Characterization of Merbau Wood Extract Used as an Adhesive in Glued Laminated Lumber

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Abstract

Polyphenolic chemical compounds were extracted from merbau (*Intsia* spp.) wood with an aqueous medium at a 1:4 ratio (wt/wt) heated to 80°C for 3 hours. The extracted compounds were characterized by matrix assisted laser desorption ionization time of flight spectrometry and included oligomers with up to six repeating flavonoid units, with resorcinol being the dominant compound paired with a minor amount of catechin units. The extract had a Stiasny number of 92.4 percent. The extract was combined with formaldehyde to produce a resin that was used to manufacture five-layer glued laminated lumber using four wood species, namely, pangsor (*Ficus callosa*), mindi (*Melia azedarach*), pine (*Pinus merkusii*), and mangium (*Acacia mangium*). The modulus of rupture and shear strength of mangium glued laminated lumber met the requirements of the Japanese standard (''Japanese Agricultural Standard for Structural Glued Laminated Timber,'' 2003), and all products had a low formaldehyde emission.

Within the wood-processing industry in Indonesia, several types of synthetic adhesives are currently being used. These adhesives include thermoplastic adhesives, such as polyvinyl acetate, and thermosetting adhesives, such as urea-formaldehyde, melamine-urea-formaldehyde, and phenol-formaldehyde resins. Thermoplastic adhesives are widely used in the furniture industry, while thermosetting adhesives are widely used in manufacturing plywood and particle board. Other synthetic adhesives are cold setting and include resorcinol-formaldehyde, resorcinol-phenol-formaldehyde, and phenol-resorcinol-formaldehyde. These adhesives are particularly used in the manufacture of laminated timber (Santoso 2011), and they are still largely imported.

Pizzi and Roux (1978a) developed cold-setting adhesive made from resorcinol, wattle flavonoid condensate, and trichloroacetic acid mixed with para formaldehyde, and the resulting shear strength met the British Standard BS 1204 part 2 for synthetic resin adhesive (British Standards Institution 1979). Furthermore, Pizzi and Roux (1978b) set up tannin-based weather- and boil-proof cold- and fast-setting adhesives for wood. The adhesives were made from commercial wettle extract mixed with formalin, methanol, and sodium hydroxide, and the resulting adhesives satisfy the requirements of international standard specifications and are comparable to those of phenol-resorcinol-formaldehyde cold-setting resin.

Resorcinol derived from aqueous extracts of merbau (*Intsia* spp.) sawdust may serve as a possible phenol-based resin with weather- and boil-proof qualities from a renewable resource. Santoso et al. (2014) have reported that extractives from merbau sawdust could be used in phenolic-based resins if they were reacted with resorcinol and formaldehyde under basic conditions (pH 10 to 11) and if the weight mixture of merbau-resorcinol-formaldehyde (MRF) were 100:5:10, with a maximum of 10 percent tapioca extender added to the liquid resin MRF (by weight).

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The resin could be used to manufacture glued laminated lumber (glulam) and composites or laminated bamboo flooring (Santoso et al. 2013, 2014).

The goal of the current study was to characterize the chemical compounds in merbau wood liquid extract by matrix assisted laser desorption ionization time of flight (MALDI-TOF) spectrometry. The merbau wood liquid extract was then copolymerized with resorcinol and formaldehyde to create an adhesive for the manufacture of glulam. Physical and mechanical properties, shear strength, and formaldehyde emission of the resultant products were then evaluated.

Methods

Adhesive preparation

Manufacture of the adhesive was based on the explanation of Santoso et al. (2014) that air-dried merbau wood sawdust was mixed with water at a 1:4 ratio (wt/wt) and heated at 80°C for 3 hours. The mixture was filtered to separate the liquid extract from the sawdust, and the extraction process was repeated twice, with a final ovendried extractive yield of 6.5 percent (wt/wt) based on the original ovendried weight of the sawdust. The extract was mixed with resorcinol and formaldehyde and called MRF. MRF consisted of two components: resin (merbau wood liquid extract, resorcinol technic, and 40% NaOH) and formaldehyde (37%) as a cross-linker or curing agent. Merbau liquid extract (M) was mixed with resorcinol (R) at weight ratios of 100:5, respectively, and NaOH was added to adjust the pH to 10 to 11. The mixture was added to formaldehyde (F) at 10 percent M (wt/wt) and mixed until homogenous at room temperature, which was followed by a 1-hour conditioning period. The solid content of MRF was 29.5 percent with pH 11.

