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Original Research Article

Effectiveness of sulfuric acid and hydrochloric acid catalysts in the esterification of frankincense cinnamic acid with ethanol and methanol

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ABSTRACT

This research aims to compare the effectiveness of sulfuric acid and hydrochloric acid catalysts in the esterification of frankincense cinnamic acid (STYRAX paraleoncomud PERK). Esterification of sulfuric acid catalyst is carried out with ethanol and for hydrochloric acid catalyst with methanol. Esterification was carried out by refluxing a mixture of 1:20 cinnamic acid - ethanol and methanol, with 3 mL of each catalyst at a temperature of 60oC for one hour. The results were rinsed with 3 x 50 mL distilled water and dried with anhydrous sodium sulfate. The results were filtered and verified for functional groups using FTIR and composition analysis using GC – MS. The results of FTIR interpretation show a decrease in absorption intensity (-OH) at 3500 cm-1 as a functional group that reacts compared to the ester results as an indication of the ongoing esterification reaction. The resulting ethyl cinnamate has a high conversion of 84.42%. Methyl cinnamate also has a distinctive ester aroma but is clearer and based on GC-MS, the content of methyl cinnamate is relatively low, namely 34.40%, the remaining cinnamic acid is 37.28%, and various side products of 28.32%. Thus, the catalyst that provides better conversion is sulfuric acid, but it requires further purification by examining the appropriate absorbent and bleaching agent. The brown color of the ester product catalyzed by sulfuric acid is thought to occur due to the oxidation of the cinnamic acid double bond by the catalyst.

Introduction

Esterification is a reaction between an acylation substrate and alcohol as a nucleophile. The most classic esterification is Fisher esterification, namely the reaction between a carboxylic acid as an acylatjng agent and an alcohol as a nucleophile catalyzed by a protolytic acid (Fakhry & Rahayu, 2016). Nowadays, more reactive acylating agent are used for esterification reactions, namely carboxylic acid halides and carboxylic anhydrides (Minami & Saka, 2006; Supaya, 2019). In general, the mechanism of the esterification reaction by acylating carboxylic acids is as follows (Fig-1) (Gui et al., 2004; Klimkiewicz, 2014).

The acid catalyst (H+) that is commonly used is concentrated sulfuric acid (H_2SO_4) which aims to activate the acylium ion by protonation of the carbonyl, so that the carbonyl carbon atom becomes more reactive because it has a more positive charge so that it is more reactive towards alcohol nucleophile (Setyawardhani et al., 2005).

The weakness of sulfuric acid as a catalyst is that if the acylation substrate contains alkenes, it can cause side reactions, namely becoming epoxides, diols and cleaving to carbonyls, so that it does not produce optimal esters (Wang et al., 2023; Kon et al., 2023). In this study, the effectiveness of sulfuric acid and hydrochloric acid catalysts was studied in esterification by acylating cinnamic acid isolated from frankincense (Chehri et al., 2018). For ethanol, sulfuric acid is used because it requires a higher level of catalyst and also the ethanol molecules are relatively larger than methanol which uses a hydrochloric acid catalyst which is relatively low in content but is not oxidative (Khan et al., 2021). The optimal results are interpreted based

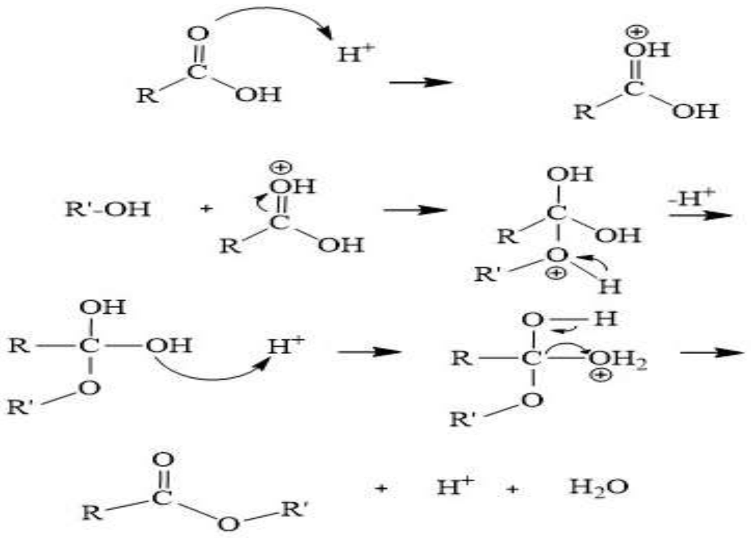


Fig-1. Esterification reaction mechanism with acid catalyst.

