Characterization of Merbau Extractives as a Potential Wood-Impregnating Material

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This study aimed to investigate the major content of merbau extractives (ME) and their potential use as an impregnating material for low-quality timber. Extraction was done by maceration with ethanol, ethyl-acetate, and hot-water. Physico-chemical, phyto-chemical, UV-visible, and infrared spectroscopy, as well as py-GCMS analysis were then performed on dried extract. The results showed that organic solvent extractions resulted in much higher yields, by 12.50% than that of hot water (1.10%). The merbau extractives liquid obtained had a low acidity, with a pH ranging from 5 to 6, which is typical of phenolic compounds. Flavonoids and phenolics were found as the major compounds. UV-vis spectra showed that ME (λ=279 nm) consists of conjugated or aromatic systems, similar to standard resorcinol, which was used as the reference (λ=274 nm). The FTIR spectra showed the absorption bands at 3369 cm^{-1} that represent the functional group of hydroxyl (OH) bonds, and 1619 and 1510 cm^{-1}, representing the aromatic ring (C=C), which could be associated with resorcinol. The Py-GCMS showed that ME is predominated by resorcinol ($C_6H_6O_2$) with a 79% concentration. The ME could be potentially used for producing phenolic/resorcinolic resin through polymerization, which could be applied for wood impregnation.

Keywords: Major content; Merbau extractives; Density; Phenolic compound; UV-vis; FTIR; Py-GCMS; Resorcinolic resin

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INTRODUCTION

Extractives, a type of chemical compound that can be found in wood or bark, can be extracted using polar and non-polar or neutral solvents (Roffael 2016). Specifically, extractives are defined as compounds that are soluble in an organic solvent. There are also water-soluble carbohydrates and their derivatives, as well as polymerized polyphenols, which require a small amount of alkali to fully dissolve (Hillis 1987; Fengel and Wagener 1989; Umezawa 2001). In wood, extractives occupy certain morphological sites. For example, resin acids can be found in resin ducts, while fat and wax reside in parenchyma cells, and phenol is found in heartwood and bark (Sjöström 1993). The amount of extractives in wood is small, generally ranging from 5% to 10% in temperate zones. However, in some tropical woods, relatively high amounts of extractives can be found (Umezawa 2001). An example of a tropical wood species that contains high levels of an easily removable extractive is merbau wood (*Intsia* sp.). Using methanol as the solvent, Hillis and Yazaki (1973) obtained 29% extractives from *Intsia bijuga* wood from Papua New Guinea.

In general, extractives function to protect the living tree from destructive agencies; however, the resistance in the native habitat varies (Hillis 1987). Extractives are also the predominant contributors to wood color and fragrance. Many extractives have specific bioactivities, and various wood species have been used as sources of crude drugs and medicines for centuries (Umezawa 2001; Shimizu *et al.* 2002; Castro *et al.* 2012). Conversely, the presence of extractives may cause disadvantages in wood processing; for example, they influence the pulping, drying, adhesion, hygroscopicity, and acoustic properties of wood (Hillis and Yazaki 1973; Umezawa 2001). Therefore, some wood processing researchers consider merbau extractives disadvantageous. Hu *et al.* (2012) conducted heat treatment on merbau wood, which exhibited discoloration because of the presence of extractives. The extractives can be readily leached, staining adjacent materials. The results showed that heat treatment is an efficient technique to overcome discoloration caused by the extractives.

Instead of trying to overcome the disadvantages of merbau extractives, some researchers have studied the utilization of the aqueous-soluble material. Hillis (1987) explained that polyphenols, which naturally occur in wood, causes color in heartwood, infiltrate the cell wall of regular heartwood, and reduce the wood’s shrinkage and swelling capacity, thereby increasing its durability. Tohmura (1998) showed that the addition of merbau extractives slightly increased the gelatinous rate of the phenolic resin. Santoso *et al.* (2014) used liquid of merbau extract to form wood adhesives, utilizing a formaldehyde reaction. Applying the bio-adhesive to three-layer flooring caused the composite flooring’s performance to be similar to flooring produced with synthetic phenolic adhesives, which are classified as exterior quality products with low formaldehyde emissions. The reason for using this extractive was that it consists of phenolic compounds, especially 1,3-benzenediol resorcin, commonly called resorcinol. It is well known that resorcinolic resin, made by polymerization with formaldehyde at ambient temperature, exhibits good performance in external conditions (Pizzi and Roux 1978; Durairaj 2003). One of the benefits of resorcinol is that it can be used to develop various kinds of synthetic resins and adhesives with excellent properties. For example, resorcinolic adhesives (developed from the reaction of resorcinol and formaldehyde) are primarily used for the fabrication of plywood aircraft and the lamination of hardwood helicopter propellers (Durairaj 2003).

This study aimed to investigate the composition of merbau extractives and their potential use, based on the major content and its characteristics, as an impregnating material to enhance the properties of low-quality plantation timber species.

