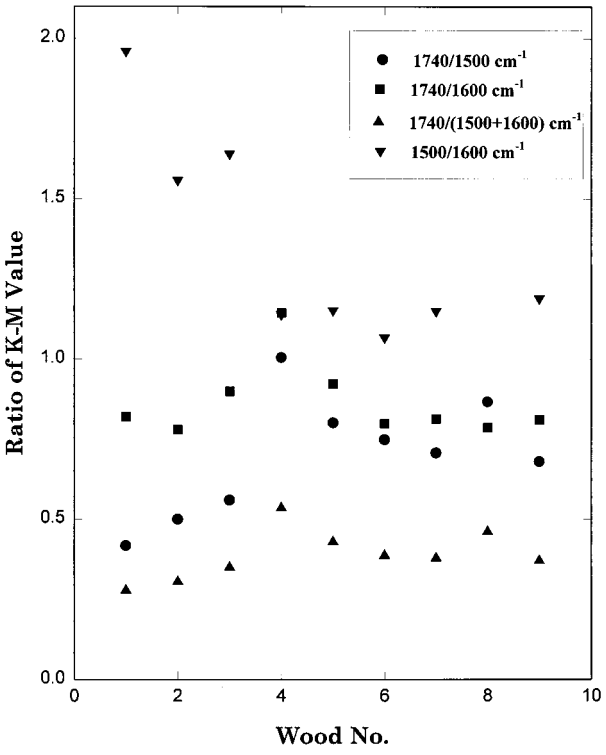


Figure 3 Variation of relative intensities of various absorption bands. The wood species are as follows: (1) *Pinus roxburghii*, (2) *Cupressus lusitanica*, (3) *Cupressus goveniana*, (4) *Adina cordifolia*, (5) *Acacia auriculaeformis*, (6) *Pterocarpus marsupium*, (7) *Grevillea robusta*, (8) *Eucalyptus tereticornis*, and (9) *Mangifera indica*. Numbers (1)–(3) are softwood species; numbers (4)–(9) are hardwood species.

RESULTS AND DISCUSSION

DRIFT and Transmission Spectra

FTIR spectra of softwood and hardwood species, measured by transmission and DRIFT methods, are shown in Figure 1(a) and (b). Distortions in the intensities of the bands of strongest absorption occur in the region 1150–950 cm^{-1}, when DRIFT spectra were measured directly from wood surfaces. A similar effect is observed in the DRIFT spectra measured from undiluted wood powder. This anomaly in DRIFT spectra is attributed to the contribution from specular component. The undesired specular component in DRIFT spectra can be minimized by either diluting the sample to a concentration $< 2\%$ in a nonabsorbing matrix like KBr[5–7] or by increasing the roughness of wood surfaces and using a metal blocker.[6] The effect of specular component can also be reduced by measuring DRIFT spectra using a silicon carbide disc.[6] Apart from concentration, DRIFT spectra are also influenced by the particle size of the ground sample and the anatomical direction of solid wood block.[5,7]

IR spectra of wood show a strong hydrogen bonded O—H stretching absorption around 3400 cm^{-1} and a prominent C—H stretching absorption around 2900 cm^{-1}. In the fingerprint region, between 1800–900 cm^{-1}, many sharp and discrete absorption bands due to various functional groups present in wood constituents are observed [Fig. 1(a) and (b)]. The O—H (at around 3400 cm^{-1}), C—H (at around 2900 cm^{-1}), C═O (at around 1740 cm^{-1}), and C═C (at around 1510 cm^{-1}) bands are pure, whereas other bands in the fingerprint region below 1460 cm^{-1} are complex, having contributions from various vibration modes in carbohydrates and lignin.[5,7,10]

Softwood and Hardwood

The distinction between IR spectra of softwood and hardwood species can be clearly seen in Fig-

