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A Study of Chemical Constituents in Platinum Fast-Grown Teak Wood (*Tectona grandis*) with Age Differences Using Py-GCMS Coupled with Interdependence Multivariate Analysis

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ABSTRACT

Pyrolysis gas chromatography-mass spectrometry (Py-GCMS) is a simple, rapid, and reliable analytical technique to assay lignocellulose biomass. This study aims to analyze the chemical content of various ages of platinum fast-grown teak wood using PyGCMS coupled with interdependence multivariate analysis. Fifty-eight peaks were shown in the pyrogram originating from carbohydrates, lignin, and extractive derivatives. Along with age, platinum fast-grown teak wood showed higher carbohydrate derivatives in heartwood than sapwood. Compared to teak wood grown in conventional (between 36.72-45.69%), platinum fast-grown teak wood has a higher content of carbohydrates (42.82-48.04%). A substantial amount of G-unit lignin was detected in the sapwood, while the S-unit lignin dominated the heartwood. The extractive content of 10-years-old teak wood heartwood was 4.82%, higher than 10- and 20-years-old heartwood from conventional wood (2.23% and 8.88%, respectively). Multivariate analysis of the chemical compound showed that Py-GCMS could be utilized to classify platinum fast-grown and conventional teak wood. 2-methyl anthraquinone (MAQ) content of 10-year-old fast-grown teak wood was 2.5 times higher than 20-year-old conventional teak wood. Based on the study, platinum fast-grown teak wood is promising as alternative wood material to fulfill the market demand for conventional teak wood.

1. Introduction

Teak (*Tectona grandis*) is one of the most popular tropical timber species due to its high demand for furniture, carpentry, construction building, and outdoor equipment (Fofana *et al.* 2009). Teak grows naturally in Southeast Asia and is highly valued for its natural durability and stability associated with pleasant aesthetics (Miranda *et al.* 2011). It is harvested for a lengthy rotation period between 50 to 80 years (Damayanti *et al.* 2018). This long rotation of teak wood is a challenge for industries that use it as a raw material to meet the demand. In order to overcome this problem, the Indonesian Institute of Sciences (LIPI), now mentioned as the National Research and Innovation Agency (BRIN), through the Research Center for Biotechnology, manages to establish a shorter rotation and faster growth of teak wood, called platinum. It has developed through vegetative and *in-vitro* techniques from superior teak wood as parent trees (Pramasari *et al.* 2014). A comprehensive study of platinum teak wood is needed regarding physical properties, wood durability, and chemical content. Previous research regarding physical platinum fast-grown teak revealed that platinum has good strength but is uncompleted for mechanical properties. A 5-year-old platinum teak wood's physical properties are almost equivalent to 20-30 years old conventional teak wood (Adi *et al.*

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2016). Although a comprehensive study of the effect of the age of platinum teak wood on their durability has not been carried out, it is closely related to the content of lignin and extractives (Ismayati *et al.* 2016). Lignin content and its compositional type in teak wood correspond with the wood stiffness and mechanical resistance (Koehler and Telewski 2006).

Meanwhile, the extractives compound such as anthraquinone and 2-methyl anthraquinone (MAQ) have an important role against biodeterioration agents such as fungus and termite attacks (Haupt *et al.* 2003; Thulasidas and Bhat 2017). In general, the extractives compound may not be present at effective levels in teak sapwood, considered less durable (Ismayati *et al.* 2016). Therefore, information regarding the chemical content, especially lignin and extractive, can effectively guide teak wood's durability, stability, and appropriate utilization.

Pyrolysis gas chromatography-mass spectrometry (Py-GCMS) is a simple, rapid, and reliable analytical technique to assay lignocellulose biomass. Lignin and extractive content quantification by Py-GCMS has been conducted in previous research (Windeisen *et al.* 2003) for the chemical content analysis of a 70-year-old teak wood sample from East Timor. Py-GCMS was proven helpful in obtaining the structure of lignocellulosic polymers, including wood, grass, wood pulp, and wood fossil (Lourenço *et al.* 2015). Py-GCMS became a powerful tool because of its high sensitivity, rapid analysis time without pre-treatment, and only a relatively small amount of sample is required, which makes this technique extremely environmentally friendly (Colombini *et al.* 2007). In this study, the chemical content (carbohydrates, lignin, and extractives) of different ages of platinum fast-grown teak wood was analyzed by a rapid analysis of PyGCMS coupled with interdependence multivariate analysis.

2. Materials and Methods

2.1. Preparation of Teak Wood Samples

Disks of platinum fast-grown teak wood of various ages were used from Cibinong Science Center Nurseries, Bogor, West Java. The radius of the wood disk was 5 cm, respectively. Samples of 10- and 20-year-old conventional teak wood were collected from a conventional in Bogor, West Java, Indonesia. The stem was cut and divided into axial positions (vertical cutting). Samples from trees aged 5 years and above were divided into heartwood and sapwood sections (radial variation) (Figure 1). Samples obtained from trees under 5 years old were not divided into different radial variations (horizontal cutting) due to the insignificant discrepancies between heartwood and sapwood.

2.2. Analysis of Chemical Components of Teak Wood by Py-GCMS

About 400-500 µg of teak wood samples were analyzed by pyrolysis-gas chromatography-mass spectrometry (Py-GCMS) with n-eicosane (0.1 µg) as an internal standard. Samples were inserted into the SF PY1-EC50F eco cup and were covered by glass wool. The eco-cup was pyrolyzed at 500°C for 0.1 min using a multi-shot pyrolyzer (EGA/PY-3030D) which was interfaced (interface temperature 280°C) with a GC/MS system QP-2020 NX (Shimadzu, Japan) equipped with an SH-Rxi-5Sil MS column (Restek, Germany), with electron impact of 70 eV and helium as a carrier gas. The pressure was 20.0 kPa (15.9 ml min-1, column flow 0.61 ml min-1). The temperature

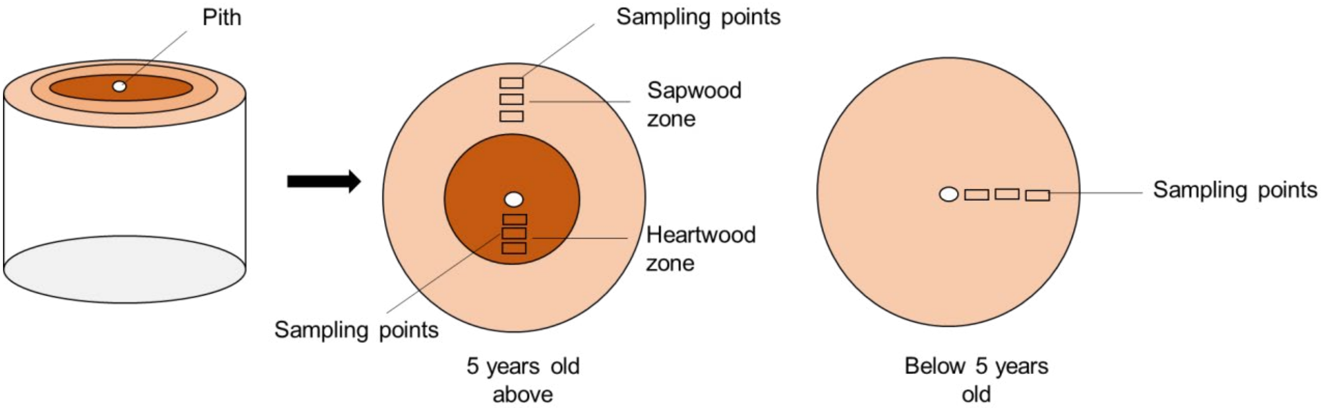

Figure 1. Schematic diagram of wood sample preparation (radial position)

profile for GC was as follows: 50°C hold for 1 min, then the temperature increased until 280°C (5°C min-1), and 13 min at 280°C. Pyrolisis products were identified by comparing their retention times and mass spectra data with NIST LIBRARY 2017.14.

