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Chemical Characteristics of Rubberwood Damaged by *Sinoxylon conigern* Gerstäcker

By

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Summary: Chemical characteristics of rubberwood damaged by a wood boring insect were investigated in comparison with those of normal wood. Ash content was higher in damaged than in sound wood. Damaged wood showed lower extractive content with hot water and with 1% sodium hydroxide solution than normal wood. Starch content was also lower in damaged than in normal wood. However, there was little difference in holocellulose and lignin content. The molar ratio of syringyl/guaiacyl unit in milled wood lignin was slightly lower in damaged wood than in normal wood. Damaged wood seemed to have lost mainly the soluble polysaccharide fraction due to attack by the wood boring insect.

1 Introduction

With the recent increase in the shortage of logs in tropical areas, rubberwood is now being utilized for the manufacture of furniture and other wood products. The rubber tree yields useful timber even after its economic rotation age (20-25 years) is reached. Harvesting and transporting the logs is easy since rubberwood is planted on a large scale in flatland plantation. And its availability is assured through systematic replanting. However, it is susceptible to insect and fungal attack. Among the harmful insects, *Sinoxylon conigern* Gerstäcker bores into a rubberwood and converts it into fine wood meal. Sound rubberwood has a light cream-colored appearance while damaged wood has a slightly dark-brownish color. There must be a chemical difference between these. Although there are many reports on latex from rubber trees, the chemical characteristics of rubberwood itself have not been fully elucidated yet. In this report, chemical characteristics of rubberwood damaged by a wood boring insect were investigated in comparison with those of normal wood.

2 Methods

2.1 Plant material

Rubberwood samples were obtained from 21-year-old trees (*Heave brasiliensis* Muell-Arg.) planted at the Rubber Research Institute of Malaysia experimental station in Sungai Buloh in Malaysia. Damaged wood had many holes in its xylem after being attacked by *Sinoxylon conigern* Gerstäcker and this porous fraction was easily crushed into fine powder (Photo 1). Since the damaged wood fraction contained many insect bodies, the wood meal was screened to remove them before sample preparation.

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Photo. 1. Rubberwood damaged by *Sinoxylon conigern* Gerstäcker

2.2 Chemical analyses of rubberwood

Chemical analyses of rubberwood were carried out according to the JIS method.

2.3 Determination of starch content

Wood meal which had been passed through 200 mesh screen was prepared for the determination.

Starch content was determined as described by HUMPHREYS (1961).

2.4 Determination of protein content

Protein content was determined by alkaline hydrolysis followed by the KCN-ninhydrin method (FUKUDA, 1976).

2.5 Preparation of milled wood lignin (MWL)

Extractive free wood meal was milled for 100 hours using a vibratory ball mill. The MWL was extracted and purified according to the standard method of BJÖRKMAN (1956).

2.6 Measurement of UV and IR spectra of lignin

UV and IR spectra of lignin were measured in a solvent of dioxane-water (9 : 1) using a Hitachi U-3210 spectrophotometer and as KBr discs using a JASCO FT/IR-3 spectrophotometer respectively.

2.7 Alkaline nitrobenzene oxidation

Nitrobenzene (0.24 m*l*) and 2 N potassium hydroxide (4 m*l*) were added to the lignin sample (10 mg) in a stainless micro tube and the mixture was heated for 2 hours at 160°C with vigorous shaking. After cooling, the solution was then extracted with ethyl ether to remove the residual nitrobenzene. Then the solution was acidified with hydrochloric acid and extracted again with ethyl ether. The extract was dried over anhydrous sodium

sulfate and evaporated to dryness. The resultant phenols were converted to trimethylsilyl (TMS) derivatives and analysed by gas chromatograph (GC) using acetovanillon as an internal standard. GC was performed on Shimazu GC-14 A with a capillary column HiCAP-CBP1.

2. 8 Sugar analysis

Sugar composition of the rubberwood was determined by HPLC using the spent liquor from Klason lignin preparation. Sugar composition of hot water solubles, 1% NaOH solubles and MWL was determined by HPLC with the hydrolysate by 2 M trifluoroacetic acid at 120° C for 1 hour. HPLC was performed on Shimazu LC-3 A with column ISA 07/S 2504.

2. 9 Gel permeation chromatograph (GPC) analysis of MWL

Approximately 1 mg acetylated MWL was dissolved in 10 m*l* terahydrofuran and 2 m*l* of the solution was applied to TOSOH HLC-8020.

2. 10 ^{13}C NMR spectroscopy

Approximately 100 mg of samples were dissolved in 0.5 m*l* DMSO-d_6 and the spectra were obtained on JEOL JNM GXS-400.