Reactivity of polyphenolic compounds in the liquid extract with formaldehyde (Stiasny precipitation number) was determined as follows. Twenty grams of dehydrated extract was weighed into a beaker containing 40 mL of water. The solution was adjusted to pH 7 by adding sodium hydroxide pellets. One hundred milliliters of 37 percent formaldehyde and 15 mL of concentrated HCl were added, and the mixture was heated at 90°C for 85 minutes. The resulting solution was vacuum filtered, and the solid residue was washed with hot water, dehydrated, and dried at a temperature of 105°C in an oven until reaching a constant weight. The Stiasny number was determined as follows:

$$\text{Stiasny precipitation number} = \frac{\text{dry weight of solid residue}}{\text{dry weight of extract}} \times 100$$

The total phenolic content present in the extract was quantitatively determined by colorimetric assay using the Prussian blue reagent (Akoto and Brefoh 2014). The MRF resin was produced according to Santoso et al. (2014) by copolymerizing the liquid extract with formaldehyde and resorcinol in alkaline conditions to yield 1,3-benzenediol, 4,5-dimethyl-resorcinol.

Glulam manufacture and testing

The sample specimens were two types of five-layer boards, namely, cross-laminated timber (CLT) and glulam. The CLT was prepared with cross-band laminas that were perpendicular to the fiber direction of the face, core, and back laminas (Fig. 1), and for the glulam all laminas were arranged parallel to the fiber direction. Each board was manufactured from a single wood species—pangsor (*Ficus callosa*), mindi (*Melia azedarach*), pine (*Pinus merkusii*), or mangium (*Acacia mangium*)—and was 70 mm thick, 150 mm wide, and 980 mm long. Each board type was replicated five times for each wood species.

The adhesive gluemix was spread at a rate of 150 g/cm^2, and the laminas were cold pressed for approximately 3 hours at room temperature, followed by conditioning for 7 days. The boards were tested for moisture content, density, shear strength, delamination, modulus of rupture (MOR), modulus of elasticity (MOE), and formaldehyde emission based on the Japanese Agricultural Standard 234 (JAS 2003).

MALDI-TOF analysis

Samples of merbau wood liquid extract were dissolved in water-acetone for analysis (Merck, supplied by VWR, France; 4 mg/mL, 50/50 volume). The solutions were mixed with 2,5-dihydroxy benzoic acid (10 mg/mL in acetone; Laser Bio Labs, France) as the matrix solution, which facilitated the deposition of a sample in the instrument. Calibration was done with red phosphorous (Laser Bio Labs). To enhance ion formation, a concentrated solution of sodium chloride (10 mg/mL in distilled water; Carlo Erba Reactifs [SDS], France) was added to the matrix. The resultant solution contained three parts of the matrix solution, three parts of the sample solution, and one part of the NaCl solution, and 0.5 to 1 liter of it was placed on the MALDI target. The dry droplet sample preparation method was used (Hoong et al. 2010). After evaporation of the solvent, the MALDI target was placed in the spectrometer. The MALDI-TOF spectra were recorded on a Axima Performance instrument (Shimadzu Scientific Instruments, Manchester, UK). The irradiation source was a pulsed nitrogen laser with 3-ns intervals at a wavelength of 337 nm. The measurements were made under the following conditions: polarity, positive; flight path, linear; mass, high (20-kV accelerating voltage), and 100 to 150 pulses.

To obtain the molecular weight of the chemical species of each peak, 23 Da (the molecular weight of Na^+ from the NaCl in the matrix and attached to the oligomers) must be subtracted from each peak value in the resulting positive mode spectrum.

Measurement of formaldehyde emission

Formaldehyde emissions from the laminated lumber boards were determined using the acetyl acetone method (Nash reagent) at a wavelength of 412 nm (Roffael 1993) according to the flask method of the European Standard EN 717-3 (European Committee for Standardization [CEN] 1996), and thus the following procedure. A test sample of 25 by 25 by 10 mm was hung by string inside a 500-mL bottle containing 50 mL of distilled water about 1 cm above the water level. Another bottle containing 50 mL of distilled water was used as a control. The bottles were placed in a 40°C oven for 24 hours, and the sample was removed from the bottle. The bottles were put in the room for 30 minutes to increase formaldehyde emission captured, and the water was poured into a volumetric flask. The test setup is illustrated in Figure 2.

