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# Characterization of bark extractives of different industrial Indonesian wood species for potential valorization

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ABSTRACT

Barks are available as waste material and by-product of wood industry. They have been reported to contain interesting molecules and show some bioactivity such as antioxidant and antifungal. This study aimed at evaluating the amounts of extractives in *Acacia mangium* (acacia), *Paraserianthes falcataria* (sengon) and *Swietenia mahagoni* (mahoni) barks, to evaluate their extractive contents and the presence of potential valuable molecules. The extraction method used soxhlet with four different solvents. Antioxidant activity assays were carried out using methyl linoleate and 2,2-diphenyl-1-picrilhidrazyl (DPPH) and the antifungal activity was determinate by fungal growth inhibitions assays. 5.3%–18.5% extraction yields were obtained. All acetone and toluene ethanol extracts show high antioxidant activity by DPPH. The highest antioxidant value obtained by DPPH was obtained for mahoni bark acetone extract with 3.9 mg/L of $EC_{50}$, followed by mahoni bark toluene ethanol 6.8 mg/L, acacia bark acetone 7 mg/L, and acacia bark toluene ethanol extract 7.4 mg/L. Sengon bark extracts had the greatest antifungal activity inhibition. The greatest antioxidant and antifungal activity were obtained with phenolic compounds which were contained in the extracts.

## 1. Introduction

Nowadays, the concept of biorefinery has become a major axis for friendly environmental chemistry development by the understanding of the necessity to reach the best yield as possible from limited and precious natural resources. Thus, modern studies have to achieve an integrated exploitation of the different vegetable residues as sources of chemicals, materials, biofuels and/or energy (Fernando et al., 2006; Dugmore et al., 2017). Forest biomass and, particularly, by-products of industry dealing with it, could provide several interesting different matters able to lead to such applications (Dessbesell et al., 2017) like valorisation of fruit peel such as banana (Villaverde et al., 2013), of organosolv liquors (Villaverde et al., 2010), or of industrial waste streams such as knotwood (Pietarinen et al., 2006). In this sense, bark as a by-product of the wood first-stage processing reveals a high potential of interest.

After wood, the bark is the second most important tissue of a trunk. It amounts to about 10–20% of a stem depending on the species and growing conditions. In its chemical composition bark differs from wood by the presence of polyphenols and suberin, by lower percentage of polysaccharides, and a higher percentage of extractives (Fengel and Wegener, 1984). As in wood, the content of bark extractives can also be different depending on the species and solvent used. The following are some examples of chemical analysis of several barks. Studying the bark of loblolly pine (*Pinus taeda*) determined the total extractives content as 19.9%, using a sequence of petroleum ether, benzene, ethanol, cold and hot water, whereas other researcher received a value of 27.5% after extraction with hexane, benzene, ethyl ether, ethanol, water and 1% NaOH. A sequence of ether, ethanol and hot water dissolved about 20% of European spruce and pine barks, and 12 and 16% respectively of beech and oak barks (Fengel and Wegener, 1984).

*Acacia mangium* is one of the fast growing tree species in Indonesia,

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which has been planted for timber production, the pulpwood being usually debarked to improve the quality of the pulp. Large amount of bark derived from pulp and mill industries are indeed unexploited in Indonesia with an annual bark volume estimated to 1.665.150 $m^3$ (Pari et al., 2000). So, there are more than 15–16 tons of potential Acacia bark that could be available in Indonesia. Other tropical hardwood species used in log processing industries also generate large amounts of bark as by-product such as sengon wood and mahoni wood. The timber production of mahoni and sengon being respectively 168.000 m3/year and 2.800.000 m3/year (Forestry Statistics of Indonesia, 2014) and assuming the bark content in each tree is 10%, the bark volumes coul be estimated at 16.800 m3/year and 280.000 m3/year respectively.

Up to now, barks are mainly used for energy production or horticulture application (Pari et al., 2006; Yamato et al., 2006). For some dedicated wood species, bark is used for tannin extraction, leading to numerous applications (Hergert, 1983). Moreover, bark tannins have been reported to show different biological activity such antifungal or antioxidant activities at the origin of their protective function in the tree. In addition to previous activities, bioactive molecules have been identified to present antidiabetic, anticancer and antifeedant activities (Rajkumar et al., 2012; Miranda et al., 2016; Wang et al., 2015; Yessoufou et al., 2015). In recent years, Acacia has become a preferred tannin source for the vegetable tannin extract industry in China because of its richness in polyphenolic compounds (Chen et al., 2001).

Based on these statements, it appears interesting to explore the chemical biodiversity of barks of different hardwood species such as *Acacia mangium, Paraserianthes falcataria, and Swietenia mahagoni* widely used in wood industry in Indonesia as potential sources of molecules for further applications in cosmetics, nutraceutics, pharmaceutics applications or as starting material for polymer production.