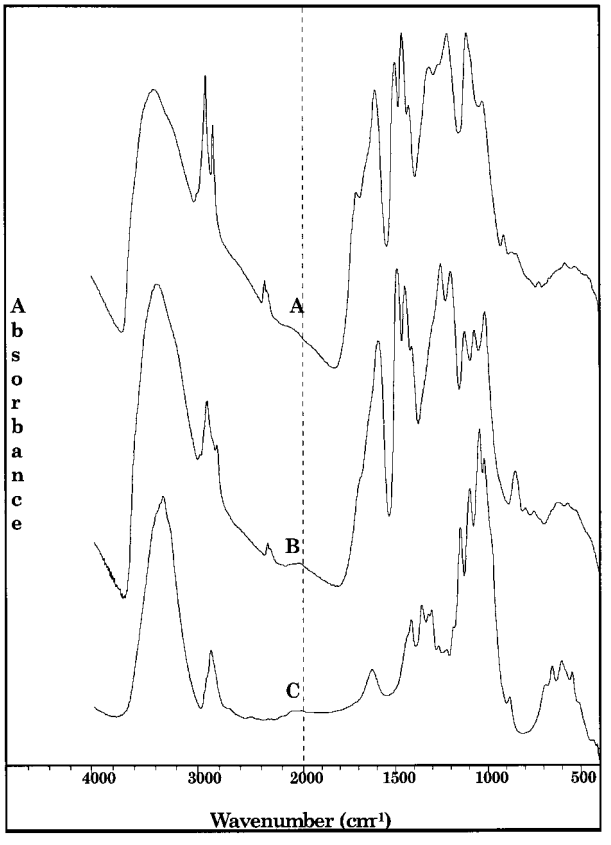


Figure 4 FTIR spectra of (A) hardwood lignin (isolated from *Acacia auruculaeformis*), (B) softwood lignin (isolated from *Pinus roxburghii*), and (C) cellulose.

Table I Summary of IR Bands Observed in Hardwood Lignin (Isolated from *Acacia auriculaeformis*) and Softwood Lignin (Isolated from *Pinus roxburghii*)

	Softwood		Hardwood		
S. No.	Band Position	Absorbance	Band Position	Absorbance	Assignment
1	3414	0.92	3419	0.82	O—H stretch (hydrogen-bonded)
2	2935	0.58	2919	0.86	C—H stretching
3	2842	0.45	2850	0.70	C—H stretching
4	1714	0.35	1711	0.50	C═O stretch (unconjugated)
5	1606	0.76	1610	0.82	Aromatic skeletal vibration + C═O stretching
6	1502	0.99	1502	0.90	Aromatic skeletal vibration
7	1462	0.93	1462	0.99	C—H deformation (methyl and methylene)
8	1425	0.75	1425	0.77	C—H in-plane deformation with aromatic ring stretching.
9	—	—	1315	0.89	C—O of syringyl ring
10	1268	1.00	1267	—	C—O of guaiacyl ring
11	1214	0.97	1218	0.99	C—O of guaiacyl ring
12	1140	0.79	1113	1.00	Guaiacyl C—H and syringyl C—H
13	1086	0.79	—	—	C—O of secondary alcohols
14	1030	0.85	1026	0.78	C—O of primary alcohol, guaiacyl C—H
15	866	0.365	912	0.68	C—H out-of-plane

ure 1(a) and (b). The position of the carbonyl peak is at a higher wave number for hardwoods (> 1740 cm^{-1}). Whereas, the lignin characteristic peak (at around 1505 cm^{-1} in hard woods) is shifted towards a higher wave number (> 1510 cm^{-1}) in the softwoods. Positions of most of the other bands in the finger print region are approximately the same in soft and hardwoods. However, the relative intensities of bands vary considerably. The relative intensities of bands at 1505, 1425, and 1270 cm^{-1} are higher in softwood, whereas bands at 1465, 1320, and 1220 cm^{-1} are stronger in hardwood. This variation is because of the different proportions of holocellulose and lignin present in soft and hardwoods. A higher lignin content in softwood than hardwood is indicated by a strong band at 1505 cm^{-1} in the spectra of softwoods. Higher holocellulose (cellulose and hemicellulose) content in the hardwood is indicated by a strong carbonyl band at 1740 cm^{-1}. These carbonyl groups occur maximum in the branched chain hemicelluloses. A representative section of molecular structure of the main polymer component of wood, that is, cellulose, hemicellulose, and lignin, are shown in Figure 2. The relative amount of cellulosic and lignin content between softwood and hardwood varies from one timber species to another. Hollocellulose to lignin ratio is found to be higher in hardwoods, as compared to the softwoods, as can be seen from Figure 3.

