Comparison of The Chemical Compounds of Malacca Bark and Malacca Fruit (*Phyllanthus emblica*) with Gas Chromatography-Mass Spectrometer (GC-MS)

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**Abstract.** Malacca (*Phyllanthus emblica*) has a chemical that contains acids that are used to treat cancer. This research was aimed to compare the content of chemical compounds malacca stem with malacca fruit (*Phyllanthus emblica*) with multilevel extraction methods. Extraction of the stem and Malaca fruit was carried out by maceration and socletation using non-polar n-hexane, semi-polar acetone, and polar methanol as solvent. Non-polar components were separated by the soxhlet extraction method using n-hexane solvent. The residue from the soxhlet extraction was then macerated using acetone solvent. Furthermore, the polar component was separated by maceration extraction method using ethanol as a solvent. The ethanol extract was then identified by chemical compounds with Gas Chromatography-Mass Spectrometer (GC-MS). Chemical compounds identified with GC-MS showed extracts on stem balakka contain the compound succinic acid dimethyl ester, dimethyl pentanedioate, and dimethyl adipate, while extracts on malacca fruit contain the compound succinic acid dimethyl ester, dimethyl pentanedioate, dimethyl adipate, methyl adipate, 1,3-Dioxolane-4-methanol.

1. **Introduction**

Malacca (*Phyllanthus emblica*) generally grows in tropical and subtropical regions including China, India, Indonesia and Peninsular Malaysia. Malacca in North Sumatra this fruit is known as Balakka fruit. So far this plant like the bark is widely used as a spice for traditional cuisine known as "Holat". Malacca (*Phyllanthus emblica*) has an acidic chemical that is used to treat cancer. Malacca is also believed to cure diabetes, stomach acid, rheumatism. In addition to Malacca bark, Malacca is also widely used by traditional communities as a drug that they have trusted for generations. Malacca is believed to be used as a drug that can reduce menstrual cramps, cough medicine and can be used to reduce blood sugar levels for diabetics. [1]. However, the use of Malacca as a traditional medicinal ingredient has not been equipped with scientifically convincing data on the content of active compounds that make it medicinal.

Some chemical compounds from Malacca (*Phyllanthus Emblica*) have been reported by [2] Dhale and Mogle using the Phytochemical Skrinning method, from the research results obtained data that the Malacca contains compounds including: alkaloids, glyceroids, carbohydrates, phenols, tannins, lignin,
saponin, flavonoids and terpenoids. [3]. Seno Aulia through phytochemical screening experiments concluded that Malacca leaves contain compounds such as alkaloids, flavonoids, tannins, phenolics, monoterpenes, quinones and saponins. Plants can be used as traditional medicine if the plants contain chemical compounds that have biological activities (bioactive substances). Bilogis active compounds are secondary metabolites which include alkaloids, flavonoids, terpenoids, tannins and saponins. Identifying secondary metabolite compounds in plants can be done by a method one of the methods that can be used is the Phytochemical Screening Method.

Utilization of the fruit and bark of Malacca as a medicine can be estimated in the fruit of Malacca containing secondary metabolites which need to be verified. By reviewing the results of previous studies on the content of chemical compounds from Malacca Fruit through the Phytochemical Skrinning method. In this case, it is necessary to develop a method for identifying chemical compounds in malacca, namely by using the Gas Chromatography-Mass Spectroscopy (GC-MS) method. GC-MS can provide qualitative and quantitative data on compounds that are components of fruit compounds and balakka stem chips. Gas chromatographic analysis will get the possibility of the number of fruit components and the bark of Malacca and their respective levels. Meanwhile, to determine the type of component of fruit and bark of Malacca, an analysis was performed with MS. Therefore research is needed to identify the main components of Malacca fruit and bark.

2. Research Method
The materials used in this research were malacca fruit, Malacca bark, ethanol, acetone, n-hexane. The tools used in the research are a set of soxhlet tools, a set of distillation apparatus, an oven, a Shimadzu GCMS-QP2010S, a set of glassware, an analytical balance. Malacca fruit and bark used in this research came from the South Tapanuli Aekgodang area. The research was conducted at the Laboratory of Chemistry Education at the University of Muhammadiyah South Tapanuli and identification of chemical compounds from the fruit and bark of Malacca stem was carried out in the laboratory of Gadjah Mada University.

2.1 Making Simplisia Fruit and Bark of Malacca Stem
The fruit and bark of Malacca are washed, the seeds are discarded, thinly cut and then dried in an oven at 100 ° C for 8 hours. Dried Malacca fruit in a blender until powdery. The crushed Malacca bark is then dried in an oven at 100 ° C for 8 hours then blended until it is powder.

2.2 Making Malacca Fruit and Bark Extract
A total of 35 g of Malacca fruit powder and bark were extracted by Soxhlet using 350 mL of n-hexane for 10 hours. The residue from soxhlet extraction was distilled and then macerated in 150 mL acetone for 24 hours. The filtrate collected is near distillation. Distilled residue is macerated again with 150 ml ethanol for 24 hours, then the filtrate is concentrated with distillation.