2.3. Interdependence Multivariate Analyses

In this study, we performed two interdependence multivariate analyses, namely Principal Component Analysis (PCA), followed by agglomerative hierarchical clustering or Hierarchical Clustering on Principal Components (HCPCs). PCA was performed according to the previous study (Julaeha *et al.* 2020). Table 1 was transposed and converted into a matrix (row i, column k), as depicted in Table S1. The teak wood samples were assigned as observations (i), whereas pyrolysis products were as descriptors (k). Mean centering and scaling were applied to the matrix in the pre-processing stage. The mean centering procedure was performed to maintain the important variation. The scaling step was employed due to the different scales of pyrolysis products.

An orthogonal linear transformation was applied to the matrix to produce principal components (Husson *et al.* 2011). F_s (resp. G_s) indicates the coordinate vectors of the teak wood samples (resp. pyrolysis products), which can be expressed as:

$$F_s(i) = \frac{1}{\sqrt{\lambda_s}} \sum_k x_{ik} m_k G_s(k) \quad (1)$$

$$G_s(k) = \frac{1}{\sqrt{\lambda_s}} \sum_k x_{ik} p_i F_s(i) \quad (2)$$

$F_s(i)$ and $G_s(k)$ represent the coordinates of teak wood sample i and pyrolysis product k on the axis s. Notation λs is the eigenvalue corresponding to the axis s. Notations of m_k and p_i are the weights associated with pyrolysis product k and teak wood sample i, respectively, whereas x_{ik} refers to the matrix (row i, column k).

The first PCs responsible for at least 80% variance were retained and subjected to agglomerative hierarchical clustering. The most similar individual observations i were agglomerated iteratively based on the pairwise distance of Ward's criterion. The number of clusters was selected according to the hierarchical tree.

PCA and HCPC were computed in the R programming language environment (R Core Team 2019) using FactoMineR (Lê *et al.* 2008). The results were visualized using factoextra (Kassambara and Mundt 2017) or ggplot2 (Wickham 2016).

2.4. MAQ Analysis

Quantitative analysis of 2-methyl-anthraquinone (MAQ) has been carried out on the program generated from the above Py-GCMS. Calibration line were created by injection of various concentration of MAQ and n-eicosane (IS; internal standard) (1:25; 1:20; 1:10; 1:1; 5:1; 10:1 w/w). Three replicates were performed for each standard. The amount of MAQ was determined using the equation below:

$$\text{Weight of MAQ } (\mu g) = WF \times \frac{\text{Area of MAQ}}{\text{area of IS}} \times W\,IS\,(\mu g) \quad (1)$$

$$\text{Yield of MAQ (ppm)} = \frac{W\,MAQ\,(\mu g)}{Wo\,(\mu g)} \times 10^6 \quad (2)$$

Where:

WF	= weight factor (slope from calibration line)
Wis	= weight of IS
Wo	= oven-dry weight of a sample

The main ion intensity (MI) conversion factors (weight-to-MI area on the chromatogram) for the lignin pyrolysis products were obtained by making calibration lines between the weight and area ratios of commercial monomeric lignin model compounds and the internal standard. Approximately 15 mg of each compound was dissolved in 50 ml of ethanol. Calibration lines were created by injections of various amounts of the compound with 0.1 g of IS. Three replicas were performed for each sample. The amount of MAQ was calculated using the MI conversion factor of the product. The yields (in ppm) were based on the weight of the oven-dried teak wood prepared sample.

3. Results

3.1. Chemical Components Analysis by Py-GCMS Coupled with Interdependence Multivariate Analysis

The chemical components of teakwood were characterized by Py-GCMS, a rapid analysis with no preparation in a small sample. The pyrogram results of the conventional and platinum fast-grown teak wood are presented in Figure 2. 58 compounds were identified on the pyrogram and classified as derivatives of carbohydrates, lignin, and extractives (Table 1). The major pyrolysis product originated from lignin (30 peaks), carbohydrates (23 peaks), and extractives (5 peaks). In terms of lignin, it was fragmented into monomers H-unit (p-hydroxyphenyl unit), G-units (Guaiacyl unit,) and S-units (Syringyl

Table 1. Pyrolysis products (as % relative of total chromatogram area) from conventional and fast-grown platinum teak wood