EXPERIMENTAL

Extraction

Merbau wood powder, with a moisture content of 18%, was prepared using a grinding machine. Extraction was done by maceration, in which 500 mL of the powder passed through a 40-mesh screen, was dispersed in 80% ethanol, and stirred every 3 h at room temperature for two 24-h periods. The mixture was filtered with a glass filter, resulting in the separation of the first filtrate (1) and the residue. This maceration procedure was repeated for the residue, resulting in a second filtrate (2). The first (1) and the second (2) extracts were combined to make a concentrate (with the use of a rotary evaporator), which was freeze-dried to powder. The extraction of merbau wood with ethyl-acetate and hot water of 80 °C was undertaken using the same procedure.

Physico-Chemical Tests

Physico-chemical tests were used to measure the density, yield, viscosity, and acidity of the merbau extractives. The merbau extract density was measured using a pycnometer and calculated using the following equation,

$$D = \frac{p_e - p_0}{p_w - p_0} \times 1 \text{ g/mL} \tag{1}$$

where D is the density (g/mL), p_e is the pycnometer weight with extract (g), p_0 is the blank pycnometer weight (g), p_w is the pycnometer weight with distilled water (g), and 1 g/mL is the density of water. The yield was measured as the solid content from the liquid form of the extract; 75 mL of liquid was freeze-dried until a constant weight was reached. The viscosity was determined using an Ostwald viscometer made of PYREX® glass (Sigma Aldrich, USA), and the acidity was determined with a digital pH meter Hanna, USA.

Phyto-Chemical Test

The phyto-chemical test aimed to determine the group of chemical composition of the merbau extract. In total, 0.3 g of dried merbau extract was prepared for the phyto-chemical analysis. The screening involved qualitative chemical tests (*i.e.*, alkaloid, flavonoid, phenolic, steroid, and saponin tests) to investigate the merbau wood extract's composition. The alkaloid detection refers to Mayer's test (Evans 1997) in which to a few mL of filtrate, a drop or two of Mayer's reagent are added by the side of the test tube. A white or creamy precipitate indicates the test as positive. In Wagner's test (Wagner 1993), a few drops of Wagner's reagent were added by the side of the test tube into a few mL of filtrate. A reddish brown precipitate confirms the test as positive. The alkaloid was also tested by Dragendorff's reagent (Waldi 1965), where to a few mL of filtrate and 1 or 2 mL of Dragendorff's reagent are added. A prominent yellow precipitate indicates the test as positive.

The phenolic and flavonoid contents were examined using ferric chloride and alkaline reagent tests (Mace 1963 *in* Raaman 2006). The amount of merbau extract (50 mg) was dissolved in 5 mL of distilled water, then few drops of neutral 5% ferric chloride solution is added. A dark green colour indicates the presence of phenolic compounds. For alkaline test, an aqueous solution of merbau extract is treated with 10% ammonium hydroxide solution. Yellow fluorescence indicates the presence of flavonoids.

The detection of phytosterols/steroid was done by Liebermann-Burchard's test (Finar 1986) in which the extract (50 mg) was dissolved in 2 mL of acetic anhydride. To this, one or two drops of concentrated sulphuric acid are added slowly along the sides of the test tube. An array of colour changes shows the presence of phytosterols.

Saponin detection refers to Kokate (1999). A few drops of 0.5 N alcoholic potassium hydroxide solution was added to a small quantity of merbau extract along with a drop of phenolphthalein. The mixture was heated on water bath for 2 h. Formation of soap or partial neutralization of alkali indicates the presence of saponin.

UV-Visible Spectroscopy Analysis

UV-visible spectroscopy analysis was conducted on the ME by comparing it to standard resorcinol, with the aim of visualizing the similarities in the absorption wavelengths between ME and resorcinol. Similar spectra showed comparable compounds for the analyzed material.

A total of 1.25 mL of homogenous ME and standard resorcinol were measured at the same wavelength range. UV-visible spectra were recorded for wavelengths ranging from 200 to 800 nm using a UV-Vis spectrophotometer Shimadzu Series UV-1700, Shimadzu Corporation, Japan.

FTIR Analysis

The amount of 15 mg of merbau extract (ME) of 120 mesh size was directly used in the FTIR spectroscopy measurement. The dried powder sample was then embedded in potassium bromide (KBr) pellets and analyzed using a MB3000 (ABB, Canada) spectrometer. They were scanned in the absorption mode in the range of 4,000 to 500 cm^{-1} with the resolution of 2 cm^{-1}.

Pyrolysis GCMS

Pyrolysis was carried out with a pyrolyzer type Py-2020iS from Frontier Labs was used, coupled with a gas chromatograph-mass spectrometer (Shimadzu series QP2010 GC/MS) from Shimadzu Corporation, Japan that used a capillary type phase of column (60 m × 0.25 mm × 0.25 μm). The inlet temperature was set at 280 °C, and pyrolysis occurred at 600 °C. The intermediate products were identified by comparing the mass spectra with the standard spectra stored in the NIST 98 Library.