on the physical properties of the ester produced and functional group verification of functional group recording by using FTIR and composition analysis by using GC-MS (Ashish et al., 2014). The novelty of this research is the use of hydrochloric acid as a catalyst, because generally the catalyst used in esterification is sulfuric acid. Sulfuric acid is thought to be oxidative towards double bonds in cinnamic acid substrates (Cao et al., 2020).

Methods

Materials

The chemicals used in this research were frankincense from the Garoga area, North Tapanuli Regency, ethanol, methanol, sodium hydroxide, anhydrous sodium sulfate, concentrated sulfuric acid, concentrated hydrochloride acid, distilled water and universal pH paper.

Instruments

The equipment used is various glassware, a set of reflux equipment, a Prestige 21 FTIR Spectrophotometer and a GC-MS QP2010.

Method

Esterification is carried out by refluxing a mixture of 1:20 cinnamic acid - ethanol (sulfuric acid catalyst) and methanol (hydrochloric acid catalyst), with three milliliters of catalyst each. temperature 60oC for one hour. The results were rinsed with 3 x 50 mL distilled water and the ethyl and methyl cinnamate results were dried with anhydrous Na_2SO_4. The results were filtered and verified for functional groups using FTIR and composition analysis using GC – MS.

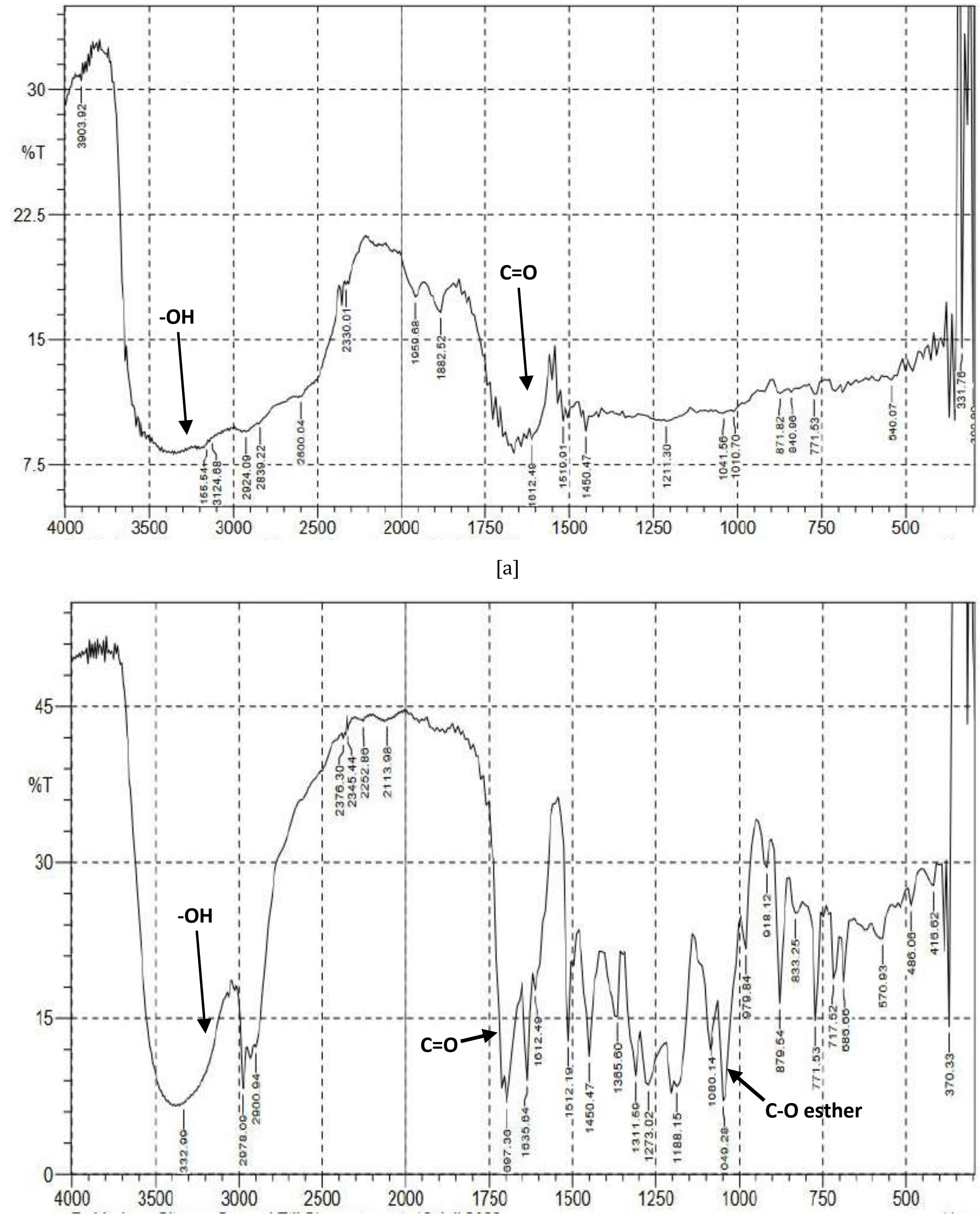
Results and Discussion

Synthesis of Ethyl Cinnamate

Esterification of cinnamic acid-ethanol at a mole ratio of 1:20 with concentrated sulfuric acid catalyst ethanol by reflux at a temperature of 60oC for one hour produces ethyl cinnamate as shown in Fig-2.

Fig 2. Ethyl cinnamate is the result of esterification of cinnamic acid - ethanol with concentrated sulfuric acid as catalyst.

The ethyl cinnamate produced has a characteristic ester or essence smell, but the blackish brown color indicates a side reaction to the double bond which produces diol, epoxide and carbonyl (Wai et al., 2019). The results of FTIR spectra recording of a compound can be used as an indication of whether a reaction is taking place based on analysis of its functional groups. The reaction of organic compounds is essentially a transformation of functional groups so that by comparing the functional groups before and after the reaction it can be concluded that the progress of a reaction is as in Fig-3.

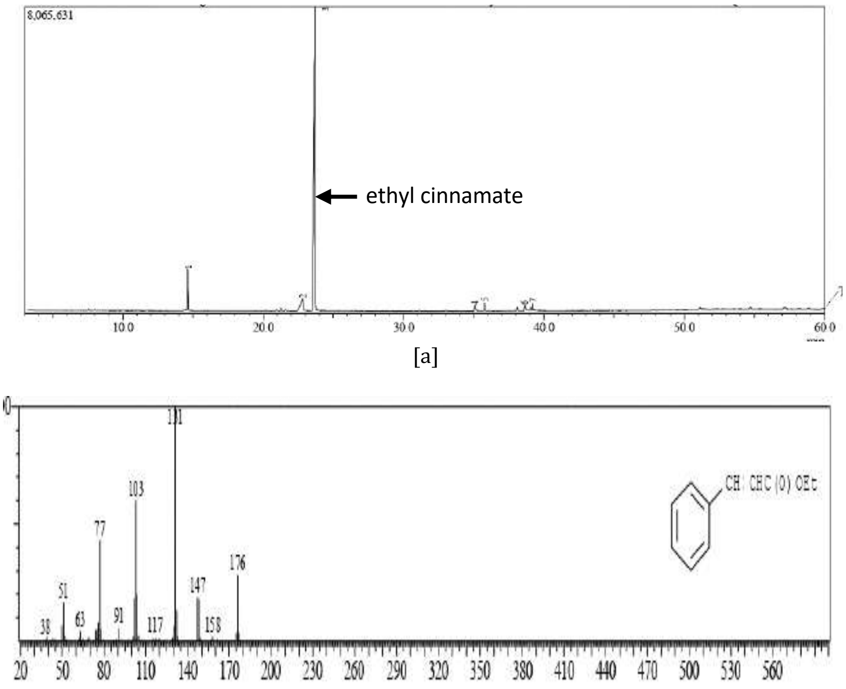


[a]

