

COMMUNICATION V

FT-IR Spectroscopic Studies on Lignin from Some Tropical Woods and Rattan.

ABSTRAK

Kajian ke atas lignin Klason dari empat jenis kayu keras tropika dan rotan dengan menggunakan spektroskopi FT-infra merah telah dijalankan. Ketahanan dan kekuatan sesuatu jenis kayu berhubung rapat dengan kandungan ligninnya. Terdapat perbezaan pada spektra FT-infra merah di antara lignin-lignin yang dikaji. Kayu yang mudah reput mengandungi lebih kumpulan guaisil di dalam lignin berbanding dengan yang lebih tahan reput.

ABSTRACT

Klason lignin of four different types of tropical hardwoods and rattan was studied using FT-IR spectroscopy. There were observable differences in the FT-IR spectra of the lignin studied. Lignin from the more durable and more resistant wood were found to contain less guaiacyl groups than that from the softer and less resistant wood. The strength and resistance of the wood might be related to its lignin content.

INTRODUCTION

Lignin in wood fibres has been associated with the mechanical strength of the wood and its resistance towards microorganism attack (Higuchi 1981). The elucidation of the structure of lignin has been difficult, giving rise to controversies as to the actual roles played by lignin. Moreover, the structure of lignin has not been completely understood. However, lignins are generally classified into three major groups (Higuchi 1981). They are (i) the gymnosperm lignin which is a dehydrogenated polymer of coniferyl alcohol, (ii) the angiosperm lignin which is a mixed dehydrogenated polymer of coniferyl and sinapyl alcohols and (iii) grass lignin which is composed of a mixed dehydrogenated polymer of coniferyl, sinapyl and p-coumaryl alcohols.

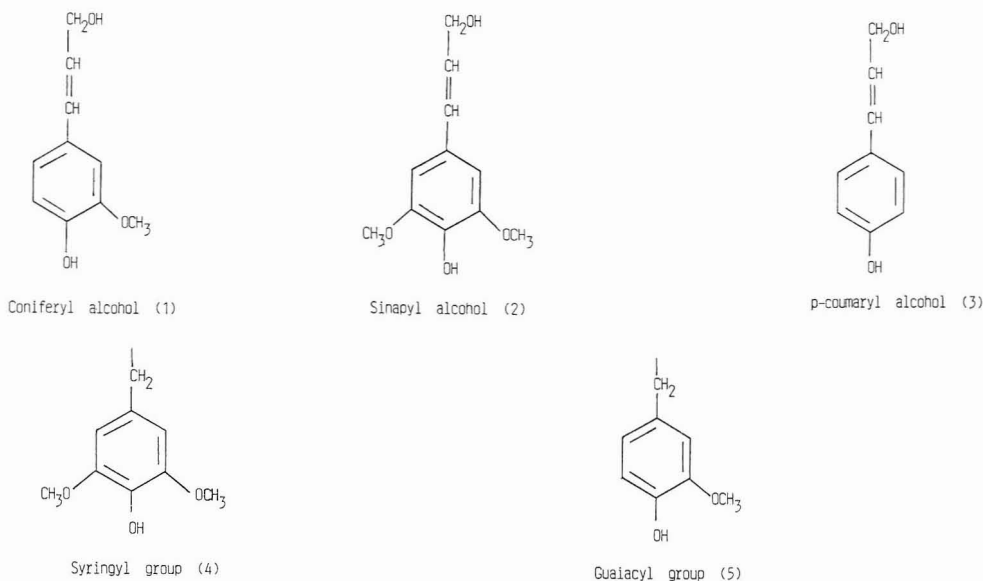
All lignins that have been isolated were found to have undergone a certain amount of structural modification either chemically or physically (Harkin 1969). As lignin is a complex polymer, there is bound to be some structural deformation during extraction.

There has been considerable work on the application of FT-IR spectroscopy in lignin analysis. FT-IR spectroscopy has been used to monitor the degradation of lignin in wheat straw and significant differences were found in the FT-IR spectra of the lignin in the region of 1400 - 1750

cm⁻¹ (Buta *et al.* 1989). The absorption band at 1510 cm⁻¹ has been used as an internal standard for quantitative analysis of lignin content (Roy *et al.* 1987). Pioneering work on this aspect was carried out by Morton and Sparkes in 1967. The deconvolution of FT-IR spectra of lignin has enhanced the fine structures and resolutions making it possible to elucidate the differences between two lignin samples using FT-IR spectroscopy (Faix and Beonhoff 1988).