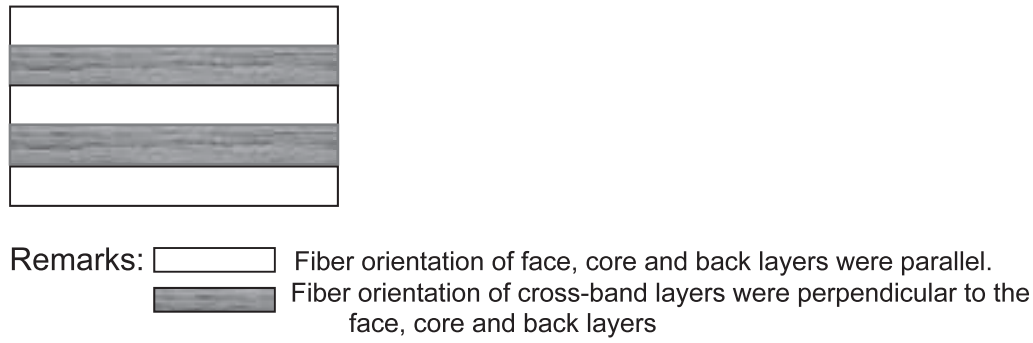

Figure 1.—Laminated beam cross section of five layers.

We next evaluated the amount of formaldehyde emitted by the samples in the water. From a formaldehyde standard solution of 3 mg/liter, we pipetted 0, 5, 10, 20, 50, and 100 mL into six 100-mL bottles, respectively, and then diluted each by adding water up to the 100-mL line. The bottles contained concentrations of 0, 0.15, 0.3, 0.6, 1.5, and 3 mg/liter formaldehyde, respectively. We pipetted 25 mL of sample solution into an Erlenmeyer flask (100 mL) with a stopper, and put 25 mL of acetyl acetone–ammonium acetate into the Erlenmeyer flask and mixed it until homogeneous. The solution was heated for 10 minutes in a water bath at 65°C and then cooled to room temperature. The same procedure was used for the standard solutions, and both solutions were evaluated with a spectrophotometer at the 412-nm wavelength.

Data analysis

To evaluate the effect of product types (two levels) and wood species (four levels) on the boards properties, a completely randomized factorial two by four design was used to analyze the data. The first factor was the product type (namely, CLT and glulam), and the second factor was wood species (namely, pangsor, mindi, pine, and mangium).

Results and Discussion

MALDI-TOF analysis of merbau wood liquid extract

Figure 3 shows a representative MALDI-TOF spectrum of merbau wood extract with a molecular weight ranging from 100 to 600 Da. The spectrum shows that merbau wood extracts contain flavonoid oligomers up to six repeating units, based on the largest oligomer components detected in the sample, which had a peak at 445 Da. The MALDI-TOF mass spectra showed clear repetitive patterns of peaks that allowed identification of specific oligomer series present in the merbau wood extract sample. The major peak-to-peak mass increments were 133, 227, 297, 315 to 319, 429, and 445 Da, which corresponded to structures (I) resorcinol, (II) stilbene type, (III) fisetinidin, (IV) catechin, (V) fisetinidin-resorcinol, and (VI) catechin-resorcinol repeating units, respectively (Table 1).

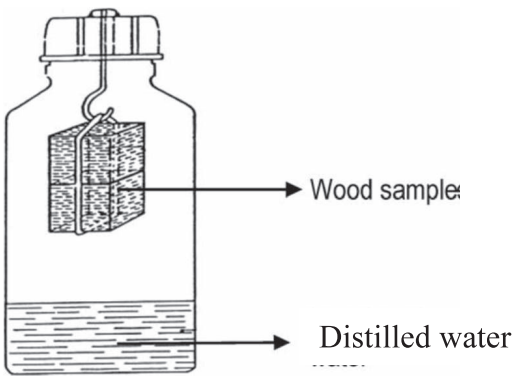

Figure 2.—Scheme of the formaldehyde emission test.