[b]

Fig-3. FTIR spectrum of cinnamate acid [a] ethyl cinnamate resulting from esterification [b].

Based on the interpretation of the FTIR spectrum in Fig-3[a] it is verified that it contains the main functional group of cinnamic acid, namely a wide and strong band at 3000 – 3500 cm-1 from the hydroxyl group (-OH). This widening is due to the very strong hydrogen bonds of the (-OH) group of cinnamic acid. Furthermore, the carbonyl group is absorbed at 1600 – 1700 cm-1 which overlaps with the alkene group (C=C) from both the benzene ring and the propanoid. Furthermore, the FTIR spectrum ethyl cinnamate of the esterification results in Fig-3[b] shows the conformation of the reaction taking place to produce ethyl cinnamate. The hydroxyl group still appears in the product but its intensity has decreased indicating that most of the cinnamic acid has been converted into ethyl cinnamate (Berthomieu, & Hienerwadel, 2009). This is supported by the very high resolution absorption between the carbonyl group (C=O) in the absorption band 1607 cm-1 and the alkene group in the absorption band 1635 cm-1. To support the conclusion that the esterification reaction took place. Furthermore GC-MS recording of the results was carried out with the chromatogram in Fig-4.



[a]

[b]

Fig-4. Chromatogram of GC-MS ethyl sinamate [a] and Library GC-MS fragmentation of ethyl cinnamate [b].

Based on the GC-MS chromatogram in Fig-4[a] ethyl cinnamate (conformation from Lybrari chromatogram fragmentation) has a very high content, namely 84.42%, namely peak 3 with an elution retention time (tr) of 23.706 minutes. The MS fragmentation pattern Fig-4[b] confirms that the peak is ethyl cinnamate, namely m/z = 176 is the M+ peak (Molecular Weight of ethyl cinnamate). The basic peak (highest peak) with m/z = 131 is the result of M+ fragmentation by releasing ethoxy radicals (CH_3-CH_2-O.). Furthermore, the m/z = 103 peak is the release of carbon monoxide from the m/z = 131 peak and the m/z = 77 peak is the benzelium peak formed due to the release of acetylene from m/z = 103. The fragmentation pattern above confirms that the peak is ethyl cinnamate (Nugraha & Nandiyanto, 2021; Cao et al., 2021).

Synthesis of Methyl Cinnamate

The synthesis of methyl cinnamate was carried out by refluxing the extracted cinnamic acid with methanol at a mole ratio of 1:20 with concentrated hydrochloric acid as catalyst. The mixture was refluxed for one hour at 60^{o}C. The results of methyl cinnamate have a typical ester aroma and are quite clear as in Fig-5. The functional group of methyl cinnamate was verified using an FTIR spectrophotometer with a spectrum as in Fig-6.

Fig-5. Methyl cinnamate is the result of esterification of cinnamic acid - methanol with concentrated hydrochloric acid as catalyst.