2. 11 Analysis of functional groups in MWL

The non-conjugated phenolic hydroxyl group content and α-carbonyl group content in MWL were determined by the $\Delta\varepsilon i$ method (GOLDSCHMID, 1952) and by the $\Delta\varepsilon r$ method (MARTON, 1961), respectively.

3 Results and Discussion

Table 1 shows the amounts of extractives in normal and damaged wood. There was no difference in alcohol-benzene solubles but in hot water solubles and in 1% NaOH solubles, significant differences were observed. The low amounts of these fractions in damaged wood may be ascribed to the decrease of soluble polysaccharides which were consumed by the wood boring insect. In order to investigate the chemical changes of these fractions, acid hydrolysis of extractives was carried out and the resultant sugar was analyzed. In this case, successive extraction with hot water and 1% NaOH solution were applied. Fig. 1 shows the HPLC chromatogram of sugar composition in hot water soluble fractions. The main product was glucose in both woods. But the amount of glucose from damaged wood was 3% lower than that from normal wood (Table 2). In 1 % NaOH soluble fractions xylose and glucose were the main products (Fig. 2). The amount of xylose was almost the same in both woods while glucose content was also 0.6 % lower in damaged wood than in normal wood (Table 3). From these results it is clear that the boring insect has eaten glucose polymers, such as starch.

Table 4 shows the results of chemical analyses of both woods. Ash content was quite different between normal wood and damaged wood. Damaged wood may contain secretions such as the excrement of the insect. There were little differences in holocellulose and lignin content. Starch content was higher in normal wood than in damaged wood. PLANK (1952) investigated powder-post beetle infestation in freshly harvested bamboo and found that starch was mainly consumed. In the present case *Sinoxylon conigern* Gerstäcker also seemed to have eaten starch in damaged wood.

Table 1. Soluble fractions of rubberwood (%)

	Alcohol-benzene solubles	Hot water solubles	1% NaOH solubles
Normal wood	6.5	14.1	27.5
Damaged wood	6.5	9.5	19.5

Table 2. Sugar composition of hot water solubles (%)

	Glucose	Xylose	Mannose	Galactose
Normal wood	4.1	+	+	+
Damaged wood	1.1	+	+	+

(%) based on original wood meal

Table 3. Sugar composition of 1% NaOH solubles (%)

	Glucose	Xylose	Galactose
Normal wood	0.9	1.9	+
Damaged wood	0.3	1.8	+

Successive extraction
(%) based on original wood meal

Table 4. Chemical analyses of rubberwood (%)

	Ash	Holocellulose	Klason lignin(Acid soluble)	Starch	Protein
Normal wood	0.2	79.0	20.1(1.6)	6.3	0.8
Damaged wood	0.9	79.5	21.9(1.4)	3.2	0.6

However, a low percent of starch remained in damaged wood (Table 4). This starch may be on insoluble one which can be solubilized after perchloric acid treatment in the quantitative determination. Latex from rubberwood contains about 0.9% protein (ARCHER, 1963). Protein content in present rubberwoods showed 0.8% and 0.6%, where damaged wood was also lower than normal wood.

Fig. 3 shows sugar composition of rubberwood xylems. The main components were glucose and xylose. The ratio of glucose/xylose was slightly higher in normal than in damaged wood, probably because a part of the glucose polymer was consumed by the insect. MWL from damaged wood and normal wood contained 2.4% and 3.5% polysaccharide respectively. Fig. 4 shows sugar composition of MWLs. In MWLs, the main sugar was xylose and glucose but the ratio was opposite to that of the xylem.

Functional groups in milled wood lignin (MWL) are shown in Table 5. The content of the non-conjugated phenolic hydroxyl group and the α-carbonyl group of MWL from damaged wood was slightly higher than that of normal wood showing that the lignin was slightly modified. Lignin in damaged wood might be oxidized after the insect

