1. Extraction of Eugenol from Cloves

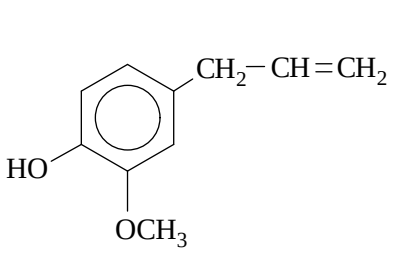
In this experiment, you will extract the essential oil of cloves, which is mostly eugenol. The procedure used is typical for isolating products from natural sources.

Introduction

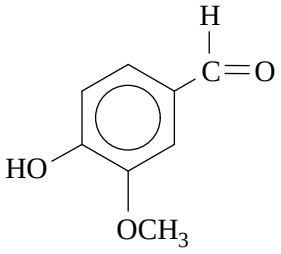
Herbs, spices, and so-called essential oils were commonly used well before organic chemistry was sophisticated enough to determine their structures. To this day, the precise composition and structure of certain ingredients of oils in perfumes have not been established.

Essential oils are volatile, ethereal liquids of oily consistency. They are extracted from plants, usually by steam distillation or extraction. The oils have odors highly characteristic of the original plants. They were thought to be the essence of plants—hence the term *essential oil*.

Essential oils differ from fatty oils in their volatility, their non-greasiness, and the fact that they are not saponifiable.* They are responsible for imparting specific odors to flowers, leaves, or woods (for example, oil of turpentine, juniper oil, peppermint oil, cedar oil) or are developed from plant components by enzyme action (for example, oil of mustard) or heat (for example, cade†). Essential oils are often flammable, soluble in alcohol and ether, and only slightly soluble in water. They can contain hydrocarbons, alcohols, phenols, ethers, aldehydes, ketones, acids, and esters.



eugenol
(cloves)



vanillin
(vanilla beans)

Eugenol is the main ingredient of the essential oil that can be isolated from the spice clove. The clove is the bud of an East Indian evergreen tree. Eugenol is used in perfumery, for the manufacture of synthetic vanillin, as a dental (topical) analgesic, and as an antiseptic.

* Saponification is the process of making soaps from fats and a base.

† Juniper tar oil, a yellow oil obtained through distillation and used in soaps, ointments, and pharmaceuticals.

Experiment Information

Time 2–2.5 hr (60 min gap during steam distillation)

Reagents Whole cloves; 5% potassium hydroxide, KOH, solution; 5% hydrochloric acid, HCl, solution; dichloromethane, CH_2Cl_2, b.p. 41°C; distilled water, H_2O; granular anhydrous sodium sulfate, Na_2SO_4; saturated sodium chloride, NaCl, solution.

Equipment Organic kit with regular condenser and 500-mL round-bottom flask, 250-mL Erlenmeyer flasks, 125-mL Erlenmeyer flasks, 100-mL graduated cylinder, 125-mL and 250-mL separatory funnels, burner with stand, ring, and asbestos gauze, glass rod, steam bath, boiling sticks, universal pH paper.

Cautions Do not breathe vapors of organic solvents. Do not burn yourself when handling the burner and hot glassware. Be careful when working with base and acid solutions. Rinse spills with large amounts of water.

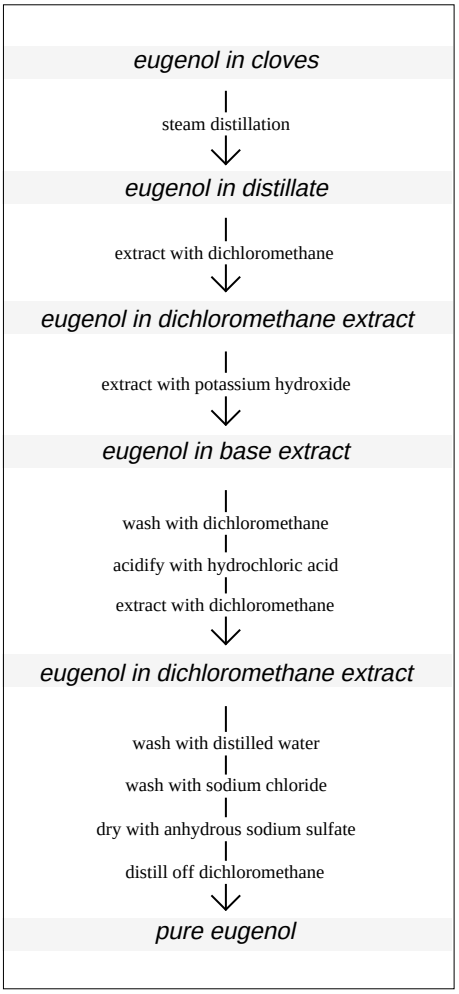
Waste

- Dichloromethane waste goes into the *Dichloromethane Waste* container.
- Cloves residue goes into the trash.
- Aqueous distillate goes into the *Aqueous Waste* container.
- Potassium hydroxide goes into the *Aqueous Waste* container.
- Hydrochloric acid goes into the *Aqueous Waste* container.
- Sodium sulfate may be dumped into the trash.
- Eugenol (product) goes into the *Organic Waste* container.