Table 1 shows the possible combinations of different repeating units and the degree of polymerization corresponding to each. These values were obtained based on the *m*/*z* value of flavonoid structures I to VI. The dominant series of peaks at 133, 297, 319, and 445 Da for flavonoid extracts were monomers, dimers, trimers, and tetramers, respectively. The main repeating unit in each oligomer group was identified as those composed of catechin (IV and VI). Chemical compounds of 155 Da or 2-methyl-5-hydroxybenzofuran + Na^+, 227 Da or stilbene type, 297 Da or fisetinidin + Na^+, 315 to 319 Da or catechin or robinetinidin multi protonated + Na^+, 429 Da or fisetinidin-resorcinol adduct + Na^+, and 445 Da or catechin-resorcinol adduct + Na^+ are demonstrated in Figures 4 to 9, respectively.

It is interesting to note that cold-setting adhesives based on flavonoid-resorcinol direct adducts have been prepared synthetically (Pizzi and Roux 1978a) and that flavonoid-resorcinol-formaldehyde coreacted adhesives have already been reported (Pizzi and Roux 1978b) and commercialized. What is extremely new in the present work is that such flavonoid-resorcinol adducts exist naturally in the extract of merbau, rendering such an approach to cold-setting glulam adhesives particularly of interest both technically and economically.

The results support previous research (Santoso et al. 2014) that found merbau wood liquid extract consisted of the functional groups C–H and C=O with absorption bands below 2,850 to 2,750 per cm and 1,820 to 1,600 per cm, which indicated functional aldehyde (CHO) groups. Further analysis by pyrolysis–gas chromatography–mass spectrometry showed that merbau wood liquid extract was dominated by resorcinol compounds, especially 1,3-benzenediol.

Stiasny numbers close to 100 have been found for polyphenol-containing extracts (Food and Agriculture Organization of the United Nations 2000). The higher the Stiasny number, the higher the amount of reactive polyphenols available in the liquid extract for polymerization. The high Stiasny number (92.4%, wt/wt) obtained from