RESULTS AND DISCUSSION

Physico-Chemical Characteristics

Table 1 presents the merbau extractive characteristics used in this study. The table shows that extraction using organic solvents composed of 80% ethanol (polarity index 5.2) and 60% ethyl acetate (polarity index 4.4) resulted in much higher yields (12.45% and 12.56%, respectively) than that of hot water (polarity index 9.0), which gave a yield of 1.10%. The higher ethanol and ethyl acetate solvent yields can be explained by the fact that the polar and non-polar solvents dissolving more compounds, including tannins and other polyphenols, color pigments, volatile compounds, fat, resin, wax, gum, and starch (Santoso *et al.* 2014). The density and viscosity of the extract from both solvents are also higher than that of hot water. The three extraction results showed that ME is a weak acid (pH 5 to 6). According to Weber and Weber (2010), weak acidity is typical of phenolic compounds, which may affect a reaction.

Organic solvents such as ethanol, methanol, ether, acetone, ethyl acetate, and hexane, or different solvent mixtures, can be used to extract most polyphenols compounds. The use of polyphenol during the extraction process is a very important step for achieving adequate recoveries (Viñas and Campillo 2014). Also, the useful purpose of the extract should be considered. The solvent choice depends on the targeted extracted compounds (Eloff 1998). However, in this study, using it was preferable to the use of hot water of 80 °C for further extraction.

According to Kislik (2012), from an environmental point of view, the best alternative for organic solvent is water because it is relatively cheap, safe, nontoxic, inflammable, and recyclable. Merbau extractive (ME), being a water-soluble material, is easily extracted using water.

Table 1. Characteristics of Raw Merbau Extract

No	Characteristics	Unit	Solvents		
			Ethanol	Ethyl-acetate	Hot water
1	Density	g/mL	1.12	1.21	1.02
2	Yield	%	12.45	12.56	1.34
3	Viscosity	poisse	1.21	1.33	1.09
4	Acidity	pH	6	5	6

Tohmura (1998) obtained considerable amounts of ME yield, especially water-soluble extractives, *i.e.*, about 15% by water, 22.5% by hot water, 21.5% by methanol, and 2% by hexane. The amount of extracts within wood tissues varies from below 1% to more than 30% depending on many factors, such as the growth rate of the tree, the time that the tree is cut down, the species, and the type of solvent (Donegan *et al.* 2007; Windeisen and Wegener 2009). Tohmura (1998) revealed that ME mostly consists of flavonoid and stilbenes groups.

Phyto-Chemical Analysis

Table 2 presents the phyto-chemical analysis results for crude ME. The phyto-chemical analysis conducted on the crude merbau extracts by ethanol and ethyl-acetate (EA) extraction revealed the presence of flavonoids and phenolic compounds. During the EA extraction, a small amount of steroid was also obtained, while alkaloids and saponins were absent from both the ethanol and EA extractions, as shown in Table 3. According to Table 3, while alkaloid, steroid, and saponin compounds were absent from the extract, flavonoid and phenolic compounds were found to be the major compounds. Harborne (1984) stated that phenolic compounds can be universally found in plants. However, they are associated with lignin, typically combined as ester groups. The flavonoids found in ME were as abundant as the phenolic compounds. The absence of alkaloid, steroid, and saponin secondary metabolites from the stem extract can be explained by their typically limited presence in leaves (Knölker and Reddy 2002). On the other hand, flavonoid and phenolic compounds are abundant in the stems as they (particularly the phenolic compounds) are the precursors for the biosynthesis of primary wood components such as lignin and cellulose (Harborne 1984; Obst 1998; Umezawa 2001).

Table 2. Phyto-Chemical Analysis of Crude ME

No	Parameter test	Results	
		Ethanol extract	Ethyl acetate extract
1	Alkaloid		
	- Dragendorf	-	-
	- Mayer	-	-
	- Wagner	-	-
2	Flavonoid	+++	+++
3	Phenolic	+++	+++
4	Steroid	-	+
5	Saponin	-	-

Remarks:
(-): Negative test (absence of turbidity, flocculation and precipitation).
(+): Weak positive test (if the reagent has a slight opacity).
(+ +): Positive test (if the reactive product and not a turbidity flocculation).
(+ + +): Test strongly positive (if the reagent produces a precipitate or heavy flocculation).

During this analysis, the presence of flavonoids and phenolics with strongly positive results (+++) indicates the possibility of using ME as a supporting material in the wood industry. Then, the question may be asked: can merbau extractives be used to produce phenolic resin?

Only a limited number of studies have been conducted regarding the use of flavonoids for wood properties improvement. A study was carried out by Ermeydan *et al.* (2012) on Norway spruce wood samples (*Picea abies*) by impregnating 3-hydroxyflavone (a type of commercial and hydrophobic flavonoid) with tosylation pre-treatment. The results demonstrated that the shrinkage values decreased by approximately 45% between untreated wood and modified wood. Additionally, the hardness and indentation modulus showed a significant increase (about 10%) from unmodified cell walls to flavonoid loaded cell walls, which indicates an improvement in the mechanical properties resulting from flavonoid insertion.