Rt (min)	Pyrolysis product	Origin	Conventional teak wood				Platinum teak wood										
			20 yo		10 yo		10 yo		9 yo		8 yo		5 yo		4 yo	3 yo	2 yo
			H	S	H	S	H	S	H	S	H	S	H	S	H/S	H/S	H/S
1.87	Pyrolysis product Furfural	C	1.08	7.29	6.87	7.39	6.62	5.95	5.97	6.23	6.24	6.41	6.50	6.66	8.54	9.47	18.24
2.15	Ethyne, fluoro-	C	3.44	2.16	2.51	2.53	3.02	2.46	2.80	2.74	2.83	2.82	3.43	4.87	2.46	2.09	47.19
2.44	CH3C(O)O(CH2)3CH=CH2	C	2.25	11.16	8.54	2.24	9.49	8.92	8.99	8.95	9.56	8.82	9.86	2.68	9.84	10.05	3.17
2.79	Ethyl Acetate	C	1.91	0.72	0.58	5.73	0.79	0.44	0.63	0.61	0.70	0.58	0.52	7.99	0.64	0.51	n.d
2.97	Acetic acid	C	3.53	2.91	4.06	4.87	4.17	4.13	4.21	4.37	4.30	4.48	4.40	0.53	4.92	5.20	n.d
3.23	2-Propanone, 1-hydroxy-	C	1.66	0.26	0.66	0.91	0.59	0.78	0.10	0.74	0.71	0.59	0.47	4.87	0.15	0.63	n.d
4.42	Acetic acid (acetyloxy)-	C	1.93	0.56	0.37	2.22	3.37	2.97	3.42	3.16	3.40	0.61	3.12	0.81	3.19	2.13	n.d
5.17	(S)-5-Hydroxymethyl-2[5H]-furanone	C	0.48	0.19	0.71	0.67	0.48	0.27	0.53	0.44	0.44	3.74	0.48	3.09	0.14	0.56	n.d
5.64	Furfural	C	1.35	1.89	1.23	1.39	1.42	1.38	1.45	1.37	1.37	1.36	1.38	1.44	1.55	1.41	1.37
5.88	1,2-Cyclopentanedione	C	2.72	1.40	1.02	1.21	0.99	0.89	1.17	1.30	1.20	1.29	1.30	1.36	1.29	1.24	n.d
6.38	trans-4-(Hydroxymethyl) cyclohexane carboxylic acid, O-acetyl	C	0.72	1.16	n.d	0.62	0.58	0.36	0.86	0.83	0.82	0.75	0.51	0.58	n.d	0.60	3.53
6.81	4-Cyclopentene-1,3-dione	C	0.34	0.49	0.4	0.41	0.32	0.13	0.42	0.38	0.38	0.37	0.38	0.38	0.44	0.30	0.66
7.40	2,4-Dimethylfuran	C	0.25	0.59	1.95	0.39	0.37	0.43	0.38	0.55	0.42	0.54	0.40	0.46	0.77	0.40	n.d
7.61	2(5H)-Furanone	C	0.42	1.66	1.55	1.74	1.37	1.48	1.47	1.52	1.54	1.71	1.39	1.72	1.74	1.50	n.d
8.07	1,2-Cyclopentanedione	C	1.51	4.63	1.36	1.84	1.60	3.95	3.99	4.32	4.91	4.17	1.73	3.61	3.93	3.18	n.d
10.00	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	C	1.21	1.33	0.33	0.58	2.68	2.55	0.37	0.39	0.41	0.41	0.33	0.58	0.46	1.66	n.d
11.00	D-Limonene	Extractive	2.27	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	3.46	3.41	n.d	n.d	n.d
11.53	4-Methyl-5H-furan-2-one	C	0.38	0.98	0.32	0.31	0.33	0.31	0.4	0.31	0.30	0.28	0.30	0.41	0.44	0.36	n.d
11.85	Phenol, 3-methyl-	H	0.34	0.36	0.25	0.39	0.29	0.92	0.44	0.60	0.82	0.30	0.50	4.17	0.43	0.21	0.88
12.63	Pentanal	C	2.07	0.63		2.96	0.76	3.06	2.58	2.30	2.72	2.78	2.74	2.63	3.09		1.65
12.80	Guaiacol	G	2.43	4.30	2.94	3.67	2.99	4.22	3.26	4.15	3.94	4.37	3.86	0.37	2.49	3.23	4.37
13.73	Maltol	C	0.57	0.25	2.22	0.36	2.07	0.40	0.30	0.34	0.33	0.34	0.37	0.38	0.32		0.53
14.02	Benzofuran, 2,3-dihydro-	C	1.58	0.86	0.28	0.83	0.94	0.63	0.89	0.70	0.82	0.60	0.69	0.78	0.65	0.39	0.4
14.72	N-[3-(Cyano-dimethyl-methyl)-1-methyl-cyclopentyl]-acetamide	C	0.80	0.29	0.89	0.15	0.16	1.12	0.18	0.20	0.19	0.20	0.19	0.20	0.12	0.10	0.98
15.11	1,4-Dioxaspiro[2.4]heptan-5-one, 7-methyl-	C	0.98	1.24	0.12	1.17	1.54	0.36	1.50	1.23	1.23	0.94	1.07	2.25	1.08	0.65	0.13
15.68	5-methyl Guaiacol	G	0.82	0.35	1.12	0.37	0.39	0.37	0.33	0.36	0.35	0.36	0.32	1.29	0.22	0.22	0.67
16.01	4-methyl Guaiacol	G	2.32	3.14	2.15	2.27	2.98	2.93	3.10	3.07	2.97	2.58	2.47	0.59	2.70	1.37	1.76
16.76	Catechol	H	1.48	0.76	0.64	1.66	1.11	2.50	0.96	1.96	0.94	1.61	1.31	0.74	1.19	1.47	2.32
18.05	2-methoxy catechol	H	0.76	1.08	1.23	0.70	0.42	1.52	1.13	1.34	1.10	1.34	1.18	4.32	1.31	0.72	1.60
18.55	4-ethyl Guaiacol	G	0.62	0.84	0.41	0.55	0.61	0.85	0.60	0.82	0.72	0.76	0.73	3.64	0.56	0.53	0.55
19.55	4-vinyl Guaiacol	G	5.83	4.05	3.32	4.24	3.25	4.26	3.43	4.10	3.92	4.55	4.01	0.36	3.37	3.56	1.36
20.65	Syringol	S	4.03	3.65	3.60	4.49	2.87	3.08	2.99	3.02	3.00	2.95	3.30	0.22	3.28	5.62	3.41
20.82	Eugenol	G	0.83	1.03	0.78	0.63	0.85	0.98	0.90	0.92	1.00	0.93	0.84	0.63	0.72	0.59	0.52
22.24	Vanillin	G	1.71	1.26	0.92	1.11	1.01	1.23	1.22	1.18	1.18	1.07	0.94	0.90	1.08	0.49	n.d
22.86	4-methyl Syringol	S	1.07	2.36	n.d	1.90	n.d	n.d	1.98	n.d	n.d	1.41	n.d	1.58	1.92	n.d	1.21