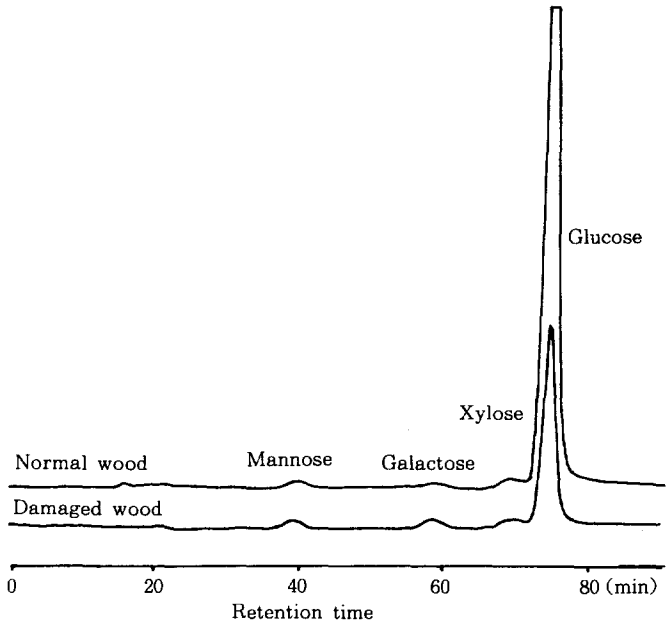

Fig. 1. HPLC chromatogram of sugar analysis of hot water solubles

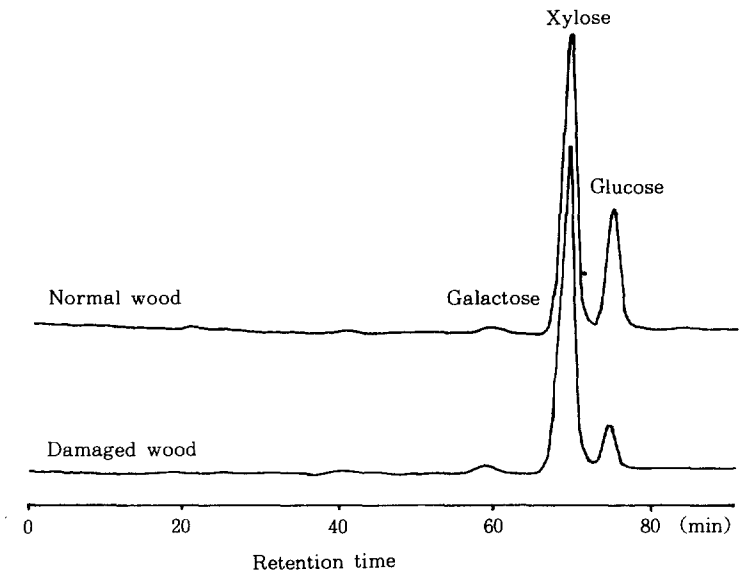

Fig. 2. HPLC chromatogram of sugar analysis of 1% NaOH solubles

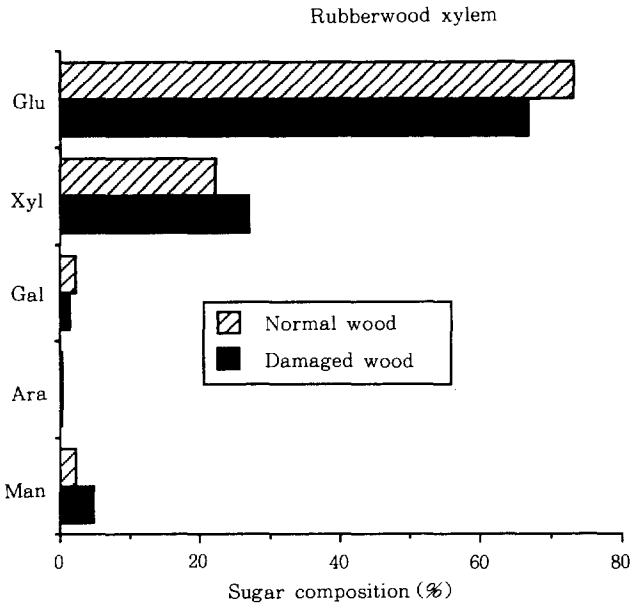

Fig. 3. Sugar composition of rubberwood samples

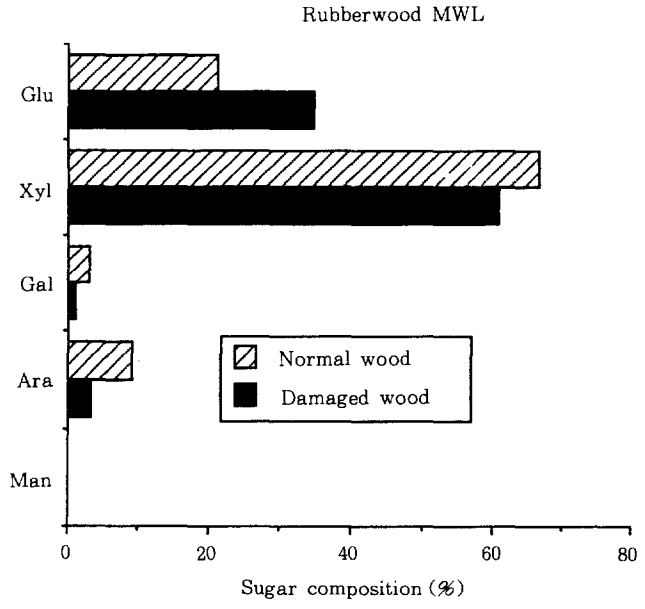

Fig. 4. Sugar composition of MWLs

attack. Table 6 shows the results of alkaline nitrobenzene oxidation of MWLs. The ratio of the syringyl unit/guaiacyl unit was lower in damaged wood MWL than in normal wood MWL, as was often observed for decayed wood. But in this case, 1% NaOH solubles of damaged rubberwood were extremely low compared to those of normal wood (Table 1). This was quite different from decayed wood, where 1% NaOH solubles usually increase. The lower content of the syringyl unit may be because of degradation by air oxidation after pulverization due to insect attack, since the syringyl unit is known to be more susceptible to autooxidation than the guaiacyl unit.

IR spectra of MWLs are shown in Fig. 5. Both spectra were almost the same except inclination from 1 505 cm^{-1} to 1 460 cm^{-1}. KAWAMURA (1964) investigated IR spectra of MWLs from various plants and classified them by the absorption intensity at 1 505 cm^{-1} and 1 460 cm^{-1} as softwood type (1 505 cm^{-1}>1 460 cm^{-1}), hardwood type (1 505 cm^{-1}<1 460 cm^{-1}) and tropical