2.3 Analysis of Malacca Fruit and Bark Skin Chemical Compounds
The filtrate obtained from the distillation results was analyzed using GC-MS. Filtrate is injected as much as 1 µl into Rtx 5 MS column, EI (Electron Impack) 70 EV, column length 30 meters, column temperature 70-300 ° C, Helium carrier gas, injector temperature 300 ° C. Components of chemical compounds are identified based on fragmentation patterns and retention times. The spectrum pattern is compared with the WILEY and NIST databases and then the spectrum is selected and identified the top of the component that has a similarity index (SI) ≥ 100%.

3. Results and Discussion
Extraction uses three types of solvents, namely non-polar n hexane solvents, semi-polar acetone solvents and ethanol polar solvents [4]. Solvent extraction can be carried out by multilevel extraction
and single extraction methods [5]. Multilevel extraction is a way to soak samples with different solvents in sequence according to their level of polarity. Non-polar, semi-polar and polar solvents are used so that liquid extracts will be obtained containing successively non-polar, semi-polar and non-polar compounds [6]. The extraction process with solvents is based on the polarity of the substances in the solvent at the time of extraction. Polar compounds will only dissolve in polar solvents such as ethanol, methanol and water. Non-polar compounds will only dissolve in non-polar solvents such as n-hexane and ether [7].

Non-polar n-hexane solvents can extract lycopene, triterpenoids and a small portion of carotenoids while xanthin compounds and other polar compounds will be extracted into polar ethanol solvents [8]. While semi-polar solvents are able to attract compounds including lycopene, b-carotene, vitamin C. Analysis using GC-MS can provide qualitative and quantitative data on the compounds that are components of the bark and Malacca extract. Gas chromatography analysis will get the possibility of the number of components of the extract of the bark and fruit of Malacca and the massing levels [9]. Identification of the components of chemical compounds in Malacca bark extract using GC-MS showed 3 compounds as shown in Figure 1.

**Figure 1.** Chromatogram Separation Results Gas Chromatography Samples of Malaca Bark

| Peak | Compound Retention Area SI BM Estimated Compound Reference |
|------|----------------|----------------|----------------|
| 1    | I 12.393 23.43 91 146 Succinic acid dimethyl ester WILEY 229 |
| 2    | II 16.051 69.99 92 160 Dimethyl pentanedioate NIST 62 |
| 3    | III 19.219 6.58 94 174 Dimethyl adipate WILEY 229 |

Identification of the components of chemical compounds in Malaca extract using GC-MS showed 5 compounds as shown in figure 2.
Identification of the components of chemical compounds in Malacca bark extract produced 3 peaks of chromatogram which can be seen in Figure 1. All three peaks are estimated to contain succinic acid dimethyl ester, methyl pentanedioate and dimethyl adipate. While the chemical components in malaca produce 5 peak chromatograms which can be seen in Figure 2. The five peaks each are estimated to contain succinic acid dimethyl ester, dimethyl pentanedioate, dimethyl adipate, methyl adipate and 1,3-dioxolane-4-methanol. Analysis of the extract content of bark and Malacca fruit in this study was carried out with mass spectra analysis based on "base peak" and Similarity Index (SI) with a comparison of spectra from NIST 62 and Wiley 229.LIB. Base peak is the highest peak abundance in the spectrum and is priced at 100%. If the SI value is close to 100%, then the detected compound has a similarity level with comparable data.

In tables 1 and 2 it is known that the extract of fruit and bark of Malacca consists of esters, namely succinic acid dimethyl ester, dimethyl pentanedioate, dimethyl adipate, methyl adipate and 1,3-dioxolane-4-methanol. Esters can be produced from carboxylic acids. By combining acids with alcohol esters can be produced by removing water molecules. Carboxylic acid esters are widely used in various industries. Succinic acid has the largest content in Malacca fruit and stems. Succinic acid is also called butanedioic acid, with a educative point of 235 and a melting point of 185, succinic acid produces five heterocyclic compounds. Succinic acid is an important chemical and has comprehensive uses. For example, in the medical industry it can be used to synthesize sedatives and cancer cures [10]. Succinic acid can be oxidized to fumaric acid or converted to a diester, such as diethylcinninic.

The structure of Malacca bark and fruit is as follows:

![succinic acid dimethyl ester](image1)
![dimethyl adipate](image2)
![methyl adipate](image3)
![1,3-Dioxolane-4-methanol](image4)

Malacca bark and fruit extracts using multilevel extraction methods using polar, semi-polar and non-polar solvents analyzed by GC-MS showed that the extracts of Malacca bark and fruit consisted of fatty acid derivatives namely succinic acid dimethyl ester, dimethyl pentanedioate, dimethyl adipate, methyl adipate and carbohydrate-derived compounds, 1,3-Dioxolane-4-methanol [11].

4. Conclusion
Isolation of the chemical components of Malaca fruits and Malaca bark was carried out by multilevel maceration using non-polar n-hexane, semi-polar acetone and polar etnaol solvents to produce blackish brown extracts. GC-MS spectra analysis showed the compounds identified in the fruit were
succinic acid dimethyl ester, dimethyl pentanedioate, dimethyl adipate, methyl adipate and 1,3-Dioxolane-4-methanol while the chemical compounds in the Malaca stem were succinic acid dimethyl ester, imethyl pentanedioate and dimethyl adipate.

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