The variation of relative intensities of the two lignin absorption (1505 to 1600 cm^{-1}) and carbonyl-to-lignin peaks, obtained from DRIFT spectra, measured from solid wood surface, for some of the softwood and hardwood timber species are shown in Figure 3. Distinct behavior by softwood and hardwood species can be seen. The intensity ratio of two lignin peaks for different woods show a higher 1505-to-1600 cm^{-1} ratio for softwood than hardwood. The intensity ratio of carbonyl absorption to two lignin absorptions shows a higher value for hardwoods. A similar pattern is found to follow when the carbonyl peak is ratioed against the sum of the intensity of two lignin peaks. The difference between hard and softwood is most distinct when the ratio was taken against the 1505 cm^{-1} band. This is because the 1505 cm^{-1} band arises purely due to aromatic skeletal vibration of benzene ring in lignin, whereas the band at 1600 cm^{-1} has contributions from conjugated C═O group also.[11] The lignin content can be estimated from the relative area of the 1505 cm^{-1} band since a linear relationship is found to exist between its area and lignin content.[1]

Table II Summary of IR Bands in Cellulose

S. No.	Band Position	Absorbance	Assignment
1	3348	0.78	O—H stretch (hydrogen-bonded)
2	2902	0.27	C—H stretching
3	1640	0.21	Adsorbed O—H, conjugated C═O
4	1430	0.37	C—H deformation (asymmetric)
5	1372	0.43	C—H deformation (symmetric)
6	1336	0.39	O—H in-plane deformation
7	1318	0.41	CH_2 wagging
8	1201	0.35	O—H deformation
9	1163	0.67	C—O—C asymmetric vibration
10	1112	0.80	Glucose ring stretch (asymmetric)
11	1059	1.00	C—O stretch
12	1033	0.90	C—O stretch
13	897	0.12	Glucose ring stretch, C_1—H deformation

Softwood and Hardwood Lignin

The IR spectra of Klason lignin isolated from softwood (*Pinus roxburghii*) and hardwood (*Acacia auriculaeformis*) are shown in Figure 4. The spectrum measured from microcrystalline cellulose powder is also shown in Figure 4 (curve C). The peak positions of all the IR bands and their relative absorbance (the intensity of highest absorbance peak normalized to unity) of lignin and cellulose are summarized in Tables I and II respectively.

Spectral differences between hard and softwood lignin are observed in the fingerprint region between 1800 and 900 cm^{-1}. In softwood lignin, the bands at 1502 (aromatic skeletal vibration) and 1268 cm^{-1} (guaiacyl ring breathing with carbonyl stretching) dominate, whereas the bands at 1462, 1218, and 1113 cm^{-1} dominate in hardwood lignin (Fig. 4). The intensity of bands at 1609 (aromatic skeletal vibration breathing with C═O stretching) and 1462 cm^{-1} (C—H methyl and methylene deformation) is lower than that of the 1502 cm^{-1} band in softwood lignin. The intensity of 1113 cm^{-1} band (C—H in-plane deformation of the syringyl unit) is much higher than that of 1030 cm^{-1} (C—H deformation in guaiacyl with C—O deformation in primary alcohol) in hardwood lignin, whereas the intensity of band at 1030 cm^{-1} is equal to or greater than that of the 1113 cm^{-1} band in softwood lignin. In softwood lignin, 1268 cm^{-1} band is more intense than 1214 cm^{-1} and has no syringyl absorption at 1315 cm^{-1}, whereas the opposite is true for hardwood lignins, that is, a weak 1267 cm^{-1} band, a strong band at 1218 cm^{-1}, and syringyl absorption at around 1315 cm^{-1}. The presence of syringyl unit in hardwood lignin is also evident from the higher intensity of band at 1462 cm^{-1}. The intensity of band at 1462 cm^{-1} is comparable to that of the 1502 cm^{-1} in hardwood lignin. This difference in the spectrum of lignin isolated from hard and softwood is because the structure of the lignin polymer in softwood is different from that of hardwood. Lignin is an amorphous, polyphenolic material arising from an enzyme-mediated dehydrogenative polymerization of the following three phenylpropanoid monomers: (A) coniferyl, (B) sinapyl, and (C) *p*-coumaryl alcohols (Fig. 5).[12]

