Isolation of Eugenol from Cloves by Steam Distillation and its Identification by Infrared Spectroscopy

Eim A. Chemist
CHEM 303
June 16, 2005

INTRODUCTION

"Essential oils" are the volatile components associated with the aromas of many plants.[1] In this experiment, the essential oil eugenol (the main component of oil of cloves) will be isolated from ground cloves using the technique of steam distillation, which is often used to isolate liquid natural products from plants.[2]

The principle of steam distillation is based on the fact that two immiscible liquids will boil at a lower temperature than the boiling points of either pure component, because the total vapor pressure of the heterogeneous mixture is simply the sum of the vapor pressures of the individual components (i. e. $P_T = P^o_A + P^o_B$, where P^o is the vapor pressure of the pure liquids). This leads to a higher vapor pressure for the mixture than would be predicted for a solution using Raoult's Law (that is $P_T = P^o_A N_A + P^o_B N_B$, where N is the mole fraction of the component in the mixture). The higher total vapor pressure leads to a lower boiling point for the mixture than for either single component.[2] During the isolation of a liquid natural product by steam distillation, water is one of the components, and the liquid natural product being isolated (which is immiscible with water) is the other component. The product can be steam distilled from the natural source at a relatively low temperature (always less than 100 ^oC), thus avoiding decomposition of the product.[2]

Steam distillation can be carried out in two ways: the direct method and the live steam method.[3] In the direct method, steam is generated by boiling a mixture of the source of the compound of interest and water. The live steam method is carried out by passing steam from an external source into the distillation flask. The direct method of steam distillation will be used in this experiment and is carried out on a semi-micro scale using the apparatus shown in Figure 1 below:

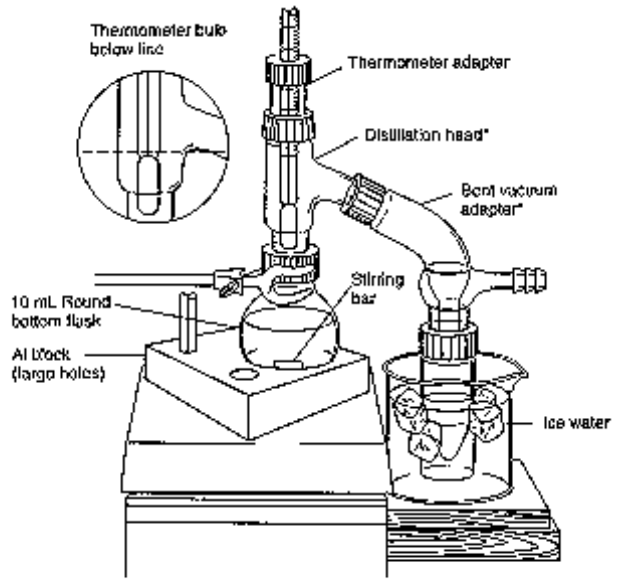
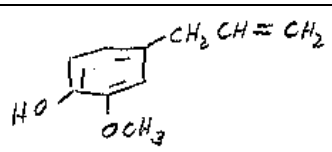


Figure 8.10 Semimicroscale distillation (*requires special pieces).

Figure 1[4]

Ground cloves and water will be charged into the distillation flask shown in the figure. The mixture will then be heated to boiling on a hot plate with an aluminum heating block and the distillate (a eugenol/water mixture) will be collected. The eugenol will then be separated from the water by extraction with methylene chloride. The methylene chloride solution will then be dried, decanted and evaporated to afford the liquid eugenol. The percent recovery from cloves will be determined, and is expected to be about 10%, based on literature data.[5] The product will be analyzed by transmission infrared spectroscopy (IR) as a neat sample using NaCl plates[6] to confirm its structure. This will be done in two ways: (1) by looking at the major absorptions in the spectrum and comparing them to a correlation table[7] and (2) by comparing the spectrum to that of an authentic sample. The major IR absorptions are expected to be 3200 – 3500 cm^{-1} (OH stretch), 3000 – 3150 cm^{-1} (sp^2 C-H stretch), 1600 – 1680 cm-1 (alkene C=C), and 1400 – 1600 cm^{-1} (aromatic C=C)[7].