Belian (*Eusideroxylon zwageri*) which is found only in Borneo is one of the most valuable woods in Sarawak and Sabah. Belian wood is very durable and resistant to microorganism attack. It is commonly used as tiles for roofs, bridges, and supports for pepper vines. The wood is able to withstand weathering for at least ten years without much deterioration. On the other hand, wood from rubber trees (*Hevea brasiliensis*) is non-durable and offers very little resistance to microorganism attack. If these properties of wood are related to its lignin composition, then there should be significant differences between the lignin from wood of the belian and that of the rubber tree.

This research was carried out to study the differences between the lignin from some tropical hardwoods and rattan (*Calamus* sp.). The findings of this project will be useful for developing a method of wood preservation.



MATERIALS AND METHODS

Lignin is known to consist of polymeric substances that differ in composition from one species of plant to another as well as from tree to tree within individual species. Factors affecting this difference are local climatic conditions, soil composition, pH, the nature of the surrounding vegetation (Harkin 1969). Wood samples of belian (*Eusideroxylon zwageri*), selangan batu (*Shorea* sp.) and kapur (*Dryobalanops* sp.) were collected as sawn timber from a sawmill at Bintulu. The species of selangan batu and kapur were not identified. Rattan cuttings were obtained from a furniture shop at Bintulu and the species was not determined. Rubberwood was obtained from the rubber plantation at Universiti Pertanian Malaysia, Kampus Bintulu. In this study, the differences within the individual species were not considered and were assumed to be less significant compared to the variations observed between the different types of plant species.

Isolation of Lignin

Lignin was isolated using the established Klason method (Ritter *et al.* 1932). Sawdust from the wood samples was ground to pass a 40-mesh sieve and dried in an oven at 50°C for 24 h. One gram of the dried sample was weighed into a cellulose extraction thimble. The thimble was placed in a Soxhlet extraction apparatus and the wood was extracted with 95% ethanol-benzene, 1 : 2 (v/v), for 8 h. The solvent was removed and air dried in a fume-cupboard. The wood was then digested in a beaker with hot distilled water (400 ml) at about 100°C for 3 h, filtered and washed with hot

distilled water (100 ml), then rinsed with ethanol (50 ml) before being air dried.

The partially digested wood was placed in a small beaker and 72% sulphuric acid (15ml) was added slowly with stirring. The mixture was allowed to stand for 2 h in a water bath at 30°C with frequent stirring. The mixture was then transferred into a 1 L flask and 560 ml of water was added to dilute the sulphuric acid to a concentration of 3%. The mixture was boiled under reflux for 4 h. The insoluble lignin was allowed to settle before being filtered into a pre-weighed filtering crucible (porosity no.3), and washed free of acid with hot distilled water (500 ml). The crucible and its contents were dried in an oven at 105°C for 12 h, cooled in a desiccator and weighed. The drying and weighing were repeated until the weight was constant.

The lignin content was calculated as a percentage of the oven-dry unextracted wood. This lignin is also known as Klason lignin. Analyses were carried out in 5 replicates for type of wood sample.

FT-IR Analysis of Lignin

Lignin samples were made into KBr discs. Approximately 2 mg of lignins were ground with 200 mg of KBr. The FT-IR spectra were taken using Perkin Elmer 1600 FT-IR Spectrometer.

Analysis of lignin in the wood was carried out using the multiple internal reflectance technique (MIR). Pieces of wood to be analysed were cut into thin strips ca. 35 x 15 mm and a thickness of approximately 1 mm. The MIR technique enabled the studies on untreated lignin to be carried out.

RESULTS AND DISCUSSION

Klason lignin contents of four different hardwoods and a species of rattan were determined and are tabulated in Table 1. Belian, selangan batu and kapur are among the tropical hardwoods that are relatively durable and have high resistance towards decay with belian being the most durable and kapur the least durable of the three (Jantan and Tam 1987). The Klason lignin contents of these three types of wood were very similar with belian having a slightly higher percentage of lignin than selangan batu and kapur. Rubberwood, which is known to decay easily, was found to contain only 18% lignin. This result indicates that a possible relationship between the lignin content of a wood and its strength might exist.