Notes The dichloromethane extraction steps should be done under the hood, if possible.

You should not discard any solutions that might have your product until the experiment is over. Store them in properly labeled Erlenmeyer flasks. A common mistake is to use a wrong solution to continue the experiment during extractions. When in doubt, check the chart.

The primary yield-determining steps are the steam distillation and the initial extraction of product with dichloromethane. The success of distillation determines the amount of organic material distilled off with water, whereas the success of extraction determines how much of that material is transferred from water into the organic solvent.



The formation of emulsion may be a serious problem during the extraction. It will slow you down significantly and cause you to lose some product. Do your best to avoid it.

In the second distillation, you distill off the solvent and your product will remain in the round-bottom flask. You should get a few drops of the product. You may get so little, though, that it may be dispersed as an invisible film on the interior surface of the flask. Weighing should reveal its presence.

When using a separatory (or addition) funnel to add water, it is possible to open the stopcock just enough so that the water drips from the funnel at the same rate as it is distilled off. The funnel allows you to add water without interrupting the boiling. If a separatory funnel is not available, close the Claisen head with a glass or Teflon stopper.

Expediency tips

This experiment requires the good planning and coordination of various tasks among team members in order to be completed on time. In particular, you need to start the steam distillation as soon as possible; it is the most time-consuming step in the procedure. Various start up tasks should be divided among team members to get things going fast.

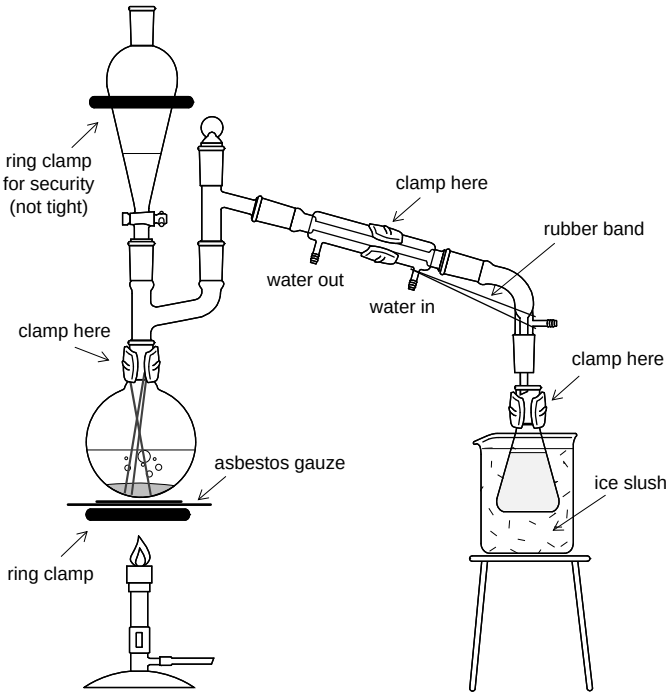
While the steam distillation is underway, the solutions and apparatus for extractions should be prepared. While some team members are doing extractions, someone should clean up the distillation apparatus and set up the second distillation.

Product Pure eugenol is a colorless liquid, b.p. 253°C, slightly soluble in water. Oil of cloves is a yellow volatile liquid, b.p. 243°C.

Experimental Procedures

Steam distillation

Set up a distillation apparatus using a 500-mL round-bottom flask. Use a Claisen as well as a regular distillation head. You will use the main arm of the Claisen head to add water. Attach the take-off adapter, securing it with a rubber band. Set the ring with asbestos gauze high enough that you can control the amount of heat easily. Use a Fisher burner if possible.



Mount the receiving flask onto a stand using a utility clamp. Use a tripod or a large ring clamp and wire gauze to position the ice-water bath. Use a steam-bath bowl or 1000-mL beaker for ice water.* At least half of the receiving flask should be immersed in ice water.

Weigh 14–16 g of cloves using a 100-mL beaker. Crack or squash them somewhat so water can penetrate them better. Weigh again and record the exact mass.

Place the cloves in the round-bottom flask. Pour 150 mL of distilled water and drop in 3 boiling sticks.† Note the level of water.

Place a 250-mL separatory funnel with a joint in the main arm of the Claisen adapter, inserting it through a ring clamp. Make sure the stopcock is closed and pour in about 200 mL of distilled water. If a separatory funnel is not available, close the Claisen head with a glass or Teflon stopper.