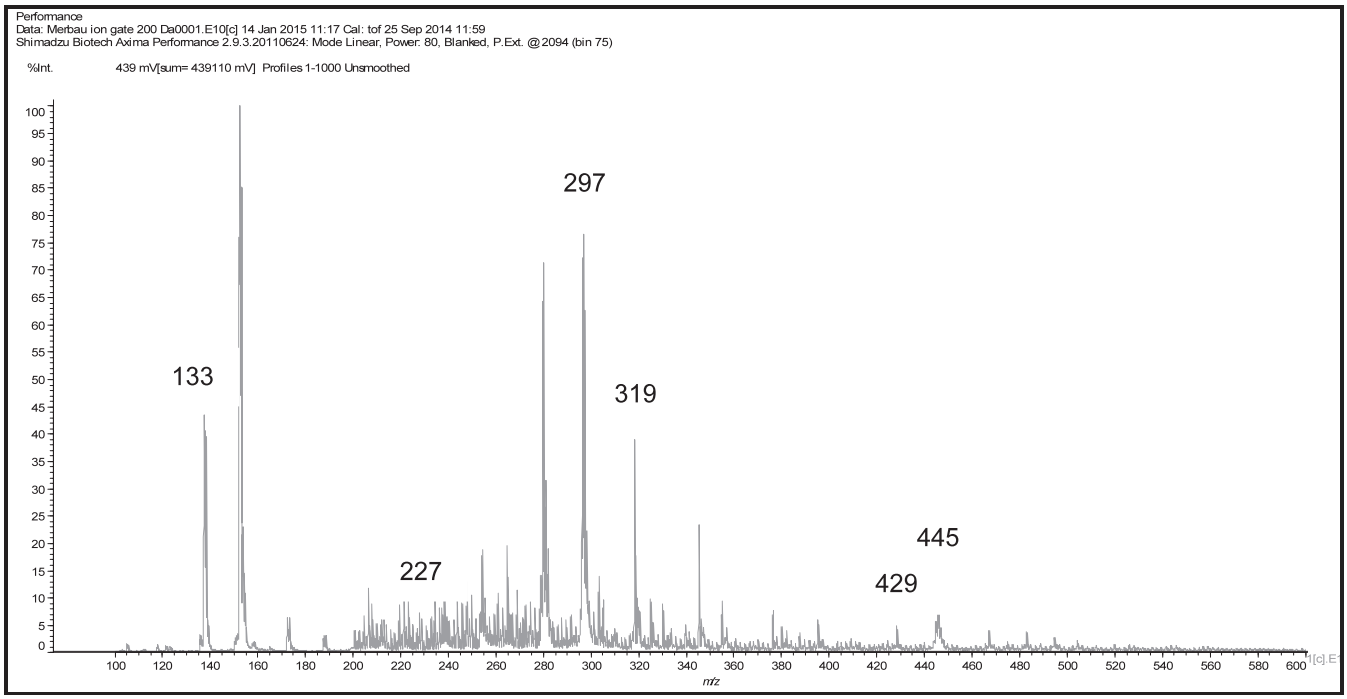

Figure 3.—Matrix assisted laser desorption ionization time of flight spectrograph of merbau wood liquid extract, 100 to 600 Da range.

the extract in the current study indicates its suitability for the resinification process.

The concentration of polyphenols (expressed as tannic acid) equivalent in the extract was found to be higher than that of phenol. The test for phenolic types yielded a pink color, which indicated the presence of flavan-3,4-ols and therefore the presence of condensed polyphenols, which are characterized as having polymerized flavonoid units. This was in agreement with Hedges (2000), who stated that condensed oligomers are ubiquitous phenolic compounds, representing the second most abundant natural phenolics after lignin and the fourth most common components in vascular plant tissues.

Table 1.—Extraction of merbau wood liquid through maceration at a warm temperature.

Molecule wt (Da)	Chemical compound	Structure no.
133	Resorcinol + Na^+	I
227	Stilbene type	II
297	Fisetinidin + Na^+	III
315–319	Catechin or robinetinidin multi protonated + Na^+	IV
429	Fisetinidin-resorcinol adduct + Na^+	V
445	Catechin-resorcinol adduct + Na^+	VI

Properties of laminated lumber

Table 2 shows the properties of the glulam specimens of four wood species bonded using the merbau extract adhesive. The moisture content of the products ranged from 10.58 to 11.21 percent. The moisture content fulfilled the guidelines of Japanese Standard JAS 234-2003 (2003), which requires the allowable moisture content in glulam to be less than 15 percent.

The shear strength of glulam was higher than that of CLT, indicating that adhesion in glulam was better than in CLT because the adhesive in glulam penetrated the adherents

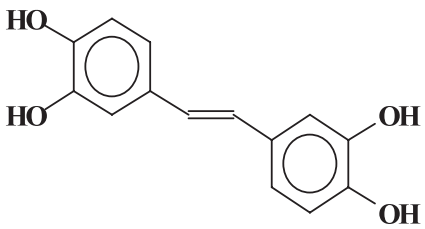

Figure 5.—227 Da = stilbene type.

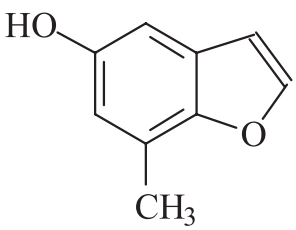

Figure 4.—155 Da = 2-methyl-5-hydroxybenzofuran + Na^+.

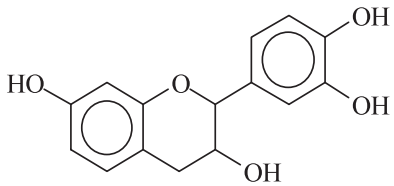

Figure 6.—297 Da = fisetinidin + Na^+.

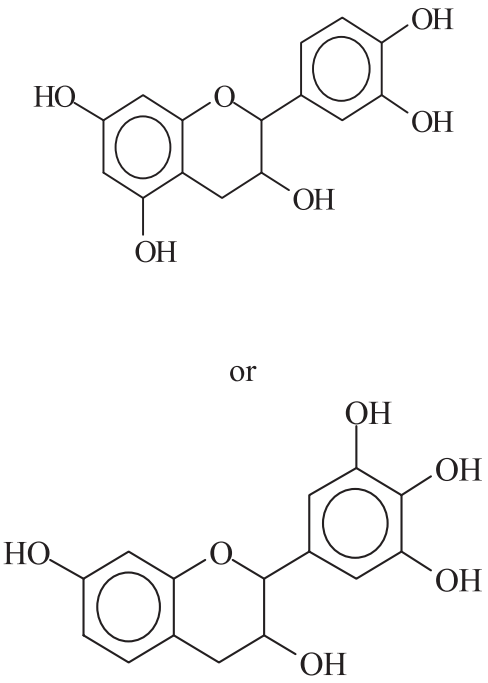

Figure 7.—315 to 319 Da = catechin or robinetinidin multi protonated + Na^+.