hardwood type (1 505 cm^{-1}≧1 460 cm^{-1}). According to this method of classification, normal rubberwood lignin was hardwood type and damaged rubberwood lignin was softwood or tropical hardwood type. This was in good accordance with the result of nitrobenzene oxidation in which the ratio of the syringyl unit/guaiacyl unit is lower in damaged wood lignin than in normal wood lignin. Fig. 6 shows the results of gel permeation chromatography of MWLs. The molecular weight distribution curve of MWLs showed two peaks. However, there was no significant difference between damaged wood lignin and normal wood lignin.

In the NMR spectra there was no significant difference between the damaged wood lignin spectrum and the normal one (Fig. 7). Both spectra showed some peaks attributable to polysaccharides. Three signals 170 ppm, 63 ppm and 20 ppm can be assigned to hemicellulose in MWLs. The spectrum from damaged wood MWL had a small peak at 195 ppm which can be assigned to α-carbonyl or γ-carbon in cinnamaldehyde. This peak was not clear in the normal wood MWL spectrum. This also suggested that

Table 5. Functional groups in MWLs (%)

	Phenolic hydroxyl group	α-Carbonyl group
Normal wood	1.61	0.22
Damaged wood	1.97	0.24

Table 6. Alkaline nitrobenzene oxidation products of MWLs

	Normal wood	Damaged wood
p-Hydroxybenzaldehyde	0.24	0.24
Vanillin	1.00	1.00
Syringaldehyde	1.57	1.25
Yield (%)	29.5	29.4