FT-IR spectra of the Klason lignins were taken for each of the wood and rattan samples (Fig. 1 a, b, c). The spectra of the lignins in the region from 1800 cm⁻¹ to 4000 cm⁻¹ did not provide much information other than broad hydroxyl and aliphatic C-H absorptions. This observation was also noted by others (Buta *et al.* 1989; Roy *et al.* 1987). This region of the FT-IR spectra will not be considered further. The aromatic absorption re-

TABLE 1
Percentages of Klason lignin in some tropical woods and rattan.

Type of wood	% Lignin mean \pm s.dev.
Belian (<i>Eusideroxylon zwageri</i>)	32.5 \pm 0.42
Selangan batu (<i>Shorea</i> sp.)	31.2 \pm 0.29
Kapur (<i>Dryobalanops</i> sp.)	29.6 \pm 0.92
Rubber (<i>Hevea brasiliensis</i>)	18.2 \pm 0.16
Rattan (<i>Calamus</i> sp.)	26.3 \pm 1.68

gion of the spectra contains bands assigned to lignin (Hergert 1971; Roy *et al.* 1987). Band assignment of the spectra between regions 1000 and 1800 cm⁻¹ is shown in Table 2. The FT-IR spectra of Klason lignin from the samples show a shift in the absorption bands between 1612 and 1500 cm⁻¹. Table 3 shows the corresponding band shifts in the five samples studied.

The spectra of wood strips using multiple internal reflectance (MIR) technique are shown in Figure 2 a, b, c. The MIR spectra of the various

TABLE 2
FT-IR absorption bands for Klason lignin.

Wave number (cm ⁻¹)	Significance of bands.
1700 - 1744	C=O in acetyl, aliphatic ester or aldehyde groups.
1600 - 1615	aromatic skeletal vibrations.
1505 - 1515	aromatic skeletal vibrations.
1455 - 1490	C-H deformation asymmetric.
1420 - 1430	aromatic skeletal vibrations.
1320 - 1330	syringyl ring (4) breathing with C-O stretching.
1270 - 1280	guaiacyl ring (5) breathing with C-O stretching.
1220	syringyl ring (4) breathing.
1160	aromatic C-H in plane deformation, guaiacyl type (5).
1120	aromatic C-H plane deformation of syringyl type (4).
1030	aromatic C-H in plane deformation guaiacyl type (5) and C-O deformation of primary alcohol.

woods and rattan show similar absorption bands as that of the Klason lignin. In addition to the absorption bands of lignin, there are extra bands observed. These bands, (1010 cm⁻¹), are most likely to be due to the presence of cellulose components of the wood. In the MIR spectra, there are two absorption bands that showed sig-

TABLE 3
FT-IR absorption band shifts between 1612 and 1400 cm⁻¹.

Wood	Absorption Bands (cm ⁻¹)			
Belian	1612*	1510*	1457	-
Selangan batu	1609	1498	1458	1424
Kapur	1609	1499	1459	1424
Rubberwood	1604*	1499	1458	shoulder
Rattan	1608	1500	1462*	1425