with greater ease in the parallel lumber components. Pangsor wood joints presented the lowest shear strength because this species has the lowest density, and the other wood species presented higher strength values. Mindi and mangium glulam fulfilled the Japanese standard requiring a shear strength of more than 54 kg/cm^2 (dry test).

The joints shear strength obtained was better compared with similar products (five plies) described in previous research (Supartini 2012). The previous products had a low density (<0.45 g/cm^3) and were manufactured from Jabon (*Anthocephalus cadamba*) and manii (*Maesopsis eminii*) wood using a commercial isocyanate adhesive. The resulting shear strength was 49 to 59 kg/cm^2 in the dry test but 0 kg/cm^2 in the wet test. Similarly, high-density products (>0.56 g/cm^3) made from mangium wood had a shear strength of 66 kg/cm^2 in the dry test and 0 kg/cm^2 in the wet test.

The MOR of the boards ranged from 63.24 to 547.73 kg/cm^2 (Table 2). Mangium glulam had the highest MOR, and mindi CLT had the lowest. Pine CLT and glulam and mangium glulam had the highest MOR, which at more than 300 kg/cm^2 fulfilled the requirements of JAS 234-2003 (2003). These results were lower than those of Supartini (2012) on five-layer CLT from manii, jabon, and mangium wood (394 to 604 kg/cm^2).

The MOE of the boards was lower than those of Supartini (2012), who produced five-layer CLT of manii, jabon, and mangium wood that had MOE values of 49,000 to 74,000 kg/cm^2. The boards in this study did not fulfill the requirements of JAS 234-2003 (<75,000 kg/cm^2).

The formaldehyde emission of the boards ranged between 0.18 and 1.10 mg/liter, with the result that all the boards were classified into E 2 (more than 0.124 mg/m^3 air; CEN 2003). Formaldehyde emission from pangsor glulam (1.10 mg/liter) was not significantly different from the glulam made from mindi (1.04 mg/liter) or mangium (1.10 mg/liter), according to the Japanese Standard the boards were classified into F** category (maximum, 2.1 mg/liter). However, the formaldehyde emission of pangsor glulam

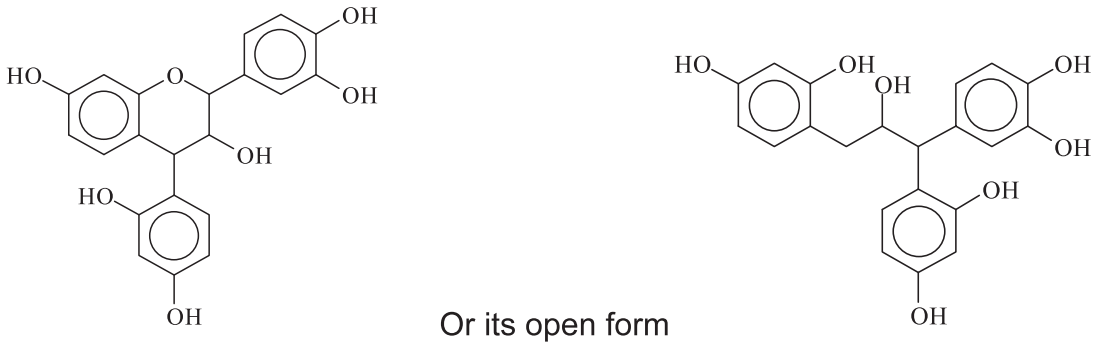

Figure 8.—429 Da = fisetinidin–resorcinol adduct + Na^+.