Another component with an abundant presence (+++) in ME identified was phenolic compounds. Phenolics or phenols, are the class of chemical compounds consisting of a hydroxyl group (-OH) bonded directly to an aromatic hydrocarbon group. Phenols are the simplest form of the class, which is also called carbolic acid (C_6H_5OH). Phenolic compounds are classified as simple phenols, or polyphenols, based on the number of phenol units in the molecule (Harborne 1984; IUPAC 1997; Croteau *et al.* 2000; Caravaca *et al.* 2006; Amorati and Valgimigli 2012; Khoddami *et al.* 2013). Free phenols and phenolic acids are best considered together, as they are usually identified together during plant analysis (Harborne 1984). Flavonoids are among the polyphenols that possess at least two phenol subunits, and compounds possessing three or more phenol subunits are referred to as tannins, specifically, either hydrolyzable or non-hydrolyzable tannins (Robbins 2003).

Phenolic substances tend to be water-soluble (Harborne 1984). Phenolic compounds or polyphenols are among the most widespread classes of metabolites in nature, and their distribution is almost ubiquitous (Umezawa 2001; Pereira *et al.* 2009). They constitute a large group, comprising at least 8000 different known substances (Caravaca *et al.* 2006).

In comparison to flavonoids, using phenolic compounds in wood treatment and products is more common. Phenolic resins or adhesives are widely used as supporting materials in the wood composite industry, with various derivatives. According to Detlefsen (2002), phenolic resin in the form of phenol formaldehyde (PF) polymers were the first product of synthetic polymers, having been developed at the beginning of the 20th century. Phenolic resin or adhesives have been developed in various types: phenol resorcinol formaldehyde (PRF), tannins (polyhydroxypolyphenolics), and lignin adhesives (Pizzi 2003; Santoso and Hadi 2004; Frihart 2005).

Phenolic compounds are also commonly used in wood modification with the aim of improving the wood’s properties. For example, PF resin can improve dimensional stability (Ryu *et al.* 1991, 1993; Sakai *et al.* 1999; Ohmae *et al.* 2002) This increase in dimensional stability appears to be caused by both the bulking of the cell wall and the cross-linking of resin components within the cell wall (Hill 2006). Treatment with this resin also enhances the decay and termite resistance of particleboards (Kajita and Imamura 1991).

This brief explanation of flavonoids and phenol presented above is important because it relates to the content of the extract merbau in further analysis by UV-visible and py-GCMS that is presented in the next section. Based on their functional groups, flavonoids and phenols are classified to a large group of polyphenols in which resorcinol is included as a simple phenol.

UV-Vis Identification

Referring to NIST (2011), the absorption wavelength range for resorcinol is visible from 200 to 290 nm. Blanco *et al.* (2005) determined the maximum absorption for this phenolic compound, at 273.8 and 290.0 nm, respectively. The results of the UV-visible analysis in this study are presented in Fig. 1

Figure 1 shows that the liquid extract of merbau wood (λ=279 nm) consisted of conjugated or aromatic systems, similar to standard resorcinol (which was used as the reference), which had a wavelength (λ) of 274 nm. In previous work (Santoso *et al.* 2014), similar spectra were found for different instruments of UV-vis spectroscopy. For example, the wavelength for merbau extractives (ME) was 279.5 nm, and the value was 273.5 for analytical resorcinol. The wavelength difference between ME and standard resorcinol is acceptable because ME is a crude extract, not a pure substance. The previous study also revealed the crystallinity degree of ME at 20.86%, and its melting or glass transition temperature at 111 °C (Santoso *et al.* 2014). All identifications indicated that ME consisted mostly of phenolic compounds, especially 1,3-benzenediolresorcin, commonly called resorcinol.

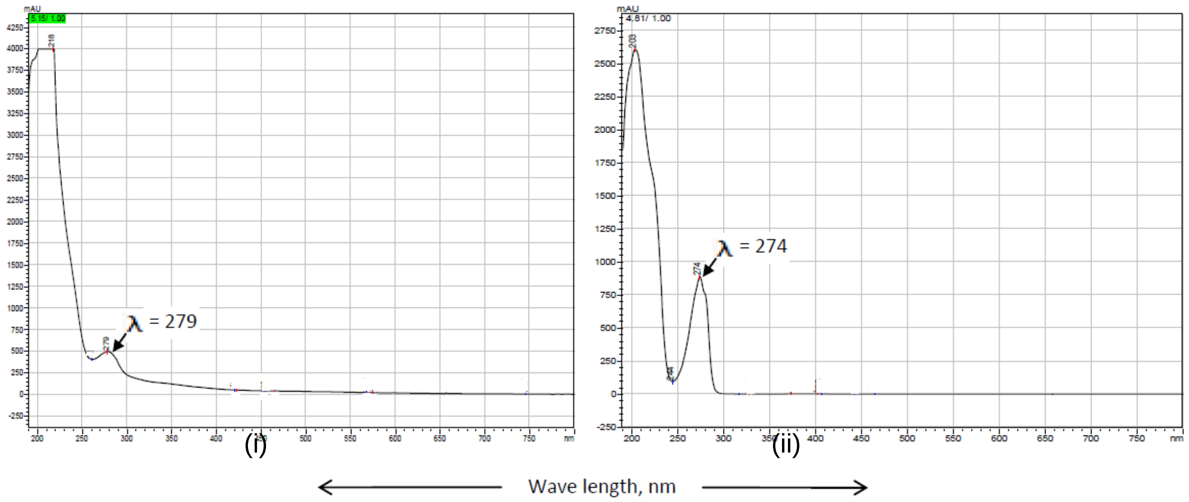

Fig. 1. UV-Vis spectrograph of (a) merbau extract and (b) resorcinol

Fourier Transform Infrared Analysis

Identification by Fourier transform infrared (FTIR) explains more details about the major compounds of the merbau extractives that was extracted with hot water, by identifying the functional groups. The FTIR analysis results for the ME are presented in Fig. 2, and details of the merbau extractive's absorption band are shown in Table 3.

