The technique for separation and purification of gondorukem (gum rosin) from pine gum (pinus merkusii) with a simple distillation method

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Abstract. This study reports the processing and separation of gum rosin from pine gum (Pinus merkusii). The research method was carried out with several stages, namely the process of tapping pine gum, the process of separation and purification. After the refining process, the gum rosin and turpentine oil are separated using a simple distillation technique. The results of gum rosin separation obtained from the distillation process were 86.67 with a soft point of 78.8°C, a vaporizing component of 0.976%, an acid number of 175.3125 and a saponification number of 178.81875. In addition to knowing the components of the gum rosin samples obtained, the identification of compounds was carried out using Fourier Transform Infrared Spectrophotometer (FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS). The results of FTIR identification showed the presence of sp²C-H, -OH, sp³C-H, C=O, -CH₂ and -CH₃ groups, while GC-MS identification showed the presence components of Caryophyllene, Pimaric acid, Dehydroabietic acid, Abietic acid, and α-Pinene. The identification results indicate that the residue from the simple distillation is gum rosin.

1. Introduction

Forest is natural resources with many benefits contained in them. Forests can also improve carbon from the atmosphere, provide food and cover wildlife [1]. In Indonesia, the utilization of forests is widely used to produce forest products both wood and non-wood. However, the existence of forests in Indonesia is currently more widely used for wood production. While the potential of forests that have high value is not only wood but non-wood forest products (NTFPs) and forest product services [2-4]. NTFPs can be calculated and high-value commodities if it can be managed well. NTFPs have an important contribution to sustainable development and forest sustainability for future generations [5,6]. In this case, NTFPs in Indonesia can support sustainable forests and conservation strategies, as well as provide alternative sources of income for the rural poor [7,8].

P. merkusii is included in a multipurpose tree species that is continuously being developed and be one of the large species enough to produce wood, resin gum production, reforestation and land conservation [9]. Almost all parts of the tree can be utilized, including the trunk that can be tapped for the sap taken. The gum is further processed to be gum rosin and turpentine oil. Pine gum can be used as the main ingredient for varnishes[10], as a raw material for soap[11], an ink material and as a raw material in the paint industry [12,13]. The results of the wood can be used as lightweight building materials, crates, matches and paper raw materials [14,15]. The gum produced by P. merkusii is
classified as oleoresin [16,17]. Oleoresin is a liquid resinous acid in turpentine which drips out when
the resin duct in the bark is cut. Oleoresin is synthesized from specialized epithelial cells in the xylem
and stored in vertical resin duct in the stems, roots, needles, and cones [18]. This type of sap mainly
contains compounds terpenoid and hydrocarbons [19,20]. P.merkusiisap in NTFPs has a high
economic value when processed by gum rosin and turpentine oil.

Gum rosin is one of the NTFPs products that have promising prospects in the present and the future
developed in Indonesia. Prospective exports from Gum rosin in Indonesia can contribute to the US $ 50
million/year [21]. The opportunity to develop the gum rosin industry is quite large, given the
potential of a large pine forest that has wide-open market opportunities, both for domestic and export
needs. During the last 2014, Indonesia exported a total of 13.6 /ton rosin (gum rosin) to India each
year, of which nearly 10% of rosin was traded on international markets throughout the world. The
processing of pine resin into gum rosin and turpentine oil is very potential and reliable as a source of
foreign exchange. Nearly 60% of total Indonesia's pine gum production is exported abroad and is able
to contribute around 67% of total non-wood forest product exports[22,23].

Gum rosin based on the source of raw materials is divided into three types, namely gum rosin
obtained from the distillation residue of the sap of pine trees, wood gum rosin (wood rosin) obtained
from the extraction of wood trunks with organic solvents then the solution is distilled and gum rosin
tall oil (tall oil rosin) which is a by-product of the pulp industry made from pine wood [24,25]. Gum
rosin can be produced by heating pine tree liquid to evaporate volatile components (terpene
components). The main components are diphenic acid, mainly abietic acid, isopimaric acid,
laevoabietat acid and pimaric acid [26,27].

During the last 10 years, research has been carried out to aim at optimizing the production of pine
gum to produce gum rosin including using paraquat, N, N-dimethyl-4,4; bipyridinum dichloride to
produce reactive oxygen species and maximize the wound effect on pine merkusii[28,29]. Using the
provision of 2-chloroethyl phosphonic acid stimulants (ethylene precursor) to obtain an additional
response to the tapping process [30,31]. However, the use of the two materials is limited in large scale
operations due to high costs. Some chemicals have been validated experimentally in the field to
increase pine gum production. One of the ways to improve the tapping method is by applying
stimulant substances to increase the productivity of the gum. The stimulants used in this study were a
mixture of sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) and nitric acid (HNO\textsubscript{3}).