Turn on cold water to flow briskly through the condenser and slowly bring the mixture to boiling. Note that it will foam while boiling. Be careful when it just begins to boil or the foam may burst and get into the condenser and contaminate the distillate. Once the mixture is boiling evenly, increase the heat.

Distill the mixture, making sure that it boils rapidly but that foam does not get into the condenser. Foam should completely fill the round-bottom flask during the distillation.

Collect the milky distillate into a 250-mL Erlenmeyer flask standing in ice water. If a clear distillate is being collected, you are distilling just water.

If you are not using a separatory funnel, add 50 mL of distilled water after collecting each 50 mL of distillate.‡ If you are using a separatory funnel, you should add water more frequently in smaller portions, so that the distillation is not interrupted.

Continue distilling until no more oily material can be seen in the condenser (it will take at least 45–60 minutes). You should collect at least 150–200 mL, but no more than 225 mL, of distillate.

Remove the clove residue from the flask while it is still warm, or at least fill the flask with tap water. To remove the solids fill the flask with tap water, swirl, pour the mixture into a 1000-mL beaker, decant liquid into the sink, and then put the solid residue into the trash (do not put the solid residue into the sink as it may clog the drain).

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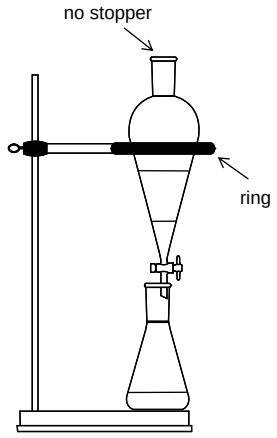
* Pour 700 mL of water into a 1000-mL beaker and add a fistful of ice. If using a steam-bath bowl, don't forget to first connect a rubber hose between lower and upper outlets. The steam-bath bowl works well because it is shallow and wide. You just need to connect the hose from the lower outlet to the upper outlet, so the ice water does not run out. You can use that hose to drain some water before adding more ice, if needed—just disconnect the hose from the upper outlet.

† These are wooden sticks not boiling chips. Do not break them. They need to stand inside the flask, so drop them through the straight arm of the Claisen adapter.

‡ To add water, stop heating, wait until foaming subsides, remove the stopper from the straight arm of the Claisen head, add water, put the stopper back, and start heating again. Slowly bring the mixture to boiling as before; then increase the heat.

Extractions Transfer the distillate to a 250-mL separatory funnel and add 25 mL of dichloromethane.



Keep turning the separatory funnel *gently* for 4–5 minutes. Too vigorous turning or shaking may cause an emulsion to form, but if the layers are not mixed somewhat, some of your product won't get extracted. If an emulsion forms, ask your lab instructor for assistance.

Position the separatory funnel in a ring clamp. Drain the organic layer into a 125-mL Erlenmeyer flask.*

Extract the remaining aqueous solution twice more with 20-mL portions of dichloromethane. Combine the dichloromethane layers.

Transfer the dichloromethane solution to a 125-mL separatory funnel and add 30 mL of 5% potassium hydroxide solution. The solution is likely to warm up as the reaction generates heat.

Save the aqueous layer into a 125-mL Erlenmeyer flask and return the dichloromethane layer to the separatory funnel.†

Extract the dichloromethane solution twice more with fresh 25-mL portions of 5% potassium hydroxide. Combine the aqueous layers.

Pour the combined aqueous solution back into the 125-mL separatory funnel and wash it with a fresh 15-mL portion of dichloromethane.

Transfer the aqueous solution to a 250-mL beaker and *slowly* acidify to pH 1 using 5% hydrochloric acid. Add the acid dropwise while stirring. Test the pH using universal pH paper. You should have to add anywhere from 20 to 50 mL of acid. You will notice that heat is evolved and that the solution turns cloudy when the pH becomes acidic.

Transfer the acidified aqueous solution back to the separatory funnel and add 20 mL of fresh dichloromethane.

Save the dichloromethane layer. Extract again with a 25-mL portion of dichloromethane and combine the dichloromethane layers. Make sure that there is no water contaminating the organic solution.

Using the same separatory funnel again, wash the combined dichloromethane solutions with 15 mL of distilled water.

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* If you are not sure which is the organic layer during any of the extractions, carefully put 2–4 drops of dichloromethane onto the surface of the liquid (using a disposable pipet) and watch whether it dissolves or sinks to the bottom layer or remains on the surface as a spot. Dichloromethane is normally heavier than water, but water saturated with salt and other substances may become heavier.

† The dichloromethane layer should be on the bottom of the separatory funnel, so you need to drain it into a clean, dry Erlenmeyer flask, then drain the aqueous layer and save it in another Erlenmeyer flask, and finally return the dichloromethane to the separatory funnel for the next extraction. If you are not sure which layer is dichloromethane, conduct the same test as before.

