Extraction of eugenol, a natural product, and the preparation of eugenol benzoate

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Abstract. This experiment was carried out to extract the eugenol from cloves in the part A, also to prepare the eugenol benzoate in part B. The experiment conducted, extraction of the essential oil eugenol from cloves. To perform this experiment cloves and water were mixed together and heated by a heating mantle in a round-bottom flask. A direct steam distillation took place, and the oil product was out aside for two weeks. After two weeks, the extraction of the eugenol and the preparation of eugenol benzoate actually took place. Next the light yellow eugenol from part A was characterized by the thin-layer chromatography (TLC) plate and 1H NMR analysis; however, eugenol benzoate from part B also was characterized by 1H NMR and Melting Point analysis. The products were analysed to check the purity, and to make sure there are no impurities. The experiment involved the use of techniques, such as steam distillation, gravity filtration, vacuum filtration to collect the product, recrystallization to purify the product, and the weigh to weight out the products.

1. Introduction
Natural products are compounds that are found in nature and are produced by plants, animals, or fungi. Molecules originating in nature have long held an important place in chemistry, and in society at large. Many of the most important and useful compounds of all time were first discovered in nature. The Clove tree is a tropical evergreen that develops clusters of flowers. These flower buds are collected and dried to give the familiar spice used in cooking. The compounds found in the essential oil of cloves are eugenol, eugenol acetate, and B-caryophyllene. The structures of eugenol, eugenol acetate, and caryophyllene are shown below:

![Figure 1. Structural Formulas – Eugenol, Eugenol Acetate and Caryophyllene.](image-url)
Smaller amounts of compounds found in the essential oil of cloves are hydrocarbons, alcohols, phenols, ethers, aldehydes, ketones, acids, and esters. Essential oils are volatile and have an odor. Essential oils are often flammable, soluble in alcohol and ether but partially soluble in water. Eugenol, C_{10}H_{12}O_2, is a one of the compounds of phenylpropanoid family. It is a pale yellow principal compound responsible for giving cloves their distinctive aroma and taste. In addition to being a natural product, eugenol is also classified as an aromatic compound. Aromatic compounds were first named due to their pleasant smells. Aromatic compounds contain a benzene ring or other aromatic ring.

In the part A of the experiment the natural product eugenol was extracted from cloves using the technique of steam distillation, which is often used to extract liquid natural products from plants. Extraction is an experimental technique used in the separation of the oil and eugenol. The steam distillation technique was used because it lowers the pressure in the flask so that it does not have to be heated at such a high temperature. High temperatures could possibly decompose organic compounds. Eugenol is the main product produced from the reagents in part A of the experiment.

In the part B of the experiment eugenol reacted with benzoyl chloride to produce eugenol benzoate. The eugenol benzoate was characterized by 1H NMR spectroscopy and melting point analysis.

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**Figure 2.** Reaction of the interaction of eugenol with benzoyl chloride with the formation of eugenol benzoate.

2. Experimental part

2.1. Part A: Extraction of Eugenol

Crushed cloves (20 g) were placed in a 500 ml round bottom flask, and water (300 ml) and a few anti-bumping chips were added. The round bottom flask with the mixture was connected to the distillation apparatuses, and using Bunsen burner the flask was distilled vigorously until approximately 150 mL of oily (some color, yellow) distillate was collected, a series of chemical extractions were performed. The collected distillate was transferred into a separating funnel, 25ml of dichloromethane was added and shaken well, then the mixture was allowed to settle and two distinct layers formed. The lower layer was organic colourless, the top one was aqueous (cloudy). The lower layer was drained into a 250 ml conical flask. Another 25 ml of dichloromethane was added to a separatory funnel, and it was shaken well, and again two layers formed, the lower organic was collected and placed into the same conical flask with organic layer. The top aqueous layer also was placed into a different 250 ml conical flask. The organic phase layer was placed into a clean separatory funnel and 20 ml of 10% sodium hydroxide solution was added to separate the eugenol acetate, more 20 ml of 10% sodium hydroxide was added to collect all of the eugenol acetate possible. The aqueous layer was collected in a conical flask then the solution was acidified to a pH of less 2 using concentrated HCl, the pH was checked using blue litmus paper, it turned to red colour, the solution is sufficiently acidified. The aqueous layer was washed with sodium chloride solution half saturated. The organic phase was collected and 25 ml of dichloromethane was added to it, the solution was dried with magnesium sulphate and filtered it over a filter paper. The gravity filtration equipment was set up to filter the solid into a reweighed round bottom flask and a rotatory evaporator at a temperature of 60°C to leave pure eugenol as a light yellow oil, the oil smelled pungent and spicy (1.01g, 5.05%) [3]. The product was characterised by TLC and H NMR spectroscopy. For the thin layer chromatography (TLC) plate the dichloromethane was used as an elution solvent. The Rf value which
was calculated from the TLC was 0.6, and 0.9. The eugenol was found in Rf = 0.6. A sample of this oil was prepared in CDCl$_3$ so that it could be analysed by H NMR spectroscopy. $^1$H NMR (CDCl$_3$): 3.3(3H), 5.5(1H), 5.9(2H) and 6.6(4H).$^3$