Based on previous publications (Coates 2000; Jacox 2003), the FTIR spectroscopy shown in Fig. 3 reveals the appearance of absorption bands for the spectrum numbers with absorption bands of 3500 to 2500, 1500 to 1675, and 1000 to 1300 (cm^{-1}), which represent the functional groups of hydroxyl (OH) bonds, aromatic rings (C=C), and ether, respectively.

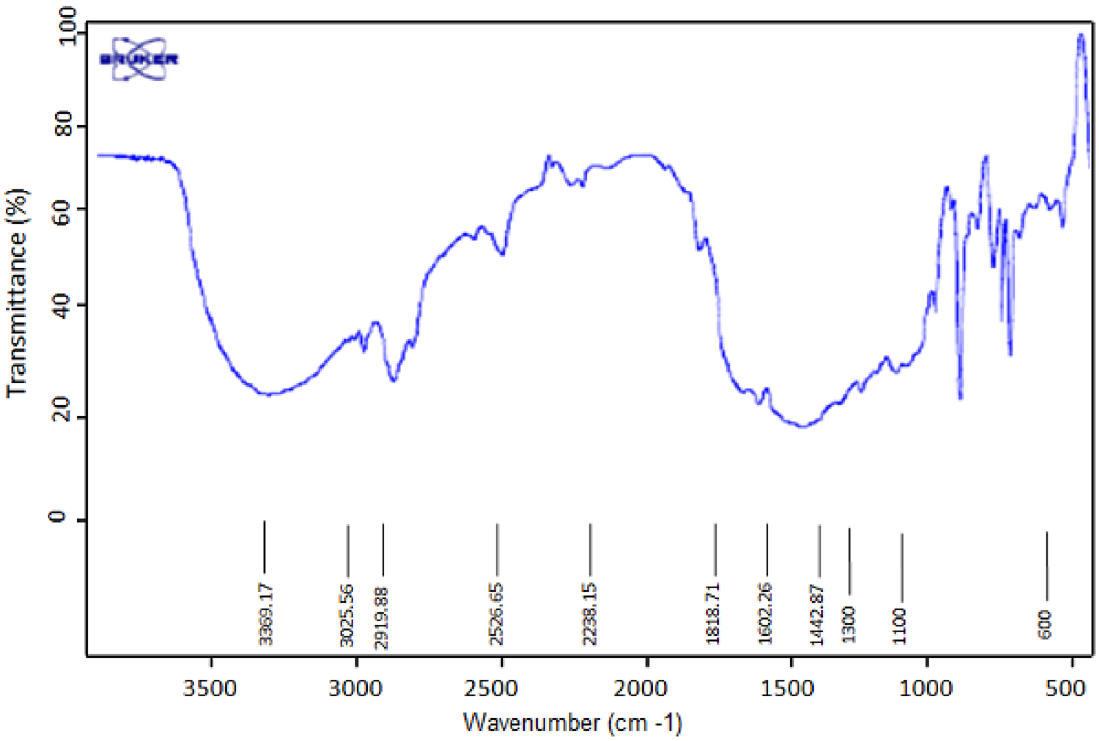

Fig. 2. Fourier transform infrared spectrograph of merbau wood liquid extract

Table 3. Spectrophotometer Absorption Band of Merbau Extractives

Wavelength (cm^{-1})	Standard range of absorbance	Description
3369.17	2500-3500	Hydroxyl functional groups- OH-stretching
3025.56		
2919.88		
2526.65		
2238.15		Alkynes- C=C Stretching
1818.71	1650-1800	Carbonyl
1602.26	1300-1675	Alkenes- C=C stretching (aromatic)
1442.87		
1300 - 1100	1000-1300	Esther- C-O- Stretching
1000 - 600		Alkene- C-H- out of plane bending

The OH bonds and the aromatic ring (C=C) functional groups can be associated with resorcinol, as it is conjugated by two functional groups of OH and one aromatic ring of C=C. Similar results were obtained by Santoso *et al.* (2014). Furthermore, a high concentration and strong appearance of OH and aromatic (C=C) bonds are shown by the absorption band of 3369.17 cm^{-1}, as it is in the range of 3200 to 3400 cm^{-1} for OH bond and 1,619 and 1510 cm^{-1} for the aromatic ring.

To confirm the functional groups of the compound shown by the FTIR, an analysis by pyrolysis-gas chromatograph-mass spectroscopy was carried out.