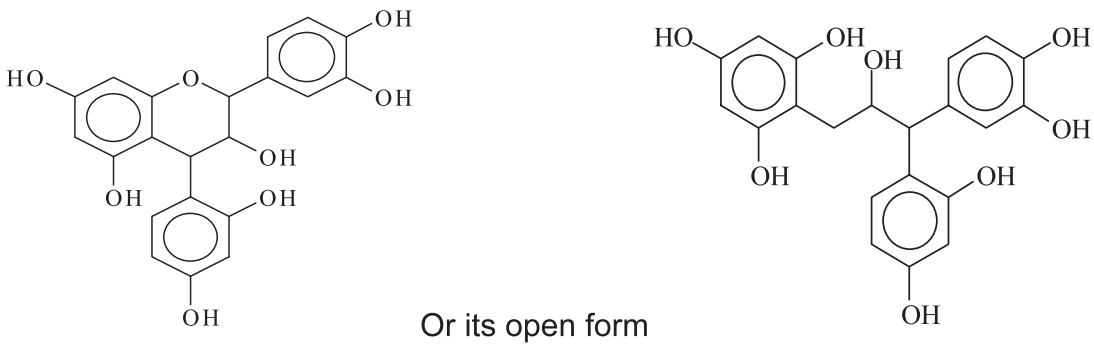

Figure 9.—445 Da = catechin–resorcinol adduct + Na^+.

Table 2.—Properties of boards.

Wood species	Product types	Properties[a]						
		Moisture content (%)	Density (g/cm^3)	Shear strength (kg/cm^2)		MOR (kg/cm^2)	MOE (kg/cm^2)	Formaldehyde emission (mg/liter)
				Dry test	Wet test			
Pangsor	Glulam	11.21 A	0.33 F	36.04 DE	19.91 D	222.5 E	31,273 D	1.10 A
	CLT	10.62 A	0.34 F	18.54 F	9.84 F	125.5 G	20,843 G	0.44 C
Mindi	Glulam	11.11 A	0.46 E	86.44 A	34.34 A	206.4 F	29,810 E	1.04 A
	CLT	11.05 A	0.49 D	36.45 DE	16.01 E	63.2 H	24,453 F	0.18 D
Pine	Glulam	10.62 A	0.54 C	48.48 C	22.25 CD	351.7 B	54,233 A	0.87 B
	CLT	10.87 A	0.55 C	30.77 E	15.41 E	342.3 C	30,653 DE	0.26 D
Mangium	Glulam	10.79 B	0.57 B	77.35 B	42.46 A	547.7 A	50,113 B	1.10 A
	CLT	10.58 B	0.63 A	37.74 D	25.24 C	295.1 D	36,020 C	0.22 D
Japanese standard		Max 15		Min 54		Min 300	Min 75,000	

[a] All values are the average from five replicates. Delamination for all samples was 0 percent. Values followed by the same letter are not significantly different. MOR = modulus of rupture; MOE = modulus of elasticity.

was significantly different from that of pine glulam (maximum, 0.7 mg/liter), which was classified in the JAS F*** category. The mindi CLT (0.18 mg/liter) was equivalent to CLT made from pine (0.26 mg/liter) or mangium (0.22 mg/liter) in terms of formaldehyde emission, and thus it satisfies the requirements of the type F**** (maximum, 0.4 mg/liter) of the JAS standard.

Conclusions

Based on qualitative analysis by MALDI-TOF spectrometry, merbau wood extracts contain flavonoid oligomers up to six repeating units. The major peak-to-peak mass increments observed were 133, 227, 297, 315 to 319, 429, and 445 Da, corresponding to resorcinol, stilbene type, fisetinidin, catechin, fisetinidin-resorcinol, and catechin-resorcinol repeating units.

Copolymerizing the liquid extract of merbau wood waste with resorcinol and formaldehyde under alkaline conditions produces a copolymer that can be used as an adhesive in the manufacture of glulam from four types of wood, namely, pangsor, mindi, pine, and mangium.

The boards of mindi and mangium glulams fulfilled the shear strength requirement of the Japanese standard, while only mangium CLT and pine and mangium glulams fulfilled JAS 234-2003 for MOR. None of the boards met the MOE requirements.

For formaldehyde emission, the boards ranged between 0.18 and 1.10 mg/liter, and according to European standards, all the boards were classified as E 2. According to the Japanese Standard, the boards belonged to F** to F****.

Thus, the preparation of cold-setting structural adhesives from merbau wood extract was possible and applicable to glulam manufacturing especially for medium-density wood. To get better adhesion quality, resin content of the adhesive should be increased.

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