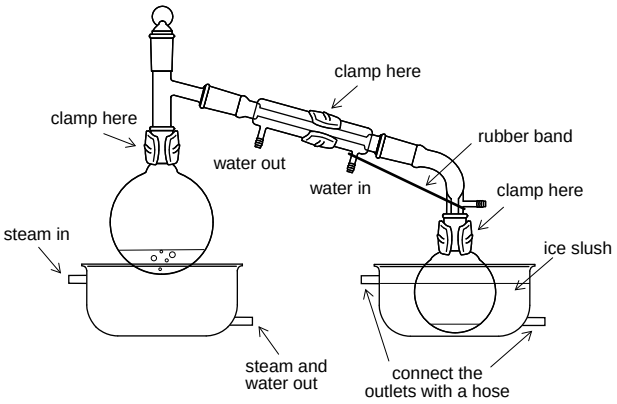
Next, wash the dichloromethane solution with 15 mL of half-saturated sodium chloride solution (made by mixing 8 mL of saturated NaCl solution with 7 mL of distilled water). Make sure that there is no water in the organic solution after the separation.

Transfer the dichloromethane solution to a clean and dry 125-mL Erlenmeyer flask or beaker. Add 15 g of granular anhydrous sodium sulfate to the flask in order to dry the organic solution. Anhydrous sodium sulfate binds any traces of water. Swirl the solution gently for about 5 minutes.

If the solution remains cloudy, repeat the drying step with a fresh portion of anhydrous sodium sulfate. If sodium sulfate dissolves or cakes, you might be working with an aqueous (not an organic) solution.

Distillation Weigh a 150-mL round-bottom flask. It will be used as the distilling flask, not to collect the distillate. Decant* the dichloromethane solution of eugenol into this flask.

Set up an apparatus for distillation using steam as a heat source. You don't need to use the Claisen head, but you should attach a 100-mL round-bottom flask as the receiving flask to the take-off adapter and place it in an ice bath. The flask and take-off adapter may be twisted (that is, not in a vertical position) so there is no need to lift the distillation flask.



Distill off dichloromethane.† Do not heat too fast or foaming may become a problem. Stop the distillation when solvent no longer drips into the receiving flask.

When the solvent is gone, you will be left with a pale yellow oil that has the pungent, spicy odor of cloves and that is about 98% eugenol.

Yield Weigh your product and calculate the yield.‡ Make sure that the instructor evaluates your product on the report sheet.

What could have affected your yield? Explain what happens to eugenol in each of the extraction steps. If we replaced the steam distillation step with a reflux extraction, would 10% aqueous HCl, NaOH, or Na_2CO_3 have to be used?

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* Let the solid settle on the bottom; then carefully pour the liquid off, leaving the solid behind. Decanting is faster and simpler than filtering if the liquid separates easily from the solid and the solid stays on the bottom.

† Do not add boiling chips. Dichloromethane evaporates so easily that we can simplify life here.

‡ If our procedure were perfect, it would be the percent of eugenol in cloves.

Study Questions

- What is an essential oil?

- What do we use essential oils for?

- What are the sources of essential oils?

- What are two common methods of obtaining essential oils?

- What are the differences between essential oils and fatty oils?

- What do we use steam distillation for in this experiment?

- Why is a steam bath, not a burner, used for separating dichloromethane from the product?

- What do you do to dry the dichloromethane solution?

Report: Extraction of Eugenol from Cloves

Date: ..... Student name: .....

Course: ..... Team members: .....

Section: .....

Instructor: .....

Extraction yield

Mass of cloves	.....	g
Mass of the round-bottom flask	.....	g
Mass of the flask with product	.....	g
Mass of eugenol	.....	g
Percent yield (show work below)	.....	%

Calculation of percent yield:

Questions

What could have affected your yield?

Instructor's evaluation of your product

You first extracted your product from the distillate using dichloromethane. Then you extracted it from dichloromethane using 5% KOH. Next you acidified that solution using 5% HCl and extracted your product back into dichloromethane. What happens to eugenol during each step? What does each step accomplish?

extraction from distillate using dichloromethane:

extraction from dichloromethane using aqueous KOH:

acidification of aqueous solution using HCl:

extraction from aqueous solution to dichloromethane:

If we replaced the steam distillation step with a reflux extraction, would 10% aqueous HCl, NaOH, or Na_2CO_3 have to be used? Justify your answer.

Student name: ..... Course/Section: ..... Date: .....

Problems

- Derive the IUPAC name of eugenol. Look at it as a phenol derivative. The $-OCH_3$ group is called methoxy.

- Draw and name structural formulas for all aldehydes and ketones that have the formula $C_5H_{10}O$. There are seven of them.