The values are expressed as molar ratios based on vanillin

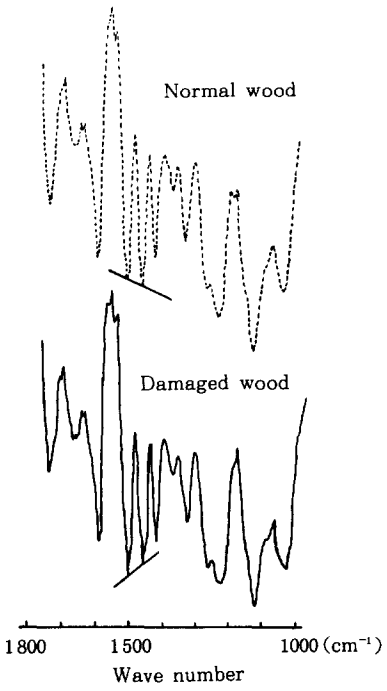

Fig. 5. IR spectra of MWLs

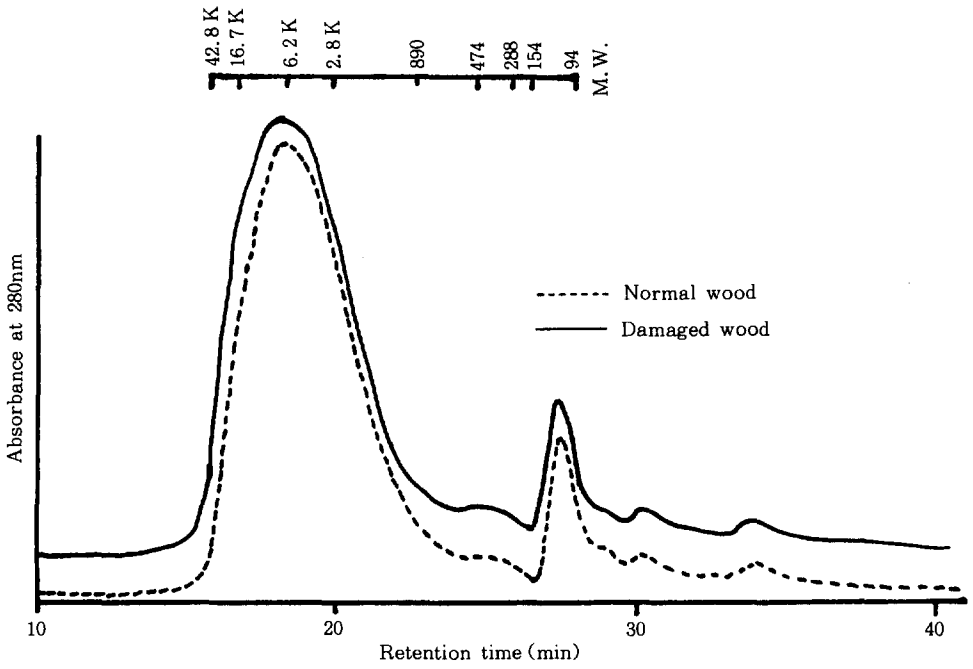

Fig. 6. GPC chromatogram of MWLs

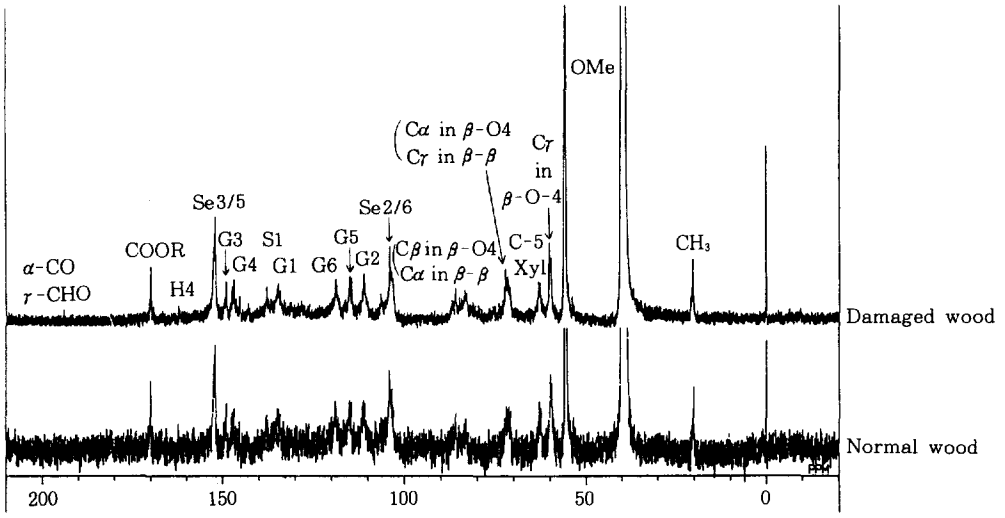

Fig. 7. ^{13}C-NMR spectra of MWLs

Notes : G = guaiacyl, S = syringyl, H = p-hydroxyphenyl, Xyl = xylose, e = etherified

damaged wood lignin was slightly oxidized compared to normal wood lignin. Tropical hardwoods often contain phenolic acids in their lignins (NAKANO, 1958). Judging from NMR spectra, however, rubberwood lignin seems to contain no such phenolic acids.

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虫害パラゴム材の化学的特性

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摘　　要

21年生マレーシア産パラゴム材の化学成分の特性を，正常材と虫害を受けて木粉化したものとを比較しながら調べた。虫害材は熱水抽出物，1% 水酸化ナトリウム溶液可溶部が正常材よりも少なく，糖組成はグルコースの割合が，ほかの単糖類に比べて少なかった。リグニン量やホロセルロースの量にはほとんど変化がみられなかったが，灰分は虫害材の方が数倍多く含まれていた。また，虫害材は正常材に比べて澱粉含有量が減少していた。このことから，虫害材は可溶性の糖類を主として食害されたものと思われる。リグニンの構成単位の比較では，虫害材リグニンはシリンギル核が正常材リグニンよりも少ない値を示した。

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