* band shifts of significant difference

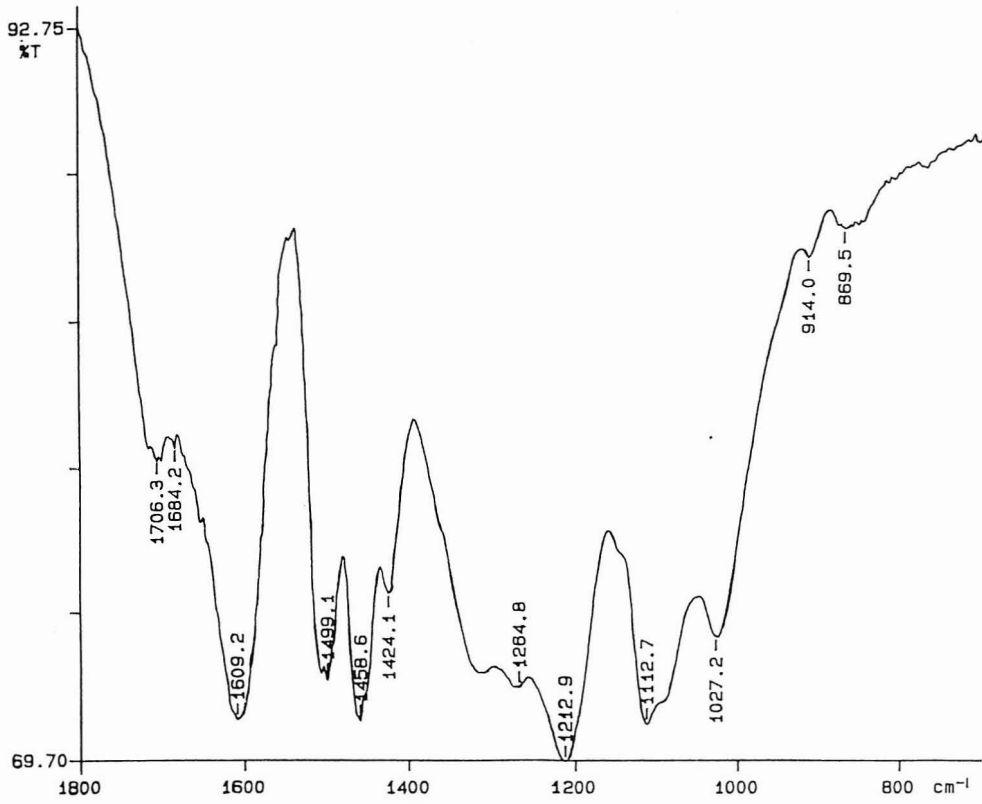


Fig. 1 (a) FT-IR spectra of lignin from kapur obtained using KBr pellet cell.

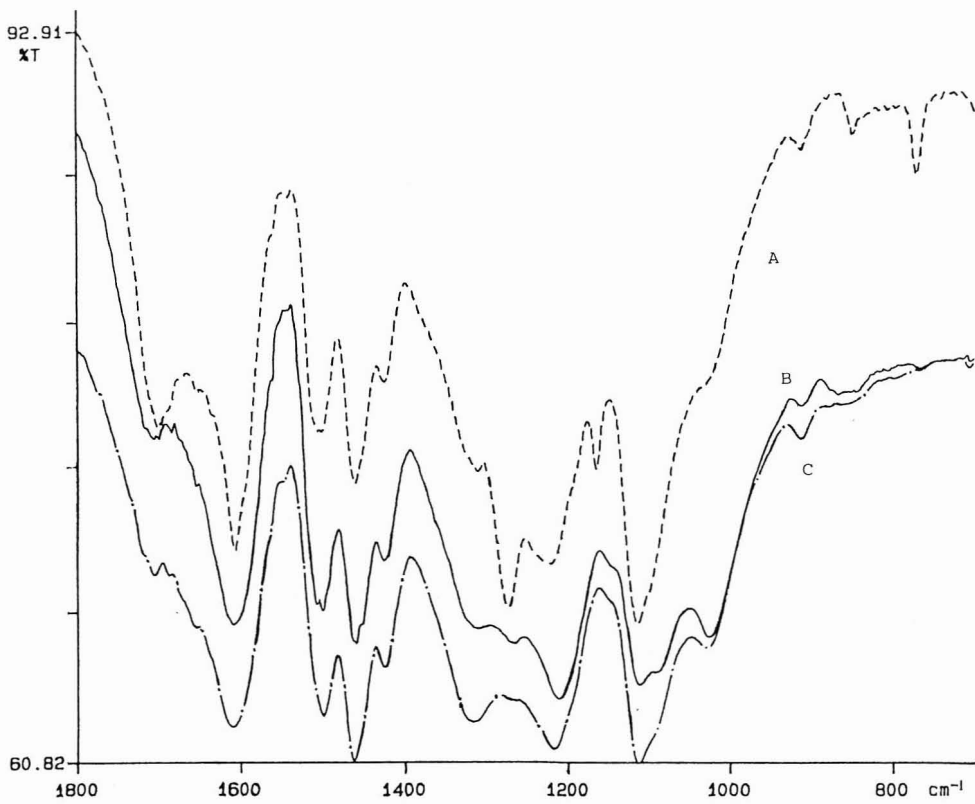




Fig. 1(b) and 1(c) Comparison FT-IR spectra of lignin obtained using the KBr pellet cell. (A) - Rattan; (B) Kapur; (C) - Rubberwood; (D) - Selangan Batu and (E) - Belian.