Table of Chemical Substances[8]

Reagent	Structure/Formula	Role	Mol. Wt.	Mp	Bp	Density
Cloves	---	Other	---	---	---	---
Methylene chloride	CH_2Cl_2	Solvent	84.93	-97 °C	39 – 40 °C	1.32 g/mL
Sodium sulfate	Na_2SO_4	Drying agent	---	---	---	---
Eugenol	 $C_{10}H_{12}O_2$	Product	164.20	-12 to -10 °C	254 °C	1.06 g/mL

Safety Information[8]

Compounds:

Material	Toxic?	Corrosive?	Flammable?	Carcinogenic?
Cloves	No	No	No	No
Methylene chloride	No	No	No	Yes
Sodium Sulfate	No	No	No	No
Eugenol	No	No	No	No

Techniques:

When heating a reaction apparatus, be sure that it is open to the air so that pressure build up and subsequent rupture of the apparatus does not occur.

When heating liquids, make sure the liquid is stirred (or a boiling chip is added) to prevent "bumping".

When performing an extraction, make sure to vent the centrifuge tube often to prevent pressure build-up.

EXPERIMENTAL

The apparatus shown in Figure 1 was assembled using a 25-mL round bottom flask as the distillation pot. The distillation pot was charged with 1.032 g of ground cloves and 15 mL of distilled water. The cloves were allowed to soak in the water until thoroughly wetted (about 15 min), then the mixture was distilled, the distillate being collected at the rate of about one drop every 2 – 3 seconds. After about 6 mL of distillate were collected, the distillate was extracted with 2.0 mL of CH_2Cl_2 (aka DCM), then again with (2 x 1.0 mL) of DCM. The DCM extracts were combined, dried over Na_2SO_4, and evaporated to give the product eugenol as a pale yellow oil.

Product mass: 0.340 g

FTIR (film, NaCl plates): 3560 (OH), 3080 – 3000 (sp2 CH), 2980 – 2940 (sp3 CH), 1640 (alkene C=C), 1514 (aromatic C=C) cm^{-1}. These values closely correspond with those of an authentic sample.[9]

[13]

RESULTS AND DISCUSSION

Steam distillation of cloves produced 0.0770 g of an oil which contained in its IR spectrum the functional groups O-H (at 3560 cm^{-1}), sp^2 C-H (3080 – 3000 cm^{-1}), aliphatic C-H (2980 – 2940 cm^{-1}), and both alkene C=C (at 1640 cm^{-1}) and aromatic C=C (at 1514 cm^{-1}). The IR spectrum is attached to this report. These data are consistent with the structure of eugenol, shown in Figure 2 below:

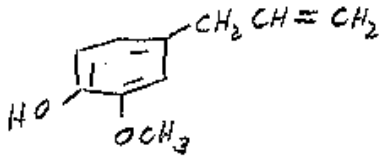


Figure 2: Eugenol

In addition, the IR of the product from the steam distillation of cloves closely corresponds with that of an authentic sample of eugenol shown in the lab text.[9] Therefore, it can be concluded that the oil which was isolated from cloves is in fact, eugenol.

0.0770 g of eugenol was recovered from 1.032 g of cloves. This corresponds to a percent recovery of 7.46%:

$$\% \text{ Recovery} = \frac{\text{Amt. Eugenol isolated}}{\text{Amt. Cloves used}} = \frac{0.0770 \text{ g}}{1.032 \text{ g}} \times 100 = 7.46\%$$

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. Otherwise, it can be concluded that the specific sample of cloves used contains approximately 7.5% eugenol.

SUMMARY AND CONCLUSIONS

In this experiment, it was shown that about 7.5% of an oil could be recovered from cloves by steam distillation. This oil was identified as eugenol by comparison of its infrared spectrum with an authentic sample.

REFERENCES

1. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques, A Microscale Approach;* 3rd ed.; Brooks/Cole: Pacific Grove, CA, 1999; p. 139.
2. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques, A Microscale Approach;* 3rd ed.; Brooks/Cole: Pacific Grove, CA, 1999; p. 663.
3. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques, A Microscale Approach;* 3rd ed.; Brooks/Cole: Pacific Grove, CA, 1999; p. 665.
4. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques, A Microscale Approach;* 3rd ed.; Brooks/Cole: Pacific Grove, CA, 1999; p. 628.
5. Wenqiang, G.; Shufen, L.; Ruixiang, Y.; Shaokun, T.; Can, Q. *Food Chemistry*, **2007**, *101*, 1558.
6. See Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques, A Microscale Approach;* 3rd ed.; Brooks/Cole: Pacific Grove, CA, 1999; p. 743 for a description of this type of sample preparation. The holder described in Figure 19.1 will not be used for this experiment.
7. Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G. *Introduction to Organic Laboratory Techniques, A Microscale Approach;* 3rd ed.; Brooks/Cole: Pacific Grove, CA, 1999; p. A19.
8. Data taken from product descriptions and MSDS's at the Fisher Scientific website. https://new.fishersci.com (accessed June, 2005).
9. *Introduction to Organic Laboratory Techniques, A Microscale Approach;* 3rd ed.; Brooks/Cole: Pacific Grove, CA, 1999; p. 142.