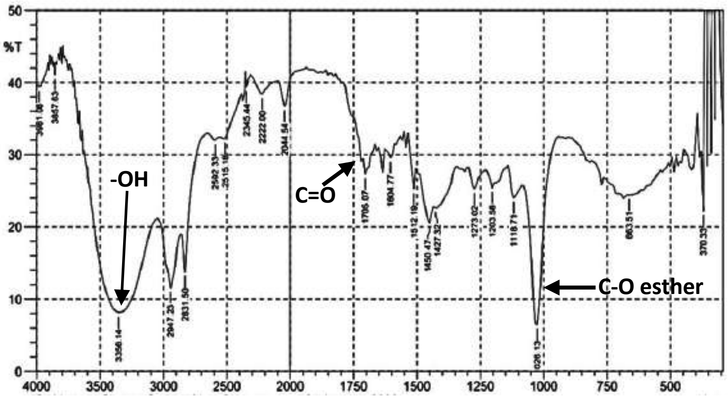
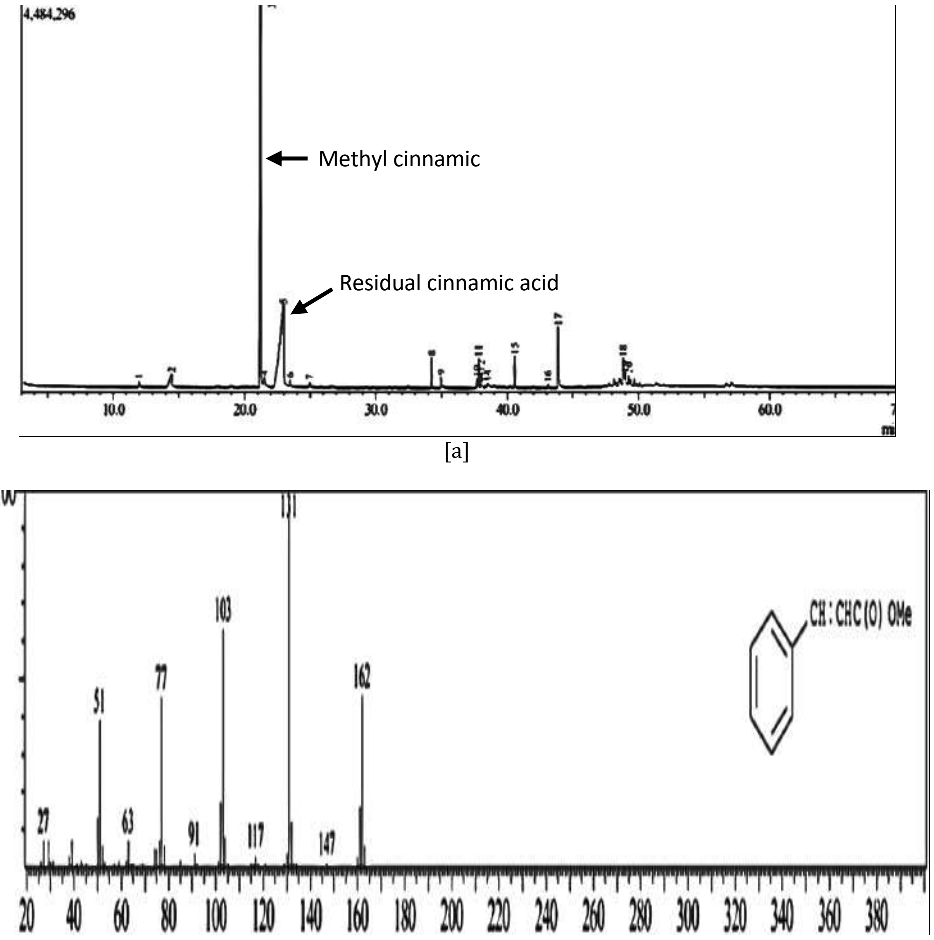


Fig-6. FTIR spectra of methyl cinnamate resulting from esterification.

Based on the spectrum of Fig-6, the absorption of the hydroxyl group (-OH) at 2947.23 cm-1 still appears even though the intensity has decreased compared to the isolated cinnamic acid spectrum (Fig-3[a]), this indicates that the esterification reaction is taking place. To find out. The composition is then analyzed by GC – MS with chromatogram as in Fig-7.



[a]

[b]

Fig-7. GC – MS chromatogram of methyl cinnamate [a] and MS spectrum of methyl cinnamate [b].