In this study gum of the tapping, results will be processed into gum rosin by using a simple
distillation technique. The residual product from the distillation process of Pinus gum is known as pine
rosin and is locally referred to as Gum rosin in Indonesia. The distillation process usually produces 15-
25% turpentine oil, which is the main commercial interest and leaves 70-80% rosin. Therefore, it is
necessary to strive for a simple method in obtaining gum rosin optimally by preserving wood and
forest ecosystems through pine gum tapping activities and pine resin processing into high economic
value gum rosin.

2. Experimental Methods

2.1. Reagents and apparatus
The materials used in this study were pine sap, aquades, acetone (C\textsubscript{3}H\textsubscript{6}O) (Merck), chloroform
(CHCl\textsubscript{3}), p.a (Merck), acid chloride (HCl) 0.5N p.a (Merck), Potassium hydroxide (KOH) 0.5 N,
indicator pp, alcohol 96% (Merck), sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) (Merck), and nitric acid (HNO\textsubscript{3}) (Merck).

2.2. Tapping pine gum
Tapping pine gum is done by scraping the bark of a pine tree then the wood was cut as deep as 1 cm
and wide 10 cm U-shaped upside down using a scoop. Then sprayed a mixture of sulfuric acid
(H\textsubscript{2}SO\textsubscript{4}) and nitric acid (HNO\textsubscript{3}) 2-3 times spray using a sprayer on the injured pine tree trunk. The
final stage is to installation a plastic bag at the bottom of the wiretapping wound so that the gum can
flow and be accommodated into the plastic. On the 4th day after tapping, a tapping wound was renewed with a thickness/tapping distance of 5 mm and then spraying was carried out again.

2.3. Pine gum processing

Pine gum processing was carried out with a simple distillation technique. Pine gum was weighed as much as 1.5 kg then put into a distillation container and heated at 165 °C using a gas stove for 60 minutes. Furthermore, pine gum vapor from heating results was channeled through condenser pipes and accommodated into turpentine oil, while the residue of the heating becomes gum rosin. Finally, it was characterized by Fourier-transform infrared (FTIR) and using gas chromatography-mass spectroscopy (GC-MS).

3. Results and Discussion

3.1. Characterization of Gum rosin using Fourier Transform Infra-Red (FTIR)

FTIR analysis was intended to see the functional group characteristics of a compound. In general, the FTIR spectrum can be divided into four regions and functional groups can be determined based on the location of the spectrum. The four areas include the X-H strain area (4000-2500 cm⁻¹), the triple bonding area (2500-1500 cm⁻¹), and the fingerprint area (1500-600 cm⁻¹).

![Figure 1. FTIR spectrum of gum rosin](image)

| No | Peak (cm⁻¹) | Intensity | Corr. Intensity | Base (H) | Base (L) | Area | Corr. Area | Compound |
|----|-------------|-----------|----------------|----------|----------|------|------------|----------|
| 1  | 1384.89     | 5.428     | 9.254          | 1421.54  | 1348.24  | 74.462 | 13.396     | CH₃      |
| 2  | 1463.97     | 4.447     | 19.437         | 1527.62  | 1423.47  | 90.45 | 24.756     | CH₂      |
| 3  | 1693.5      | 0.146     | 35.346         | 1855.52  | 1571.99  | 295.607 | 167.419    | C=O      |
| 4  | 2650.19     | 9.426     | 4.972          | 2702.27  | 2382.09  | 259.235 | 24.921     | sp³C-H   |
| 5  | 2870.08     | 0.966     | 0.797          | 2881.65  | 2704.2   | 234.362 | 2.048      | sp³C-H   |
| 6  | 3412.08     | 5.978     | 0.249          | 3639.68  | 3408.22  | 234.203 | 13.065     | -OH      |
The FTIR spectra (Figure 1) and the corresponding signal analysis presented in Table 1, show the characteristics of the infrared absorption band of the rosin used (Pinus merkusii). The FTIR spectrum shown in Figure 1 shows the characteristic absorption for -CH\textsubscript{3}, -CH\textsubscript{2}, C=O, sp\textsuperscript{3}C-H, -OH and sp\textsuperscript{2}C-H. Uptake of -CH\textsubscript{3} is shown by the wavelength of 1384.89 cm\textsuperscript{-1}[32]. Uptake of -CH\textsubscript{2} is shown at a wavelength of 1463.97 cm\textsuperscript{-1}. Uptake of C=O is shown at a wavelength of 1693.5 cm\textsuperscript{-1}. Uptake of sp\textsuperscript{3}C-H is shown by peaks of 2650.19 cm\textsuperscript{-1}. Uptake of sp\textsuperscript{2}C-H is shown by peaks of 2870.08 cm\textsuperscript{-1} and Uptake of -OH is shown by peaks of 3412.08 cm\textsuperscript{-1}.