Table 1. Continued

Rt (min)	Pyrolysis product	Origin	Conventional teak wood				Platinum teak wood										
			20 yo		10 yo		10 yo		9 yo		8 yo		5 yo		4 yo	3 yo	2 yo
			H	S	H	S	H	S	H	S	H	S	H	S	H/S	H/S	H/S
22.99	trans-Isoeugenol	G	1.19	n.d	0.46	n.d	0.62	0.70	3.25	0.64	0.61	n.d	0.6	3.07	2.75	0.40	n.d
23.34	5-methyl Syringol	S	2.41	n.d	1.85	n.d	2.00	1.66	n.d	1.74	1.72	0.65	1.69	n.d	n.d	1.96	n.d
23.50	Eugenol (cis)	G	2.96	3.21	2.65	2.71	3.33	3.39	0.63	3.38	3.33	3.38	3.14	n.d	n.d	2.30	n.d
24.54	Acetoguaiacone	S	1.35	1.30	1.04	1.21	1.16	1.26	1.21	1.23	1.19	1.16	0.94	0.93	1.04	0.66	1.01
25.31	4-ethyl Syringol	G	1.06	1.06	1.68	0.42	0.83	1.00	0.56	0.83	0.77	1.40	1.51	0.76	0.86	2.13	n.d
25.58	Guaiacyl acetone	S	0.76	0.87	2.62	0.76	0.69	n.d	0.62	0.95	0.82	2.76	2.53	1.49	0.87	3.12	n.d
26.29	4-vinyl Syringol	S	1.78	2.88	4.37	4.94	3.33	n.d	3.39	3.38	3.16	3.22	3.64	3.92	3.82	5.86	1.21
26.46	5-vinyl Syringol	S	2.17	n.d	n.d	n.d	n.d	3.33	n.d	n.d	n.d	n.d	n.d	0.82	n.d	1.11	n.d
27.28	4-allyl Syringol	S	0.58	1.14	1.01	1.12	1.08	0.84	1.02	1.19	0.81	0.68	0.82	0.34	0.99	0.98	n.d
27.77	Levoglucosane	C	5.54	3.04	6.83	3.36	4.38	2.64	3.95	2.34	2.41	1.06	1.26	n.d	2.83	n.d	n.d
28.51	4-propenyl Syringol cis)	S	1.11	0.66	1.28	0.47	0.71	0.60	0.65	0.85	1.15	0.72	1.08	n.d	1.30	n.d	0.60
28.88	Syringaldehyde	S	1.52	1.06	1.56	1.43	1.08	0.88	1.18	1.06	0.98	0.69	0.93	0.79	1.45	1.28	n.d
29.83	4-propenyl Syringol (trans)	S	3.98	3.49	3.30	3.64	3.57	2.72	3.30	2.79	2.60	2.35	2.74	1.03	3.29	3.89	n.d
30.55	Acetosyringone	S	1.59	0.99	1.18	1.20	6.25	0.84	1.10	0.89	0.82	0.72	0.76	2.74	1.05	1.11	0.70
30.97	Coniferyl alcohol cis)	G	5.18	6.53	8.34	8.03	0.84	7.89	7.61	8.43	8.20	9.60	7.86	0.65	7.22	6.25	n.d
31.34	Syringylacetone	S	1.78	0.97	1.22	1.23	1.05	0.92	0.99	0.90	0.84	0.82	0.93	7.44	0.98	1.35	n.d
32.60	Propiosyringone	S	0.74	0.63	0.44	0.53	0.38	0.43	0.38	0.43	0.39	0.32	0.41	0.84	0.38	0.28	n.d
34.67	Sinapyl alcohol (cis)	S	0.48	0.62	0.91	0.89	0.68	0.62	0.75	0.67	0.65	0.55	0.72	n.d	0.82	0.87	n.d
36.40	Sinapyl alcohol (trans)	S	1.53	2.96	3.72	4.39	2.43	2.19	2.44	2.33	2.34	2.48	2.63	0.7	3.08	4.68	n.d
38.82	2-methyl anthraquinone (MAQ)	Extractive	1.74	0.96	1.41	0.19	2.69	0.52	2.15	0.29	0.80	0.12	0.19	2.97	0.06	0.11	n.d
40.79	1-hydroxy-3-methyl anthraquinone	Extractive	0.48	0.34	0.30	0.15	0.57	0.24	0.46	0.18	0.32	0.18	0.15	0.15	0.09	n.d	n.d
48.17	(E)-3,3'-Dimethoxy-4,4'-dihydroxystilbene	Extractive	1.32	1.27	0.52	0.83	0.58	0.95	0.99	1.01	1.03	1.13	0.98	n.d	0.67	0.39	n.d
50.95	Squalene	Extractive	3.07	0.21	n.d	n.d	0.98	0.08	0.64	n.d	0.30	n.d	n.d	0.86	0.00	n.d	n.d
	Total carbohydrate (%)		36.72	45.69	42.8	43.88	48.04	45.61	46.56	45.32	47.23	44.85	42.82	48.28	48.59	42.43	77.85
	Total H (%)		2.58	2.20	2.12	2.75	1.82	4.94	2.53	3.90	2.86	3.25	2.99	9.23	2.93	2.40	4.80
	Total G (%)		24.95	25.77	24.77	24.00	17.7	27.82	24.89	27.88	26.99	29.00	26.28	12.26	21.97	21.07	9.23
	Total S (%)		26.88	23.58	28.1	28.2	27.28	19.37	22.00	21.43	20.47	21.48	23.12	22.84	24.27	32.77	8.14
	Total Lignin (%)		54.41	51.55	54.99	54.95	46.8	52.13	49.42	53.21	50.32	53.73	52.39	44.33	49.17	56.24	22.17
	Total extractive (%)		8.88	2.78	2.23	1.17	4.82	1.79	4.24	1.48	2.45	1.43	4.78	7.39	0.82	0.50	0.00
	S/G Ratio		1.08	0.92	1.13	1.18	1.54	0.70	0.88	0.77	0.76	0.74	0.88	1.86	1.10	1.56	0.88
	L/C Ratio		1.48	1.13	1.28	1.25	0.97	1.14	1.06	1.17	1.07	1.20	1.22	0.92	1.01	1.33	0.28

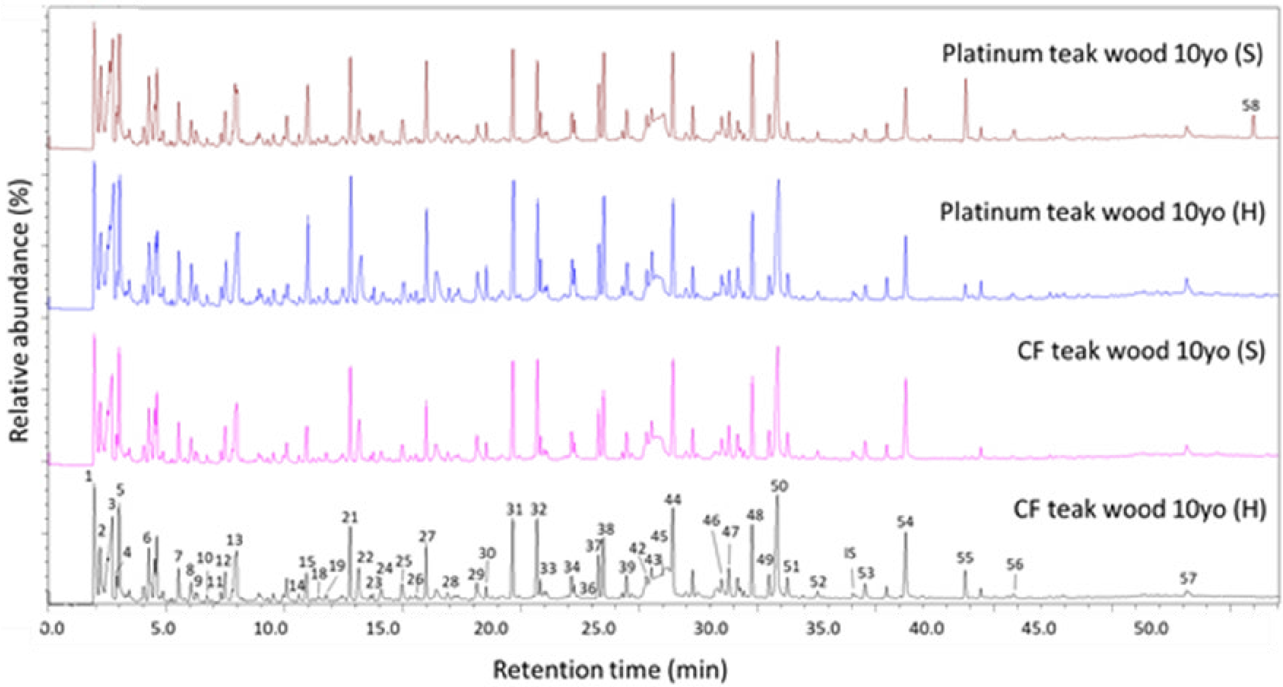

Figure 2. Py-GCMS pyrogram of 10 years-old Tectona grandis for fast-grown platinum and conventional teak wood. The Pyrolysis product peaks (1-58) are presented in Table 1, and n-eicosane for internal standard (IS)

unit). The carbohydrate derivatives were mostly detected in earlier retention time, followed by lignin and extractive. Levoglucosane (45) was the major pyrolysis product and was identified at 27.77 min retention time, originating from carbohydrates, both cellulose and hemicellulose. Extractive derivatives such as 2-methyl-anthraquinone (MAQ), 1-hydroxy-3-methyl anthraquinone, (E)-3,3-dimethoxy-4,4'-dihydroxystilbene, and squalene) were detected at the fingerprint area at the end of the pyrogram. We employed multivariate interdependence analysis techniques to further elucidate the chemical fingerprints from teak wood pyrolysis products.