Softwood lignin (called guaiacyl lignin) is a polymer largely based on coniferyl alcohol (unit A) as a basic unit, which is more than 95% of the total number of structural units with the remainder consisting mainly of *p*-coumaryl-alcohol-type units (unit C) and a trace amount of sinapyl-alcohol-derived-unit (unit B). Hardwood lignin (called guaiacyl–syringyl lignin) are composed of coniferyl- and sinapyl-alcohol-derived units in varying proportions. In hardwood lignin, the methoxyl content per phenylpropanoid unit typically is in the range 1.2 to 1.5 (Dence and Lin).[12] Guaiacyl-type lignin absorbs near 1270 and 1230 cm^{-1} and the syrngyl type (the major type in hardwood lignin) absorbs at about 1230 cm^{-1}. The guaiacyl-to-syringyl ratio can be estimated from the relative intensity of bands at 1270 and 1230 cm^{-1}.

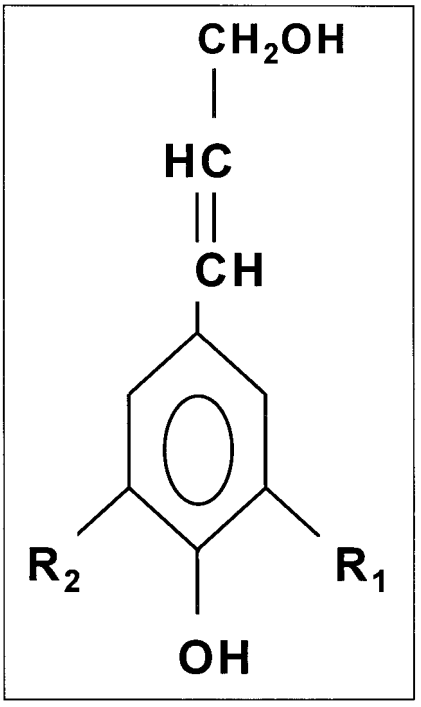


Figure 5 Lignin precursors: (A) R_1 = OCH_3, R_2 = H, (B) R_1 = R_2 = OCH_3 and (C) R_1 = R_2 = H

CONCLUSIONS

The structural difference between hardwood and softwood and wood polymers (cellulose and lignin) extracted from them has been explained by FTIR spectroscopy. Characteristic absorption peaks for cellulose and lignin were identified. The relative variation in the intensities of IR bands in hard and softwood has been explained on the basis of different proportion of constituent polymers present in it. The holocellulose-to-lignin ratio for some of the soft and hardwood species was estimated from the DRIFT spectra measured directly from solid wood. The intensity ratio for two lignin peaks show a higher value of the 1505-to-1600 cm^{-1} ratio for softwood than hardwood. The ratio of intensity of carbonyl absorption (1740 cm^{-1}) to lignin absorption peaks is higher for hardwood than softwoods. Further study on the reaction of wood and its constituent polymers with various organic and inorganic reagents and changes in wood surfaces due to its exposure to varying environmental conditions is in progress.

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