## 2. Materials and methods

### 2.1. Material

Bark samples from *Swietenia mahagoni* (Family Meliaceae) and *Acacia mangium* (Family Leguminosae)

were collected from trees from industrial plantation forest managed by Perum Perhutani (a state-own forestry company in Jawa island, including Bogor region), while *Paraserianthes falcataria* (Family Leguminosae) came from community forest located in Dramaga region, Bogor, Indonesia. They were approximately 20 years (*S. mahagoni*) and 7 years old (*P. falcataria, A. mangium*), respectively. After air drying to approximately 15% moisture content, barks were converted to sawdust with particle size between 20 and 40 mesh. Sawdusts were then oven dried at 103 °C until constant mass.

### 2.2. Extraction

Approximately 7-10 g of bark sawdust were extracted with a soxhlet apparatus using a sequential extraction with four different solvents, dichloromethane, acetone, toluene/ethanol (2/1, (V/V)), and water (purity > 99%). Absolute ethanol anhydrous and toluene were obtained from Carlo Erba Reagents (Val de Reuil, France) while the other solvents were purchased from Sigma-Aldrich SARL (St-Quentin Fallavier − France). After extraction, the crude extracts were evaporated using a vacuum rotary evaporator. Crude extracts were first oven dried at 50 °C and the drying finished under vacuum. Dry extracts were weighed and the extraction yield was calculated as the percentage of the amount of extract compared to the initial mass of dry bark.

### 2.3. GC–MS analysis

1–2 mg of dry extract was reacted and dissolved in 50 µL of N,O-bis (trimethylsilyl) trifluoroacetamide containing 1% trimethyl chlorosilane (BSTFA/1%TMCS, Sigma-Aldrich SARL, St-Quentin Fallavier − France) for 12 h and then evaporated at 70 °C before dilution in 1 mL of ethyl acetate. GC–MS analysis was performed on a Clarus 680 gas chromatograph coupled to a Clarus SQ8 quadrupole mass spectrometer (Perkin Elmer Inc., USA). Gas chromatography was carried out on a 5% diphenyl/95% dimethyl polysiloxane fused-silica capillary column (DB–5 ms, 30 m × 0.25 mm, 0.25-µm film thickness, J & W Scientific, USA) with helium as carrier gas at a constant flow of 1 mL/min. The gas chromatograph was equipped with an electronically controlled split/splitless injection port. The injection (1 µL) was performed at 250 °C in the splitless mode. The oven temperature program was as follows: 80 °C for 2 min, increase from 80 to 190 °C at a rate of 10 °C/min, increase from 190 to 280 °C at a rate of 15 °C/min and hold for 5 min, then 10 °C/min until 300 °C hold for 14 min. Ionization was achieved under the electron impact mode (70 eV ionization energy). The source and transfer line temperatures were 180 and 250 °C, respectively. Detection was carried out in scan mode: $m/z$ = 45 to $m/z$ = 700. The detector was switched off in the initial 2 min (solvent delay). Compounds were identified by comparison with spectra from the NIST (US National Institute of Standards and Technology, Gaithersburg, MD, USA) mass spectral library (Edition of 2011)

### 2.4. MALDI-TOF analysis

The dry extracts were dissolved in a solution of water/acetone (1:1) up to 7.5 mg/mL. For the enhancement of the ion formation NaCl solution was added and placed on the MALDI target. Then, the solutions of the sample and the matrix were mixed in equal amounts and 1.5 µL of the resulting solution were placed on the MALDI target. As the matrix, 2,5-dihydroxy benzoic acid (Sigma-Aldrich SARL, St-Quentin Fallavier − France) was used. Red phosphorous was used as reference for spectrum calibration. Finally, after evaporation of the solvent, the MALDI target was introduced into the spectrometer.

The spectra were recorded on a KRATOS AXIMA Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK). The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. The length of one laser pulse was 3 ns. Measurements were carried out using the following conditions: polarity-positive, flight path-linear, 20 kV acceleration voltages, 100–150 pulses per spectrum. The delayed extraction technique was used applying delay times of 200–800 ns. The software Maldi-MS was used for the data treatment.

### 2.5. Antioxidant activities

#### 2.5.1. Antioxidant activity by methyl linoleate oxidation assay

Antioxidant activity was determined by oxygen uptake inhibition during oxidation of methyl linoleate initiated by AIBN. The induced oxidation by molecular oxygen was investigated in a gas-tight borosilicate glass apparatus (Diouf et al., 2006). Solution extracts (0.1 g/L) were put into the reactor glass and were evaporated until there is no longer solvent. $9 \times 10^{-3}$M 2,2-azodiisobutyronitrile (AIBN); 0.4 M methyl linoleate; and 1 mL butanol were added to the reactor glass. The oxygen was given until the pressure was ~~145 torr~~ 193.3 hPa. Oxygen inhibition was monitored with pressure transducer to investigated antioxidant activity during 2.5 h and temperature was set at 60 °C by the external heating bath. Antioxidative capacity was determined by comparing oxygen uptakes between reactions without extract and in presence of extracts. Strong antioxidants would have hight percentage of OUI (Oxygen Uptake Inhibition) (Poaty et al., 2010). It was determined as:

$$\text{OUI (Oxygen Uptake Inhibition)} = \frac{Pcontrol - Psample}{Pcontrol}$$

#### 2.5.2. Antioxidant activity by DPPH assay

The DPPH radical scavenging activity (RSA) was performed