3.2. 2-Methyl Anthraquinone (MAQ) Analysis

The durability of teak wood was assumed due to MAQ, which has antifeedant activity or toxicity. MAQ may affect the palatability of wood or merely discourage termite feeding. However, a previous study confirmed that MAQ concentration did not influence the toxicity and feed deterrent effects. The interaction of MAQ and other extractives may contribute to the durability of teak wood.

In this study, the MAQ content was used to determine the resistance of fast-grown wood compared to conventional wood. However, further resistance tests must be conducted to determine more accurate resistance against termite or fungal attacks. The MAQ peaks in the pyrogram were detected as an extractive derivative along with (17), (56), (57), and (58). A calibration line for MAQ was obtained using Py-GCMS, which is shown in Figure 3. The slope of the calibration line was the conversion factor of the area ratio into the weight ratio using n-eicosane as the internal standard.

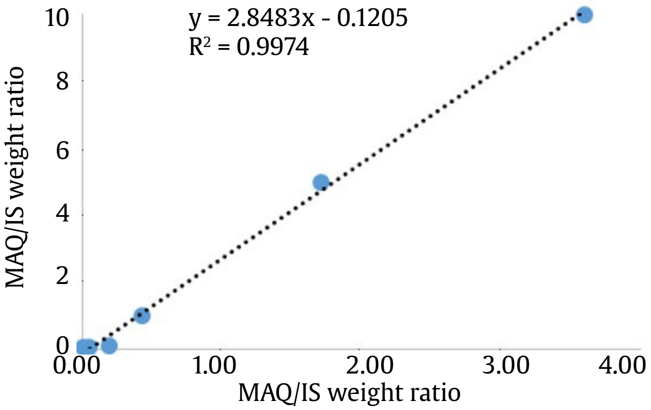

Figure 3. MAQ and IS calibration line by Py-GCMS

4. Discussion

4.1. Chemical Components Analysis by Py-GCMS

Extractive derivatives such as 2-methyl-anthraquinone (MAQ), 1-hydroxy-3-methyl anthraquinone, (E)-3,3-dimethoxy-4,4'-dihydroxystilbene, and squalene) were detected at the fingerprint area at the end of the pyrogram. The previous report of (E)-3,3-dimethoxy-4,4'-dihydroxystilbene from teak wood was unattainable, but several reports regarding its isolation from Leuzea carthamoides root were available. (E)-3,3-dimethoxy-4,4'-dihydroxystilbene from L. carthamoides displayed a stimulant (Hajdu *et al.* 1998) and anti-inflammatory (Nahar *et al.* 2014). The compound (57) was presumably a free monomer from extractive derivatives rather than a part of lignin polymer (Kishimoto *et al.* 2004; Rönnols *et al.* 2015). Pyrogram results also displayed the presence of stilbene as an extractive derivative. This compound is one of the phenolic compounds commonly found in wood and is responsible for natural resistance and the activity of flavonoids, quinones, and tannins (Nascimento *et al.* 2013; Wolcott 1950). Extractive derivatives were applicable to determine the association between wood resistance and the possibility of future genetic modification for wood properties enhancement. Sapwood and heartwood pyrogram (Figure 2) presented a significant difference between forest community and platinum fast-grown teak. Along with the differences in age and wood parts (sapwood and heartwood), the relative abundance of carbohydrates, lignin, and extractive was also observed.

Total carbohydrate derivatives were 77.85%, 42.43%, and 48.59% in 2, 3, and 4-year-old fast-grown teak wood. A notable amount of carbohydrates in the early formation of wood was caused by the role of carbohydrates in the plant growth process as a building block and energy carrier for plant metabolic processes (Hartmann *et al.* 2018). As platinum teak ages, a higher amount of carbohydrates were accumulated in the heartwood. Platinum teak showed higher carbohydrate content (42.82-48.04%) than community-forest teak wood (36.72-45.69%).

The lignin content increases as the tree ages to support the wood's mechanical and physical properties. Lignin and extractive contents will continue to increase until 5 years of cambium formation (Cordero and Kanninen 2003).

In 5- and 10-year-old fast-grown teak wood, the total carbohydrate area in the heartwood section, tends to be higher than in the sapwood section. The finding is in line with the Py-GCMS analysis of 70-year-old teak with carbohydrate values of 61.9% and 64% for sapwood and heartwood, respectively (Lourenco *et al.* 2015). Sapwood shows a higher lignin content than heartwood by the increase in the age of fast-grown wood (Raiskila *et al.* 2007). During Py-GCMS analysis, polymer lignin is fragmented into monomers: H-unit (p-hydroxyphenyl unit), G-units (Guaiacyl unit,) and S-units (Syringyl unit). The lignin content and the lignin monomer ratio were helpful in the approach to determine the mechanical properties of wood (Carrilo *et al.* 2018; Koehler and Telewski 2006; Lourenco *et al.* 2015). Higher G-unit content in lignin contributed to better mechanical properties and durability in teak. In the sapwood, most of the lignin monomer comprised syringol-unit and smaller guaiacol units. On the contrary, heartwood displayed a higher G-unit rather than S-units. The total relative abundance of G-units was higher than S-units in sapwood and, conversely, in heartwood (Table 1).

The heartwood of 9-year-old fast-grown teak wood has higher compression strength than sapwood (Hadinata and Kozakiewicz 2020). However, the compression strength of parallel and perpendicular to the grain of 8-year-old platinum teak wood tends to increase from pith to bark, which was also a parameter that the wood is still in the juvenile formation (Adi *et al.* 2020). A lignin with more G-units, structurally more complex and condensed (more C–C inter-unit bonds), could indicate the wood stiffness and mechanical properties (Carrillo *et al.* 2018; Lourenco *et al.* 2015). Compared to conventional teak wood, a 10-year-old platinum teak wood has almost an equal amount of lignin and carbohydrate, with an L/C value between 0.97-1.14. The L/C values of 10- and 20-year-old conventional teak ranged between 1.13-1.48. In the previous report, five years old platinum teak has a higher modulus of rupture, modulus of elasticity values, and better physical and mechanical properties than 10-year-old conventional teak wood (Darmawan *et al.* 2015; Rizanti *et al.* 2018). Furthermore, the platinum teak density reached 0.52 g cm3 -1 (Adi *et al.* 2020), higher than conventional teak wood.

4.2. Multivariate Interdependence Analysis

In the initial exploratory data analysis, pairwise Pearson correlations among pyrolysis products to evaluate the collinearity were calculated. The correlation plot (Figure S1) showed the collinearity of some pyrolysis products. Twenty-one pyrolysis products displayed high correlations, above 75%. Seven are carbohydrate origin, including acetic acid, ethyne, furfural, 1-hydroxy-2-propanone, O-acetyl trans-4-(hydroxymethyl)cyclohexane carboxylic acid, 1,2-cyclopentadiene, and 2,3-dihydro-benzofuran. The other five pyrolysis products with high collinearity come from lignin-G: 4-vinyl guaiacol, 4-ethyl guaiacol, 4-methyl guaiacol, vanillin, and 4-ethyl syringol. Two high collinearity pyrolysis products, 3-methyl-phenol and 2-methoxy catechol, originated from lignin-H. In contrast, lignin-S contributes five pyrolysis products with high correlations: sinapyl alcohol (cis), 4-propenyl syringol (trans), 4-allyl syringol, syringylacetone, and 5-methyl syringol. Meanwhile, (E)-3,3'-dimethoxy-4,4'-dihydroxystilbene is the only pyrolysis product from extractive with high collinearity. In contrast, the correlation plot of teak wood samples does not display collinearity above 75% (Figure S2). The highest collinearity is shown by heartwood of 8-years-old and sapwood of 9-years-old fast-grown platinum teak woods, which are 73% positively correlated.