Based on the GC-MS chromatogram data in Fig-7[a], a relatively low level of methyl cinnamate (peak 3, tr = 21.67 minutes) was obtained, namely 34.39 % and the residual cinnamic acid (peak 5, tr = 22.957 minutes) was 37.28%, and a number of other components were 28.32%. Fragmentation of methyl cinnamate resulting from esterification using MS spectra in Fig-7[b] is through the following mechanism. The molecular weight is the M+ peak with (m/z) = 162, the base (highest) peak with m/z = 131 is the fragmentation of M+ by releasing methoxy radicals (CH_3O). The fragment with (m/z) = 103 is the result of fragmentation of the base peak by releasing carbon monoxide, while the fragment with (m/z) = 77 is the result of peak fragmentation (m/z) = 103 with the release of neutral acetylene molecules (Schüler et al., 2018)

Fragmentation of the remaining cinnamic acid resulting from esterification (peak 5, tr = 22.957 minutes) with the spectrum in Fig-8. The fragmentation mechanism is the peak with (m/z) = 148 which is M+ which is the molecular weight of cinnamic acid as well as the basic (highest) peak because it is most stable fragment. The peak with (m/z) = 131 is M+ fragmentation with the release of hydroxy radicals (OH). Next, the peak (m/z) = 103 is the fragmentation of (m/z) = 131 by releasing carbon monoxide. Meanwhile, the peak with (m/z) = 77 is fragmentation (m/z) = 131 with the release of neutral acetylene molecules (Masike et al., 2017).

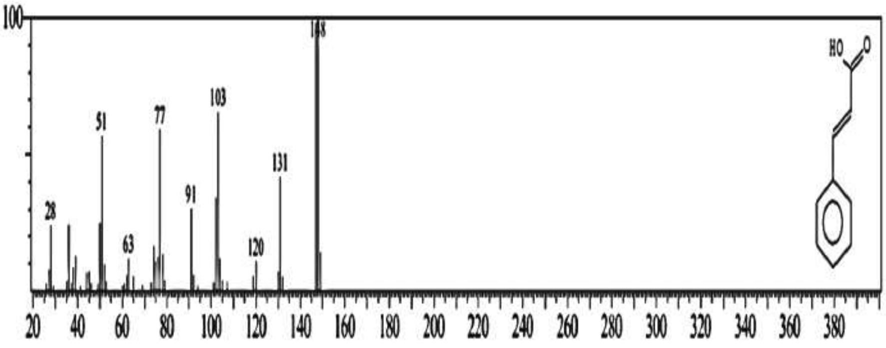


Fig-8. Fragmentation spectrum of the remaining cinnamic acid resulting from esterification.

The chromatogram in Figure 5[a] shows that there are several by-product components of around 28.32%. It is thought to be the result of addition of hydrochloric acid competing with nucleophilic substitution of the chloride ion (Costa, 2020). The results of methyl cinnamate are relatively clean compared to ethyl cinnamate because hydrochloric acid is not oxidative to alkene. The sulfuric acid catalyst has a higher conversion but the result is black chocolate due to the possibility of an oxidative double bond side reaction (Santaella et al., 2015), so further research needs to be carried out to purify it with a suitable adsorbent.

Conclusion

Based on the interpretation of the FTIR spectra and GC-MS chromatograms, the reaction conformation takes place with different functional groups corresponding to the reactants and products, namely decreasing the absorption intensity of the hydroxyl group (-OH) which changes to esters (ethyl and methyl cinnamate). The ethyl cinnamate content produced was 84.42% with a typical ester (essence) aroma but still blackish brown in color. Furthermore, the content of methyl cinnamate produced is relatively low, namely 34.40% and the remaining cinnamic acid is 37.28%, and various other trace components with a total amount of 28.32%, but it is very clear indicating that there is no side reaction of double bond oxidation and has a characteristic ester odor. Catalyst what provides a higher conversion is sulfuric acid compared to hydrochloric acid, but further purification studies with appropriate absorbents are needed. Thus, based on product efficiency, the sulfuric acid catalyst is better than hydrochloric acid.

Conflict of Interests

The author(s) declares that there is no conflict of interest in this research and manuscript.

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