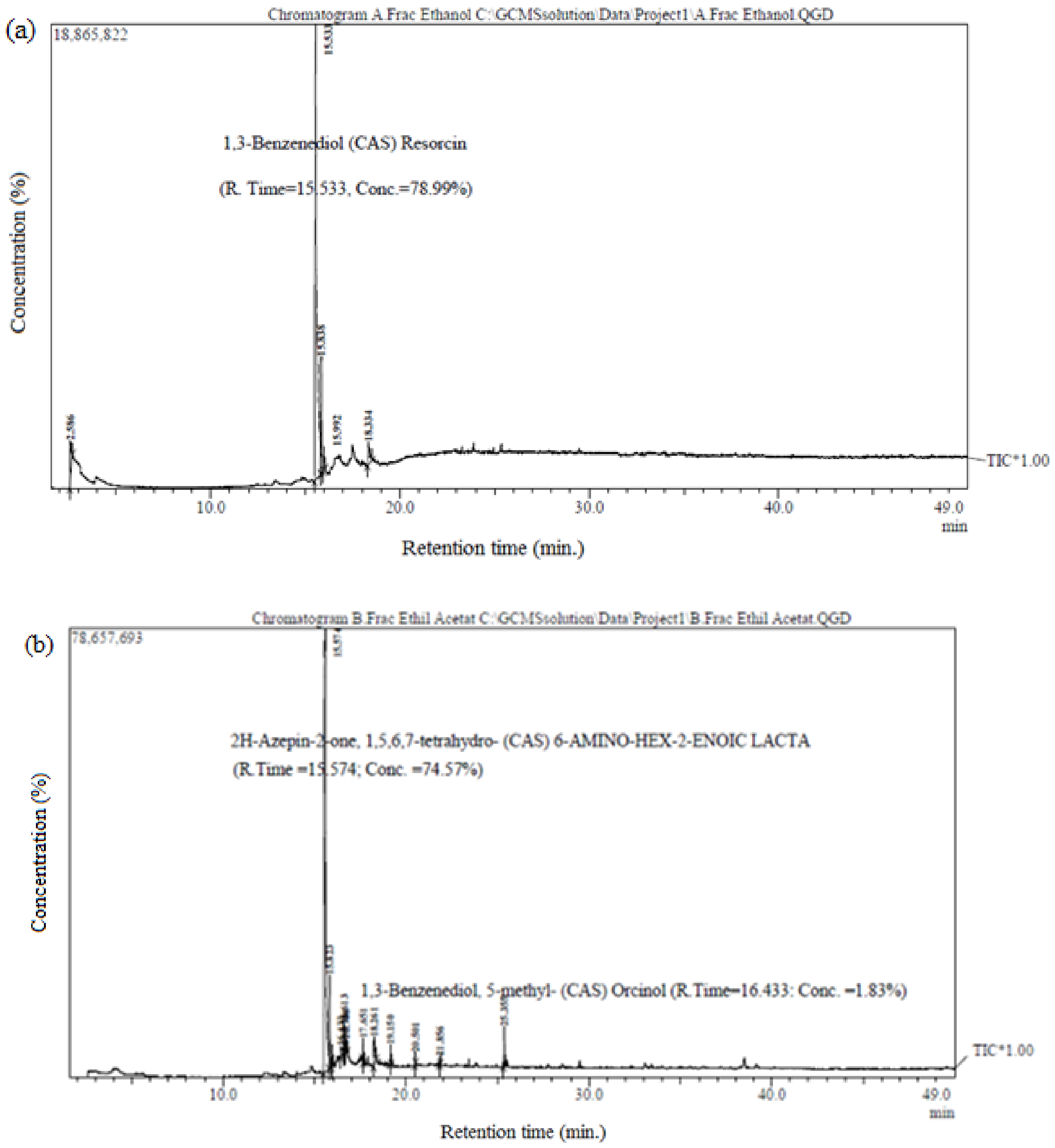

Fig. 3. Chromatogram py-GCMS of merbau wood liquid (ME) extracted by ethanol (a) and by ethyl acetate (b)

Py-GCMS Identification

Py-GCMS provides a suitable method for the quantitative and qualitative analyses of complex mixtures with high efficiency, precision, and simplicity (Zheng 2007; Mullen and Boateng 2008). In a coal pyrolysis study, flash pyrolysis-GC/MS used in the structure analysis provided *in-situ* information at the molecular level, particularly in the presence of phenolic forms (Eglinton *et al.* 1994; Liu and Peng 2008). More importantly, direct information about the amounts and species of phenols released during pyrolysis can be obtained, and the pyrolysis vapor's condensation effect on the phenolic compound analyses can be avoided (Kong *et al.* 2014). Windeisen and Wegener (2009) stated that GCMS is one of the best analysis methods for extractives.

Pyrolysis-gas chromatograph-mass spectrometry (py-GCMS) has been used for wood analysis since the late 1970s. Ralph and Hatfield (1991) stated that a mixture of relatively simple phenols may be produced from lignin pyrolysis. Previously, many researchers have used py-GCMS to isolate wood lignin (Obst 1983; Pouwels and Boon 1987; Faix *et al.* 1987, 1990; Meier and Faix 1992; Fu *et al.* 2014). This method can be also used to identify compression wood in many species (Brennan *et al.* 2014).