Additionally, a principal component analysis was conducted. Figure 3 showed that the combination of PC1 and PC2 only covered 46.3% of the total variance. Meanwhile, the cumulative variance described by the first three PCs was 58.3%, less the ideal percentage of total variance captured (80%) (Varmuza and Filzmoser 2006).

In order to further analyze the number of considered PCs, a 10-fold cross-validation procedure on PCA was conducted. The result showed that the variance captured by the first three PCs (Figure 3) was lower than the pairwise analysis result. The minimum number of the first thirteen PCs was required to explain 80% of the total variance (Figure 3).

The lack of variance captured by the first three PCs may limit the pattern recognition on the teak wood data. Nevertheless, in such a situation, PCA is still a beneficial tool. PCA can transform continuous variables, from the teak wood pyrolysis product data set, into new ones without redundancy and containing the most informative features (Husson *et al.* 2011).

Using PCA, hierarchical clustering on principal components (HCPC) was conducted. Ward's criterion based on multidimensional variance (Murtagh and Contreras 2012) was applied to PCs in the hierarchical clustering computation. Cluster dendrogram visualization suggests five hierarchical clusters (Figure 4).

Figure 4. HCPC dendrogram of teak wood pyrolysis products. The height represents the dissimilarity between clusters. FGP denotes fast-grown platinum, CF conventional, H heartwood, S sapwood, and H/S slab from teak wood under 5-year-old.

The sapwood part of 5-year-old fast-grown platinum has its cluster alone. This entire cluster may be due to a clear separation between sapwood and heartwood starting from 5-year-old. Similarly, the

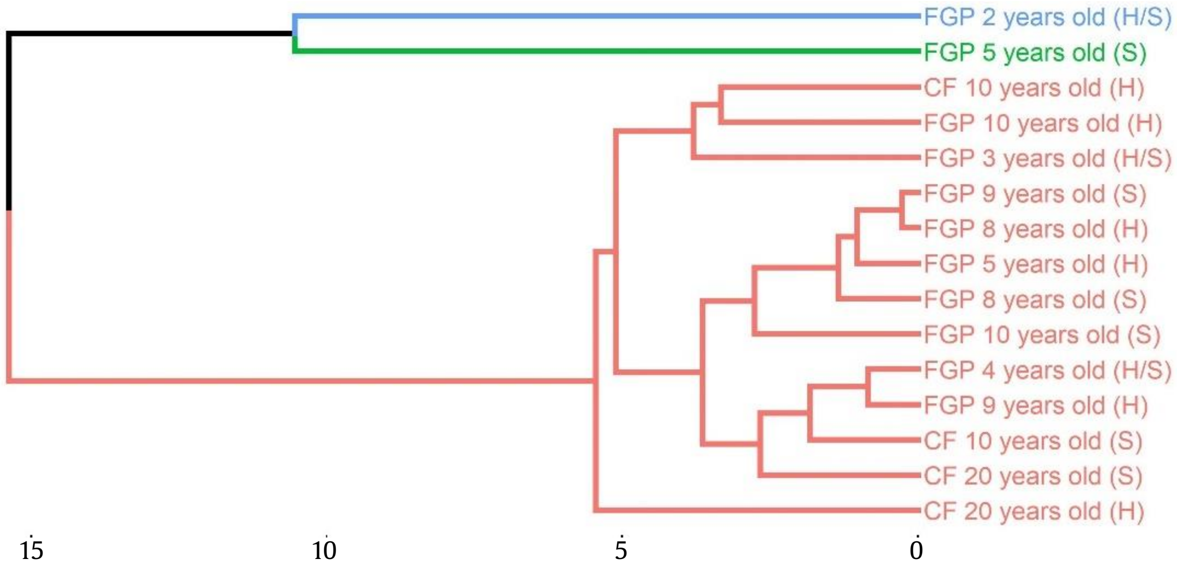

Figure 4. Py-GCMS pyrogram of 10 years-old Tectona grandis for fast-grown platinum and conventional teak wood. The Pyrolysis product peaks (1-58) are presented in Table 1, and n-eicosane for internal standard (IS)

slab sample from 2-year-old fast-grown platinum is also separated from the other clusters.

The remaining samples are in a big cluster (Figure 3, indicated by pink color). The heartwood from the oldest conventional has the highest height among other samples in the group, which may indicate its different chemical composition to other samples. Nonetheless, its sapwood is in the same sub-cluster as that of 10-year-old conventional teak wood, along with samples of heartwood and slab of 9 and 4-year-old fast-grown platinum samples, respectively.

Next, we performed PCA and HCPC calculations on pyrolysis products from lignin, which corresponds to the wood stiffness and mechanical resistance, to investigate any possible clustering pattern. The PCA results on the pyrolysis product of lignin are better than those of all peaks in better variance (Figures S3, S4, S6, and S7). Nonetheless, three first PCs only capture 66.78% of the total variance (Figure S6), whereas a 10-fold cross-validation procedure suggests at least ten first PCs to fulfill variance around 80%. Hence, we calculated an HCPC from fourteen PCs from lignin pyrolysis products of teak wood samples. The HCPC dendrogram of lignin pyrolysis products (Figure 5A) suggests a similar clustering to that of all peaks in pyrograms (Figure 3).

We further computed HCPC on pyrolysis products of lignin-S as the first highest lignin content in teak woods studied. Even the resulting HCPC dendrogram (Figure 5B) displays a similar clustering to previous ones (Figures 4 and 5A); it displays a lower height among clusters which may indicate a lower dissimilarity of lignin-S among teak wood samples. The HCPC dendrogram suggests that the heartwood of 20 -year-old conventional and the sapwood of 10-year-old fast-growing platinum samples have similar lignin-S content. Likewise, the sapwoods of 10 and 20-year-old conventional samples are similar in lignin-S content to the slab of 4-year-old and the heartwood of 9-year-old fast-growing platinum samples.

Figure 4. HCPC dendrograms of (A) all-lignin, (B) lignin S, and (C) lignin G pyrolysis products from teak woods. The height represents the dissimilarity between clusters. FGP denotes fast-grown platinum, CF conventional, H heartwood, S sapwood, and H/S slab from teak wood under 5-year-old.

The HCPC on the second highest content of lignin type in teak wood samples, lignin-G, was also conducted. The resulting HCPC dendrogram (Figure 4C) suggests that lignin-G content in the sapwood of 20-year conventional is very similar to the sapwoods of 9- and 10-year and the heartwood of 8-year fast-growing platinum teak woods.

4.3. 2-Methyl Anthraquinone (MAQ) Analysis

Table 2 shows the content of MAQ in both teak wood, conventional and fast-grown platinum on heartwood and sapwood. MAQ has been detected in 2-year-old fast-grown teak wood at 12.38% and increased as the tree ages. The distribution of MAQ tends to increase from sapwood to heartwood. Furthermore, at the age of 10 years, platinum teak wood has 2.5 times higher MAQ content compared to conventional-grown teak and almost 2 times higher than 20-year-old conventional-grown teak wood. Hence, platinum teak wood can be harvested in a shorter growth period than conventional-grown teaks.