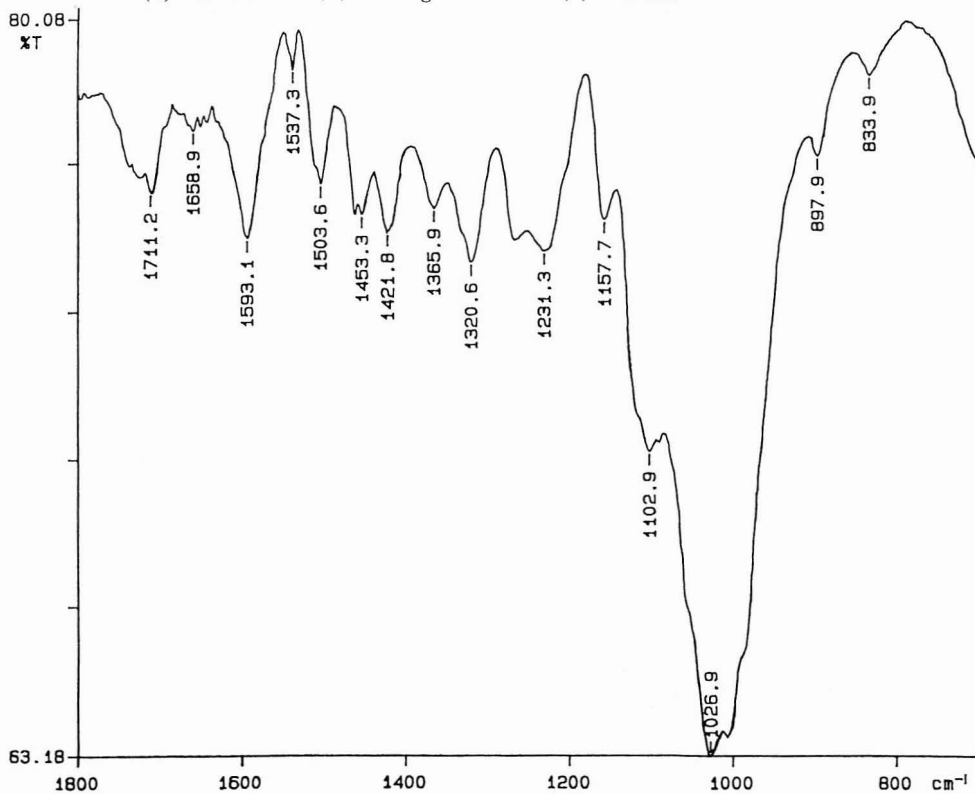


Fig. 2 (a) : FT-IR spectrum of Selangan Batu wood strip obtained using the MIR technique.