3.2. Gas Chromatography Mass Spectroscopy (GC-MS) Characterization

Gum rosin results of distillation are identified using the GC-MS component. The identification is done by comparing the fragmentation patterns of reference compounds. Data from the results of the gum rosin compound distillation results were adjusted using the WILEY229 data bank. LiIB can be seen in Table 2.

### Table 2. Gum rosin component analysis results using GC-MS

| No. | Compound            | RT   | Area (%) | SI  | Molecular weight | Molecular formula | Structure          |
|-----|---------------------|------|----------|-----|------------------|-------------------|--------------------|
| 1   | Caryophyllene       | 15.07| 1.39     | 929 | 204              | C\textsubscript{15}H\textsubscript{24} | ![Structure](image) |
| 2   | Pimaric acid        | 35.43| 0.27     | 816 | 302              | C\textsubscript{20}H\textsubscript{30}O\textsubscript{2} | ![Structure](image) |
| 3   | Dehydroabietic acid | 36.12| 7.80     | 822 | 300              | C\textsubscript{20}H\textsubscript{28}O\textsubscript{2} | ![Structure](image) |
| 4   | Abietic acid        | 36.49| 4.41     | 900 | 302              | C\textsubscript{20}H\textsubscript{30}O\textsubscript{2} | ![Structure](image) |
| 5   | á-Pinene            | 3.86 | 0.12     | 859 | 136              | C\textsubscript{10}H\textsubscript{16} | ![Structure](image) |

Based on the GC-MS analysis of the components of the gum rosin compounds distilled shown in Table 2, it was found that the main components of these results were Dehydroabietic acid with a content of 7.80% and abietic acid with a content of 4.41%. The two main components are abietic type resin acids. This result is supported by research conducted by Yadav[33] that the main ingredients of
gum rosin are abietic acid and dehydroabietic acid (diterpenoid containing 20 carbon) with a typical hydrofenantrene ring.

**Figure 2.** (A) Compound chromatogram RT 15.07; (B) mass spectrum of RT 15.07 compounds

Based on GC-MS analysis showed that compounds with RT 15.07 minutes and SI 929 similar to Caryophyllene compound with the molecular formula $\text{C}_{15}\text{H}_{24}$. So that it can be said Compound with RT 15.07 minutes is a compound of Caryophyllene. Caryophyllene is a constituent of many essential oils. Usually found as a mixture with isocaryophyllene (cis double bond isomer) and $\alpha$-humulene ($\alpha$-caryophyllene), an open ring isomer. Caryophyllene is famous for having a cyclobutane ring, as well as a trans-double bond in a 9-membered ring.
Figure 3. (A) Compound chromatogram RT 35.43; (B) mass spectrum of RT 35.43 compounds

Based on GC-MS analysis the compound with RT 35.43 minutes and SI 816 is similar to the Pimaric acid compound with the molecular formula $\text{C}_{20}\text{H}_{30}\text{O}_2$. So that it can be said Compound with RT 35.43 minutes is a compound Pimaric acid. Pimaric acid is a carboxylic acid from the resin acid group, often found in pine oleoresin. Pimaric acid is a type of pimarane and isopimaric acid and sandaracopimaric acid of the theisopimarane types[21].
Figure 4. (A) Compound chromatogram RT 36.12; (B) mass spectrum of RT 36.12 compounds

Based on GC-MS data analysis of compounds with RT 36.12 minutes and SI 822 similar to Dehydroabietic acid compounds with the molecular formula \( \text{C}_{20}\text{H}_{30}\text{O}_{2} \). Compounds with RT 36.12 minutes are Dehydroabietic acid compounds. Dehydroabietic acid is an acid compound that is classified as an abietic acid type resin.
Figure 5. (A) Compound chromatogram RT 36.49; (B) mass spectrum of RT 36.49 compounds

Based on GC-MS analysis it shows that compounds with RT 36.49 minutes and Si 900 are similar to abietic acid compounds with the molecular formula C_{20}H_{28}O_{2}. So it can be said that compounds with RT 36.49 minutes are abietic acid compounds. Abietic acid is an acid compound that is classified in the type of abietic acid resin, also known as abietinic acid or Sylvi acid. Abietic acid is the most abundant resin acid of several organic acids contained in the oleoresin solids of pine trees. Esters or their salts are called abietates.

4. Conclusion
Separation and purification of the gum rosin from pine gum have been successfully carried out using a simple distillation method. The gum rosin yield obtained from the distillation results is 86.67%. The results of FTIR identification showed the presence of sp²C-H, -OH, sp³C-H, C=O, -CH₂ and -CH₃ while GC-MS identification showed the presence of caryophyllene, pimaric acid, dehydroabietic acid,
abietic acid and á-pinene components. The identification results indicate that the residue from the simple distillation results ingum rosin.

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