ANSWERS TO QUESTIONS

1. Why is eugenol steam-distilled rather than purified by simple distillation?

   Eugenol has a high boiling point (254 ^{o}C), and many organic compounds decompose at such high temperatures. Steam distillation allows eugenol to be distilled at a much lower boiling point (< 100 ^{o}C), thus minimizing the potential for decomposition.

2. In a steam distillation, the amount of water actually distilled is usually greater than the amount calculated, assuming that both water and organic substance exert the same vapor pressure when they are mixed that they exert when each is pure. Why does one recover more water in the steam distillation than was calculated? (Hint: Are the organic compound and water truly immiscible?)

   In most cases, organic substances have some solubility in water. If this is true, then the amount of water which is required to steam distill the substance in its entirety is the calculated amount plus an amount needed to distill over the amount of substance dissolved in water.

3. Steam distillation is one way to isolate an essential oil from a plant or fruit. Describe two other methods.

   Expression (or cold-pressing) is the process of mechanically squeezing the oils out of the source, and is usually used for isolating citrus fruit essential oils. Solvent extraction is the process of treating the source with an organic solvent, such as hexane or supercritical carbon dioxide. The oils dissolve in the organic solvent, and then are isolated by evaporating the organic solvent.

6/14/05 Eugenol From Cloves

E. A. Chemist

USE ASSIGNED VOICE WINDOW WHILE WRITING UP THE 03 LAB PROTOCOL!

1. The apparatus shown in Figure 1 of the Introduction (p. 628 of Alvim, et al.) was assembled using a 25 ml round bottom flask as the distillation flask. A spin vane was used as the stirring bar.

2. The distillation flask was charged with 1.032 g of ground cloves and 15 ml of distilled water.

3. The cloves were allowed to soak in the water for about 15 min., until the cloves were thoroughly wetted

4. With cooling water running through the condenser, the mixture was heated using an aluminum block (Setting on hot plate - 2-3). After ~ 20 min, the mixture still was not boiling, so the hot plate was setting was increased to 7. The mixture began boiling, and food distillate was collected at the rate of ~ 1 drop every 2-3 seconds.

5. After ~ 6 ml of distillate were collected, the distillation was discontinued.

~~6. The distillate was placed in a 60 ml separatory funnel and extracted~~

6. The distillate was placed in a 15 ml screw-cap centrifuge tube, and 2.0 ml of CH_2Cl_2 was added. The mixture was shaken well, vented by unscrewing the cap slowly, and the lower CH_2Cl_2 layer was transferred to a dry 5 ml conical vial using a Pasteur pipet.

6/14/15 Eugenol From Cloves

E. A. Chemist

7. The remaining aqueous layer was extracted two more times w/ 1.0 ml (each) of CH_2Cl_2. These CH_2Cl_2 extracts were combined with the CH_2Cl_2 extract from Step 6.

8. The combined CH_2Cl_2 extracts were dried over anhydrous sodium sulfate. Enough sodium sulfate was added so that free-flowing crystals were present. Then the CH_2Cl_2 extracts were allowed to stand for 10-15 min.

9. The CH_2Cl_2 solution was decanted away from the sodium sulfate (using a pasteur pipet) into a dry 5 ml conical vial. The drying agent (i.e. the sodium sulfate) was rinsed with small amounts of CH_2Cl_2, and these washings were combined with the original CH_2Cl_2 extracts.

Vial wt = (w/o cap) 18.643 g

10. Under a hood(!), the CH_2Cl_2 solution was evaporated by heating on a hot plate (Setting = 3) + directing a slow stream of air over the top of the vial. This gave (after evaporation was complete) a pale yellow oil weighing

Wt of vial + oil = 18.720 g
Tare wt of vial = 18.643 g

Product wt: 0.0770 g

11. One drop of product was placed between 2 NaCl plates and a transmission IR was taken.