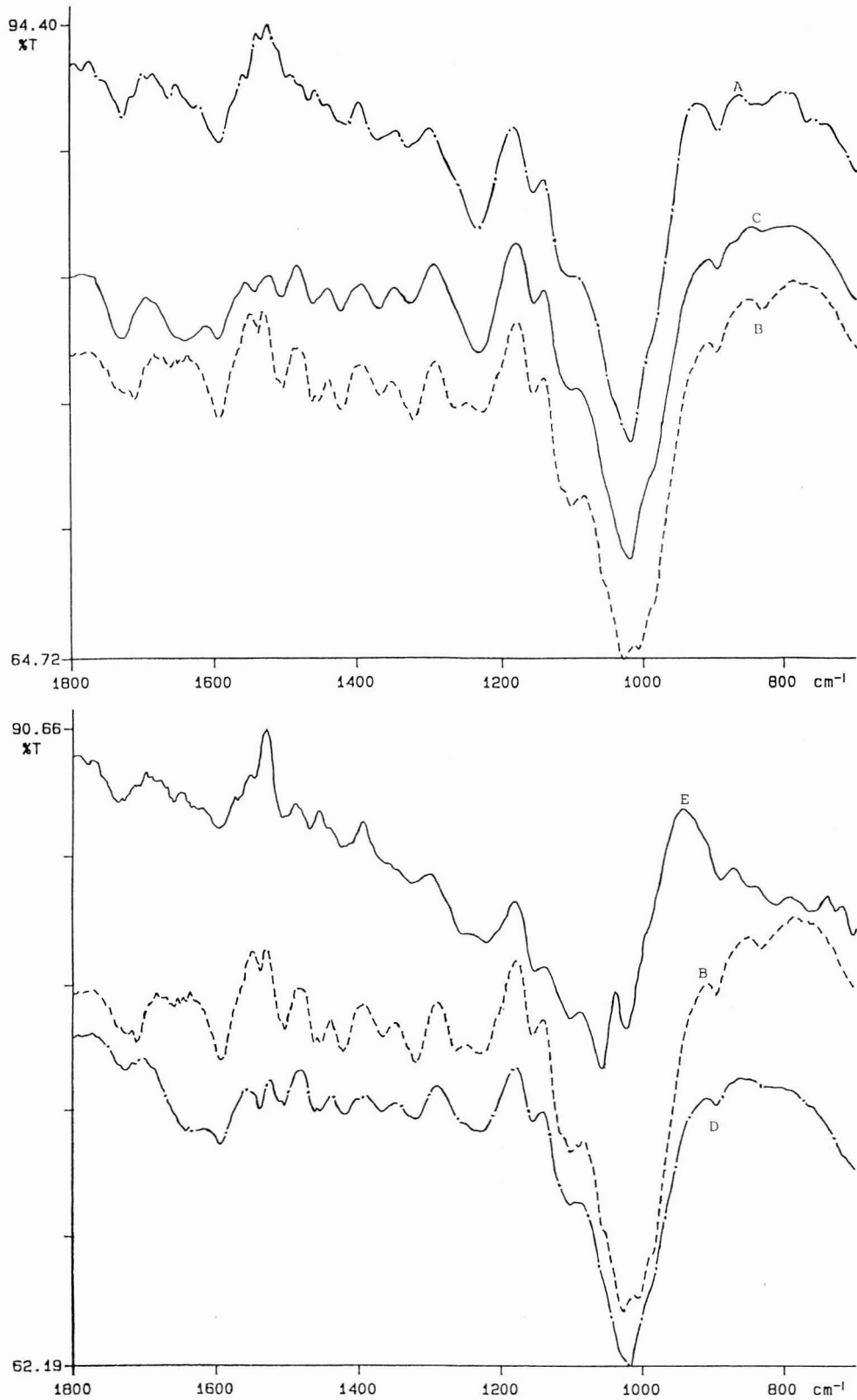


Fig. 2 (b) and 2 (c) : Comparison FT-IR spectra of wood strips obtained using the MIR technique. (A) - Rattan; (B) - Selangan Batu; (C) - Rubberwood; (D) - Kapur and (E) - Belian.

nificant differences among the various wood samples. The first was the absorption band of wave number between 1500 and 1515 cm^{-1} . Belian wood showed a relatively strong absorption at 1510 cm^{-1} while the wood showed a doublet at 1503 and 1512 cm^{-1} . This absorption band is assigned to the aromatic skeletal vibration. This indicates that belian has almost a single type of aromatic ring while the other wood contains at least two types with a more or less similar concentration. The second absorption band is at the region between 1000 and 1030 cm^{-1} . Belian and selangan batu showed a single absorption band at 1013 cm^{-1} while kapur showed a wider band which was unresolved at 1007 cm^{-1} . Rubberwood showed distinctly two equally strong bands at 1013 and 1030 cm^{-1} , while rattan also showed the two similar bands, with the band at 1030 cm^{-1} being much stronger than that of 1013 cm^{-1} . The absorption band at 1030 cm^{-1} is assigned to the aromatic C-H in plane deformation of the guaiacyl type (5). This indicates that lignins in rubberwood and rattan contain a higher proportion of guaiacyl group than those from belian, selangan batu and kapur.

CONCLUSION

This study has shown that there are detectable differences in the FT-IR spectra of the extracted lignins as well as in the untreated wood strips of various types of wood. Further studies should be carried out to elucidate the specific differences between the lignins of various woods. Separation of lignin components will be necessary to characterise the exact nature of each type of lignin in plants. Further work is being done in our laboratory.

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