2.2. Part B: Preparation of eugenol benzoate
Eugenol (1.0 g, 6.09 mmol) was added to 10% aqueous sodium hydroxide (20 ml) in a 50 ml conical flask. After swirling the flask to dissolve the oil, benzoyl chloride (2 ml, 2.42 g, and 17.18 mmol) was added in 1.0 ml portions with constant shaking. The flask was stoppered and the contents shaken for 5 minutes. The solid benzoyl derivative was collected by suction filtration and washed with deionized water (5 ml). The crude product was recrystallized from ethanol to give eugenol benzoate (0.92 g, 56.4%) as white needles, mp 63-72ºC (lit.1 70ºC). H NMR (CDCl$_3$): 7.06(1H,3), 6.83(1H,4), 6.85(1H,6), 3.80(3H,8), 3.36(2H,12), 5.95(1H,13a), 5.04(1H,14a), 5.07(1H,14b), 7.82(1H,16), 7.42(1H,17), 7.59(1H,18), 7.42(1H,19), and 7.82(1H,20).

3. Results and Discussion

3.1. Part A
Eugenol (1.01 g, 5 % recovery) was extracted as light yellow oil and with strong clove smell, from 20 g of cloves. Although the % recovery seems slightly low relative to the expected 10%, the experiment proceeded as planned. There were no spills or other abnormal physical losses. It is possible that the ratio of the size of the glassware to the theoretical amount of eugenol which can be obtained from cloves in this experiment is large, leading to adherence of a large percentage of the product on the sides of the glass apparatus. If this is so, then steam distillation of a larger sample of cloves should give an improved recovery [5]. Otherwise, it can be concluded that the specific sample of cloves used contains approximately 5.01% of the eugenol. Eugenol oil was analysed by TLC plate and H NMR spectroscopy. TLC plate and $^1$H NMR spectroscopy are attached to the laboratory book. The spectrum identifies functional groups present in the molecules in the oil. Thin layer chromatography (TLC) shows that the sample is eugenol, Rf was 0.6. The second spot on the TLC was Rf 0.9 was trace impurity it could be due to residue left in the glassware that was not washed away after the extractions [7]. H NMR spectroscopy. H NMR (CDCl$_3$): 3.3(3H), 5.5(1H), 5.9 (2H) and 6.6 (4H).

In $^1$H NMR spectroscopy, the CDCl$_3$ does not show signs of a large interfering peak, whereas regular hydrogen shows a large peak in the spectrum.

| Peak at ppm | Interpretation of the data |
|-------------|---------------------------|
| 1 3.29-3.31 | CH-O(ether)               |
| 2 5.5      | C=C-H                    |
| 3 5.9      | Aromatic H               |
| 4 6.6-6.8  | Aromatic H               |
| 5 6.95     | CDCl$_3$                 |

The product is Eugenol. This can be confirmed by analysed characteristic peaks of the H NMR data. Based upon these results and comparison of the spectra with the corresponding standard spectra of eugenol, this fraction was identified as 4-allyl-2-methoxyphenol [7].

3.2. Part B
Eugenol benzoate (0.92 g) was obtained as white needles in a 56.4 % yield, mp 63-72ºC (lit.1 70ºC) [3]. H NMR and melting point of the product confirmed its structure.
HNMR (CDCl₃): 7.06 (1H, 3), 6.83 (1H, 4), 6.85 (1H, 6), 3.80 (3H, 8), 3.36 (2H, 12), 5.95 (1H, 13a), 5.04 (1H, 14a, 5.07 (1H, 14b), 7.82 (1H, 16), 7.42 (1H, 17), 7.59 (1H, 18), 7.42 (1H, 19), and 7.82 (1H, 20).

The interpretation of H NMR data for eugenol benzoate [6]:

There is a slight difference between the literature (lit.1 70ºC), and with the experimental (63-72ºC) melting point values. It could be because there were some impurities in the compound; the product was not 100% pure. The product is Eugenol benzoate, the melting point and H NMR data confirmed that.

4. Conclusion
To conclude, while performing the experiment it was shown that about 5% of oil could be recovered from cloves by steam distillation. This oil was identified as eugenol and was characterized by TLC plate analysis and the interpreting of the ¹H NMR data. Eugenol was converted to a benzoate derivative, which confirmed the structure of the original compound. The final yield of the experiment (56.4%) was lower than expected, because of some impurities in the compound. Also, there are always could be some errors while performing the experiment.
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