The py-GCMS analysis results for this current study are presented in Fig. 3 and Table 4. The results show that merbau extractive (ME) contains five major chemical compounds, *i.e.*, (from the lowest concentration): phenol (peak-4, 1.86%), benzoic acid (peak-5, 4.86%), ammonium carbamate (peak-1, 5.59%), bifuran (peak-3, 8.71%), and benzenediol resorcin (peak-2, 78.99%) (Fig. 3(a)). All of the compounds are commonly found in plants soluble in water (Grigg *et al.* 1966; Durairaj 2003; Brooks *et al.* 2007; Qualley *et al.* 2012; Jiang *et al.* 2014). The mass analysis of the major peak, at the retention time 15.53 min, gives a mass peak of 110 (major), which is assigned as free resorcinol ($C_6H_6O_2$), shown in Fig. 4.

Table 4. Quantitative Compound Results for ME, Detected by Pyrolysis-GCMS

Peak	R.Time (min)	Area	Conc. (%)	Name
1	2.586	7658570	5.59	Carbamic acid, monoammonium salt (CAS) Ammonium carbamate
2	15.533	108293701	78.99	1,3-Benzenediol (CAS) Resorcin
3	15.838	11947282	8.71	2,2'-Bifuran (CAS) BI-(FURYL-2)
4	15.992	2545692	1.86	Phenol, 2,6-dimethoxy- (CAS) 2,6-Dimethoxyphenol
5	18.334	6657325	4.86	Benzoic acid, 2,4-dihydroxy-6-methyl-, methyl ester (CAS) Methyl orsellinate
		137102570	100.00	

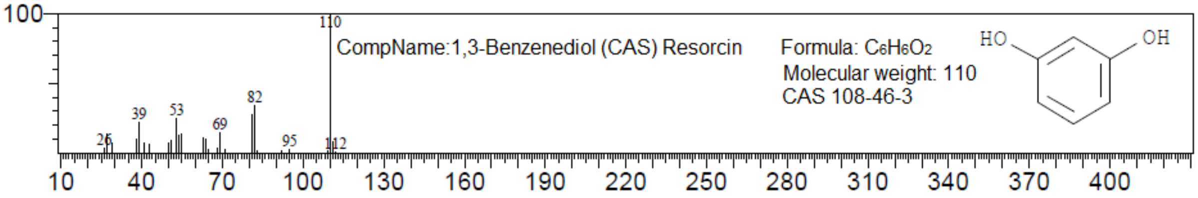

Fig. 4. Mass spectroscopy of merbau wood liquid extracted by ethanol

Regarding the chemical content, this study reconfirms that merbau extractives are dominated by resorcinol (molecular weight = 110), which is indicated by the highest peak at the retention time (R. Time) of 15.533 min, with a concentration of 78.99% (Fig. 3(a), Table 4, and Fig. 4). This result is similar to the results obtained by Santoso *et al.* (2014), who analyzed ME for its potential use as an adhesive. In that study, the resorcinol peak occurred at the retention time of 22.187 min; however, the concentration was lower, at 38.33%. In the study conducted by Malik and Santoso (2009), using the py-GCMS analysis method also revealed similar major ME compounds, with a high concentration of resorcinol (52.51%) at 21.998 min of retention time. Both the previous ME analyses showed lower concentrations of resorcinol than the current study because of the solvent used. In the previous study, merbau wood powder was macerated in hot water, whereas in the current study, merbau wood powder was extracted using ethanol as the solvent.

The results obtained in this study are very promising, as resorcinol is one of the most remarkable chemicals known in organic chemistry. It is a dihydroxybenzene with the formula $C_6H_4(OH)_2$ (Fig. 4). The compound also has other common names, such as resorcin, *m*-dihydroxybenzene, 1,3-benzenediol, 1,3-dihydroxybenzene, 3-hydroxyphenol, *m*-hydroquinone, *m*-benzenediol, and 3-hydroxycyclohexadien-1. The International Union of Pure and Applied Chemistry (IUPAC) in its 1993 “Recommendations for the Nomenclature of Organic Chemistry” recommended benzene-1,3-diol as the proper name for this substance (Dressler 1994; Panico and Powell 1994; Durairaj 2003; NIST 2011). Based on phyto-chemical classification, resorcinol is categorized as a simple phenolic compound (Harborne 1984). It has been widely recognized as a versatile chemical compound that is extensively utilized in the development of advanced and beneficial chemistries and technologies. In wood industries, resorcinol is well known as an exterior adhesive. It is usually copolymerized with formaldehyde and phenol to form RF or PRF resin. Pizzi (2003) stated that resorcinol-formaldehyde (RF) and phenol-resorcinol-formaldehyde (PRF) cold setting adhesives are primarily used in the manufacturing of structural, exterior grade glulam, finger joints, and other exterior timber structures.