In conclusions, platinum fast-grown teak wood aged five and older has the relatively same to higher chemical content than conventional teak wood. The MAQ as an essential chemical compound in wood durability showed that at the age of 10, the

Table 2. The yield of MAQ on teak wood in different ages

Sample	Teak wood ages (year old)	MAQ content (ppm)	
		Heartwood	Sapwood
Conventional teak wood	20	392.06±4.89	133.90±58.40
	10	272.83±86.04	18.87±7.70
Platinum teak wood	10	694.20±90.15	64.99±21.24
	9	542.26±7.07	50.77±16.59
	8	237.36±34.44	15.23±4.76
	5	33.41±2.56	27.80±3.56
	4	10.42±2.50	
	3	12.38±4.32	
	2	n.d	

n.d means not determined

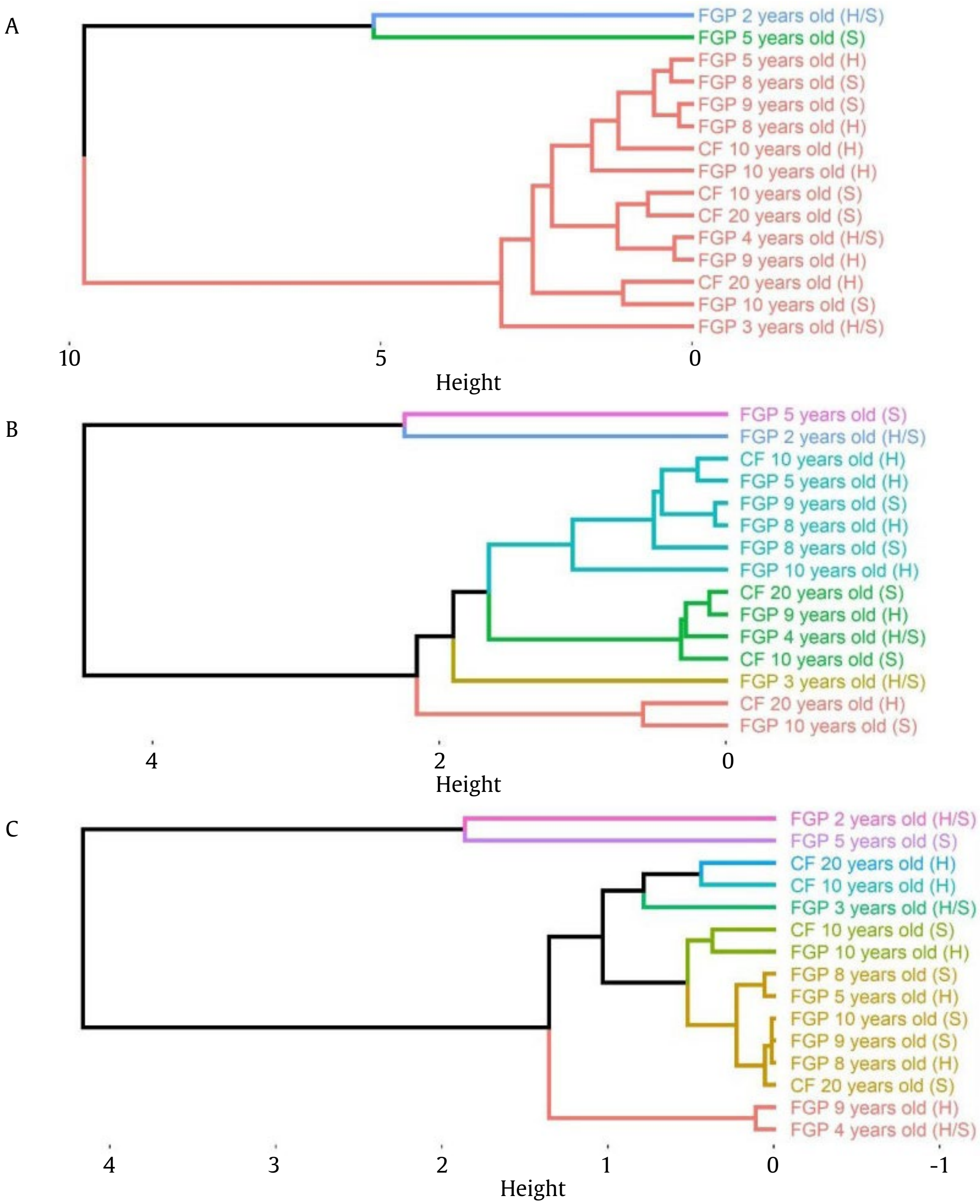

Figure 5. HCPC dendrograms of (A) all-lignin, (B) lignin S, and (C) lignin G pyrolysis products from teak woods. The height represents the dissimilarity between clusters. FGP denotes fast-grown platinum, CF conventional, H heartwood, S sapwood, and H/S slab from teak wood under 5-year-old

fast-grown teak had a MAQ content of 2.5 times higher than that of conventional teak and almost 2 times higher than that of 20-year-old. The chemical content study of fast-grown teak provided an approach to studying wood durability and its use for industry or society. Further investigation is vital to determine the durability of fast-grown teak wood comprehensively.

References

Adi, D.S., Himmi, S.K., Amin, Y., Darmawan, T. and Dwianto, W., 2020. Radial variation of wood properties of eight years-old fast-growing teak (*Tectona grandis*-Platinum teak wood). *IOP Conference Series: Earth and Environmental Science.* 591, 012035. https://doi.org/10.1088/1755-1315/591/1/012035

Adi, D.S., Sudarmanto, S., Ismadi, I., Gopar, M., Darmawan, T., Amin, Y., Dwianto, W. and Witjaksono, W., 2016. Evaluation of the wood quality of platinum teak wood. *Teknologi Indonesia*. 39, 36-44.

Carrillo, I., Vidal, C., Elissetche, J.P. and Mendonça, R.T., 2018. Wood anatomical and chemical properties related to the pulpability of *Eucalyptus globulus*: a review. *Southern Forests: a Journal of Forest Science*. 80, 1-8. https://doi.org/10.2989/20702620.2016.1274859

Colombini, M.P., Orlandi, M., Modugno, F., Tolppa, E.L., Sardelli, M., Zoia, L. and Crestini, C., 2007. Archaeological wood characterisation by py/gc/ms, gc/ms, nmr and gpc techniques. *Microchemical Journal.* 85, 164-173. https://doi.org/10.1016/j.microc.2006.05.001

Cordero, L.P., Kanninen, M., 2003. Heartwood, sapwood and bark content, and wood dry density of young and mature teak (*Tectona grandis*) trees grown in Costa Rica. *Silva Fennica*. 37, 45-54. https://doi.org/10.14214/sf.511

Damayanti, R., Ozarska, B., Pandit, I.K.N., Febrianto, F. and Pari, G., 2018. Wood properties of 5-year-old fast grown teak. *Wood Research Journal*. 9, 29-34. https://doi.org/10.51850/wrj.2018.9.2.29-34

Darmawan, W., Nandika, D., Sari, R.K., Sitompul, A., Rahayu, I., Gardner, D., 2015. Juvenile and mature wood characteristics of short and long rotation teak in Java. *IAWA journal.* 36, 428-442. https://doi.org/10.1163/22941932-20150112

Fofana, I.J., Ofori, D., Poitel, M., Verhaegen, D., 2009. Diversity and genetic structure of teak (*Tectona grandis* Lf) in its natural range using DNA microsatellite markers. *New For.* 37, 175–195. https://doi.org/10.1007/s11056-008-9116-5

Hadinata, M.E., Kozakiewicz, P., 2020. An investigation of selected properties of teak wood from 9-year-old plantation forest in Indonesia. *Annals of Warsaw University of Life Sciences–SGGW. Forestry and Wood Technology*. 110, 61-72. https://doi.org/10.5604/01.3001.0014.3929

Hajdu, Z., Varga, E., Hohmann, J., Kalman, A., Argay, G., Guenther, G., 1998. A Stilbene from the Roots of Leuzea c arthamoides. *Journal of Natural Products*. 61, 1298-1299. https://doi.org/10.1021/np980128i

Hartmann, H., Adams, H.D., Hammond, W.M., Hoch, G., Landhäusser, S.M., Wiley, E. and Zaehle, S., 2018. Experiments with trees: from seedlings to ecosystems. *Environmental and Experimental Botany.* 152, 1-6.

Haupt, M., Leithoff, H., Meier, D., Puls, J., Richter, H.G., Faix, O., 2003. Heartwood extractives and natural durability of plantation-grown teakwood (*Tectona grandis* L.)—a case study. *European Journal of Wood and Wood Products*. 61, 473-474. https://doi.org/10.1007/s00107-003-0428-z

Husson, F., Lê, S., Pagès, J., 2011. Exploratory Multivariate Analysis by Example Using R, first ed. CRC Press, Boca Raton. https://doi.org/10.1201/b10345

Ismayati, M., Nakagawa-Izumi, A., Kamaluddin, N.N. and Ohi, H., 2016. Toxicity and feeding deterrent effect of 2-methylanthraquinone from the wood extractives of *Tectona grandis* on the subterranean termites *Coptotermes formosanus* and *Reticulitermes speratus*. *Insects*. 7, 63. https://doi.org/10.3390/insects7040063

Julaeha, E., Dewi, K.S., Nurzaman, M., Wahyudi, T., Herlina, T., Hardianto, A., 2020. Chemical compositions and antioxidant activities of Indonesian citrus essential oils and their elucidation using principal component analysis. *Preprints.* 2020, 2020110586. https://doi.org/10.20944/preprints202011.0586.v1

Kassambara, A., Mundt, F., 2017. Factoextra: extract and visualize the results of multivariate data analyses. *R Package Version*. 1, 337-354.

Kishimoto, T., Ueki, A., Takamori, H., Uraki, Y. and Ubukata, M., 2004. Delignification mechanism during high-boiling solvent pulping. Part 6: Changes in lignin structure analyzed by 1H-13C correlation 2-D NMR spectroscopy. *Holzforschung.* 4, 355-362. https://doi.org/10.1515/HF.2004.054

Koehler, L., Telewski, F.W., 2006. Biomechanics and transgenic wood. *American Journal of Botany*. 93, 1433-1438. https://doi.org/10.3732/ajb.93.10.1433

Lê, S., Josse, J., Husson, F., 2008. FactoMineR: an R package for multivariate analysis. *Journal of statistical software*. 25, 1-18. https://doi.org/10.18637/jss.v025.i01

Lourenço, A., Neiva, D.M., Gominho, J., Marques, A.V., Pereira, H., 2015. Characterization of lignin in heartwood, sapwood and bark from *Tectona grandis* using Py–GC–MS/FID. *Wood Science and Technology*. 49, 159-175. https://doi.org/10.1007/s00226-014-0684-6

Miranda, I., Sousa, V., Pereira, H., 2011. Wood properties of teak (*Tectona grandis*) from a mature unmanaged stand in East Timor. *Journal of wood science*. 57, 171-178. https://doi.org/10.1007/s10086-010-1164-8

Murtagh, F., Contreras, P., 2012. Algorithms for hierarchical clustering: an overview. *Wiley Interdisciplinary Reviews: Data Mining and Knowledge Discovery*. 2, 86-97. https://doi.org/10.1002/widm.53

Nahar, P.P., Driscoll, M.V., Li, L., Slitt, A.L. and Seeram, N.P., 2014. Phenolic mediated anti-inflammatory properties of a maple syrup extract in RAW 264.7 murine macrophages. *Journal of Functional Foods*. 6, 126-136. https://doi.org/10.1016/j.jff.2013.09.026

Nascimento, M.D., Santana, A.L.B.D., Maranhão, C.A., Oliveira, L.S. and Bieber, L., 2013. Phenolic extractives and natural resistance of wood. *Biodegradation-Life of Science*. 801, 349-370.

Pramasari, D. A., Wahyuni, I., Adi, D. S., Amin, Y., Darmawan, T., Dwianto, W., 2014. Effect of age on chemical component of platinum teak wood–a fast growing teak wood from LIPI. *In: Proceedings of The 6th International Symposium of IWoRS.* Medan: Indonesian Wood Researc Society (IWoRS), pp. 211-216.

Raiskila, S., Pulkkinen, M., Laakso, T., Fagerstedt, K., Löija, M., Mahlberg, R., Paajanen, L., Ritschkoff, A.C., Saranpää, P., 2007. FTIR spectroscopic prediction of Klason and acid soluble lignin variation in Norway spruce cutting clones. *Silva Fennica.* 41, 351-371. https://doi.org/10.14214/sf.301

Rizanti, D.E., Darmawan, W., George, B., Merlin, A., Dumarcay, S., Chapuis, H., Gérardin, C., Gelhaye, E., Raharivelomanana, P., Kartika Sari, R. and Syafii, W., 2018. Comparison of teak wood properties according to forest management: short versus long rotation. *Annals of Forest Science*. 75, 1-12. https://doi.org/10.1007/s13595-018-0716-8

Rönnols, J., Schweinebarth, H., Jacobs, A., Stevanic, J.S., Olsson, A.M., Reimann, A. and Aldaeus, F., 2015. Structural changes in softwood kraft lignin during nonoxidative thermal treatment. *Nordic Pulp and Paper Research Journal.* 30, 550-561. https://doi.org/10.3183/npprj-2015-30-04-p550-561

R Core Team, 2019. R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. Available at: https://www.R-project.org/.

Thulasidas, P.K., Bhat, K.M., 2007. Chemical extractive compounds determining the brown-rot decay resistance of teak wood. *Holz als Roh-und Werkstoff*. 65, 121-124. https://doi.org/10.1007/s00107-006-0127-7

Varmuza, K., Filzmoser, P., 2016. *Introduction to Multivariate Statistical Analysis in Chemometrics*. CRC Press, Boca Raton. https://doi.org/10.1201/9781420059496

Wickham, H., 2016. *ggplot2: Elegant Graphics for Data Analysis*. Springer. https://doi.org/10.1007/978-3-319-24277-4

Windeisen, E., Klassen, A., Wegener, G., 2003. On the chemical characterisation of plantation teakwood from Panama. *Holz als roh-und werkstoff*. 61, 416-418. https://doi.org/10.1007/s00107-003-0425-2

Wolcott, G.N., 1950. The termite resistance of pinosylvin, stilbene and other new insecticides. *The Journal of Agriculture of the University of Puerto Rico*. 34, 338-342. https://doi.org/10.46429/jaupr.v34i4.12830