Different py-GCMS analysis results are shown in Fig. 4(b) because of the different solvent used (ethyl acetate). The major compound is shown by the single peak that belongs to caprolactam (2H-azepin-2-one). Caprolactam is well known as the precursor to nylon-6, a widely used synthetic polymer (Ritz *et al.* 2011). This finding will not be discussed further because the focus of this study is on the use of phenolic compounds found in merbau extractives. However, it is important to highlight that another compound, the polymer caprolactam, was found as the result of this study. As Hillis (1987) stated, merbau contains large amounts of water-soluble polymers that could be considered for other uses. This study affirms the content of merbau extractives, which can potentially be further applied in wood treatment or modification.

Potential Utilization of Merbau Extractives as an Impregnating Material

The results of phyto-chemical analysis (Table 2) show that merbau extractives contained major amounts of phenolic compounds (+++). This result can be potentially used to produce phenolic resins. Spectroscopic and chromatographic analysis, as shown in Fig. 2, Fig. 3(a), Fig. 4, and Table 4, substantiated that ME is dominated by resorcinol – one of the simplest phenolics. Weber and Weber (2010) explained that the presence of a hydroxyl group and an aromatic ring can be complementary to each other in facilitating both electrophilic and nucleophilic reactions. Phenol has an extremely high reactivity toward electrophilic substitution and assists its acid-catalyzed reaction with formaldehyde, leading to phenolic resins. Furthermore, phenol is a weak acid. This study demonstrated ME’s weakness in acidity, as presented in Table 1. Thus phenol’s properties show an ability to react with formaldehyde under acidic or basic conditions (Weber and Weber 2010), leading to either novolac resins (*via* acid conditions) or resole resins (basic conditions).

It is well known that resin made from resorcinol is resorcinol-formaldehyde (RF). It has the advantage over PF resins of being curable at room temperature because it has a reaction time 10 times faster than that of PF resin (Frihart 2005). In the polymerization process, resorcinol is very reactive because of the combined effect of the two hydroxyl groups on the aromatic ring in activating the 2-, 4-, and 6-positions toward reaction with formaldehyde, and with hydroxymethylresorcinol in the condensation step as well. As phenol and resorcinol have three reactive sites, they are able to crosslink. In addition, the resorcinol copolymerizes well with formaldehyde at room temperature (Pizzi 2003). The excellent performance of phenolic/resorcinolic resins or polymers is also well known. In particular, its durability, its hydrophobicity, good structural strength, and unique low-temperature properties, as well as resistance to many kinds of conditions including boiling water and high humidity, make using phenolic/resorcinolic resins very advantageous (Durairaj 2003). The properties of the resin will enhance the properties of wood which is not durable, unstable and hygroscopic, if the wood is impregnated with resin.

Based on the aforementioned literature review describing the excellent performance of resorcinolic resin, the advantages of the resin are as follows: it has a high reactivity, it reacts very quickly and easily, the resin can be reacted both in acidic and basic conditions, it is curable at room temperature, able to make crosslinks, can copolymerizes well with formaldehyde at room temperature, and has good physical properties (durable, hydrophobic, good structural strength, and resistant to many kinds of conditions including boiling water and high humidity).

Such properties can be useful for impregnation application because, according to Hill (2006), to make the impregnation process effective, it is essential that the impregnating material is non-leachable in service conditions. The fixation of the impregnating compound can occur through two main mechanisms: (i) monomer (or oligomer) impregnation, with subsequent polymerization within the cell wall; and (ii) diffusion of a soluble material into the cell wall, with subsequent treatment to render the material insoluble (immobile).

Another issue to consider when using ME as an impregnating compound is its penetration. The principle behind impregnation modification is to impregnate the wood's cell wall with a chemical, or a combination of chemicals, which then react to form a material that is bonded into the cell wall (Norimoto 2001; Hill 2006). A study on the characteristics of polymerized merbau extractive (PME) as a potential material for wood impregnation has been conducted and will be published as a separate paper.

CONCLUSIONS

1. Extraction using the organic solvents ethanol and ethyl-acetate resulted in much higher yields, of 12.45% and 12.56%, respectively, than that of hot water, 1.10%. The density and viscosity of the extract from both solvents were also higher than that of hot water. Merbau extractives (ME) has a weak acidity (pH of 5 to 6), which is typical of phenolic compounds. Phyto-chemical analysis proved that ME flavonoid and phenolic compounds were found to be the major compounds of ME.
2. Analysis using UV-vis spectroscopy showed that ME (λ=279 nm) consists of conjugated or aromatic systems, similar to standard resorcinol that was used as the reference, which had wavelength (λ) of 274 nm. Pyrolysis GCMS showed that the major compound of ME is resorcinol ($C_6H_6O_2$, mol. weight 110), which was detected at min 15.533, with a concentration of 78.99%. Further, analysis by FTIR spectroscopy showed that absorption bands contained the OH bonds (3,361 cm^{-1}) and aromatic ring (1,619 and 1510 cm^{-1}) functional groups.
3. ME can be a promising material for wood impregnation application in the form of phenolic or resorcinoilic resin because of its excellent physico-chemical properties.

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