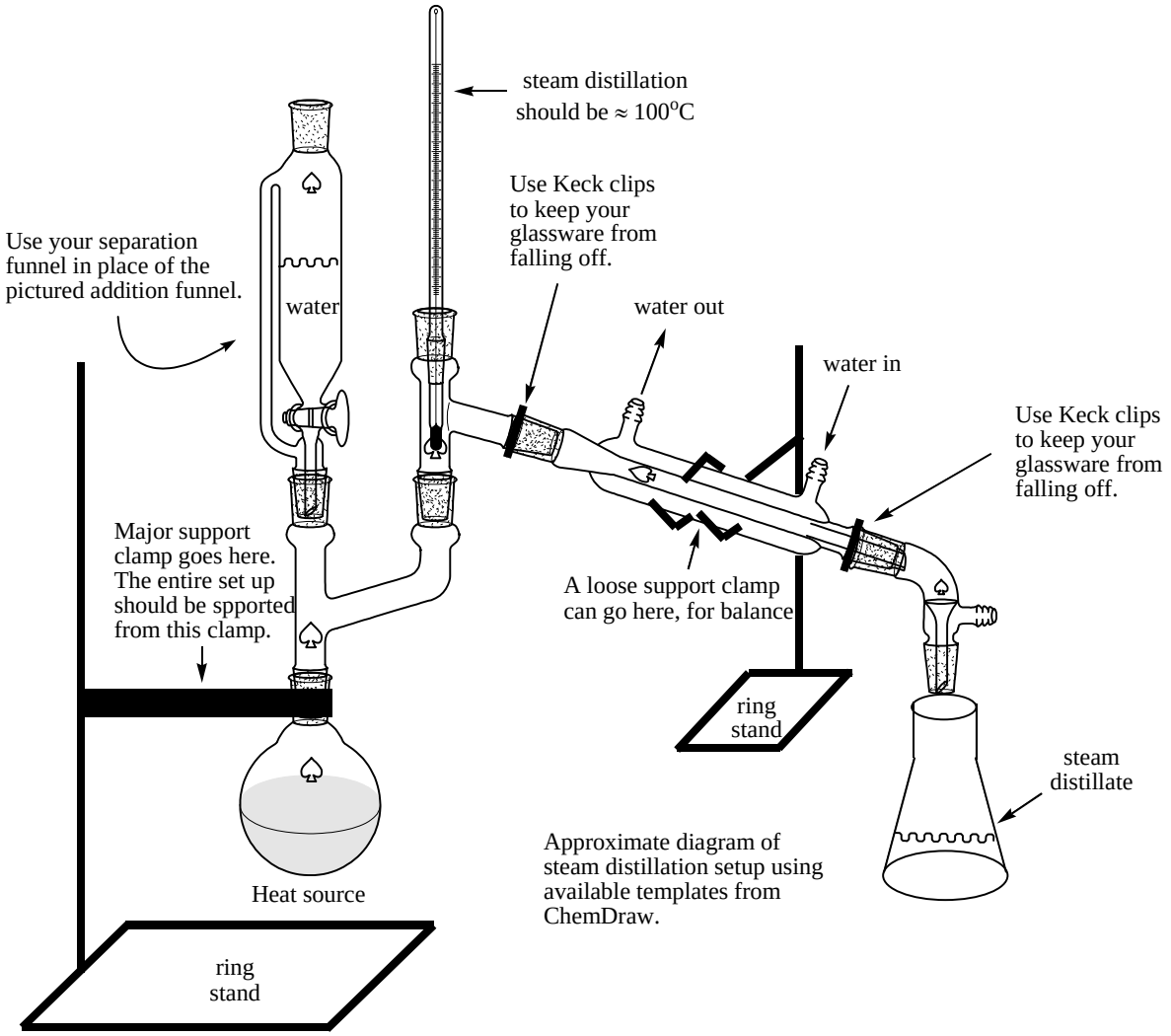
Eugenol extraction from cloves using steam distillation

The goal of this experiment is to isolate the natural product, eugenol, from cloves using the following procedure. You will need to acquire an IR, H-NMR, C-NMR and GC-MS and provide a complete explanation to show how these confirm the structure. You will also need to turn in your lab notebook pages for the work done on this project. Someone else should be able to repeat the entire procedure by just using your lab notebook pages. (20 points for your spectra and explanation and 20 points for your lab notebook pages = 40 total points)



Approximate diagram of steam distillation setup using available templates from ChemDraw.

It is possible that there are some esters of eugenol, along with eugenol itself. Weigh out 15 grams of cloves and place them in a 250 mL round bottom flask. Add about 125 mL of water and 3-4 boiling chips. It must be at least half full and a little more is ok. Set up a distillation apparatus, approximately as shown above. Heat the contents using a <u>low flame</u> (acceptable here because you are essentially distilling water) until the water starts to boil. Occasionally this mixture will foam, so boil at a steady rate that keeps the foam from bumping over. You can transfer out your distillate periodically to a graduated cylinder to keep it separate in case your distillation does bump over (and you monitor the amount of liquid that has distilled out). Collect about 80 mL total, making sure to keep the liquid volume in your distilling flask approximately constant by adding water from your separatory funnel (or addition funnel) to replace the water distilled.

Place the distillate in a 125 or 250 mL separatory funnel and extract with 3 x 15 mL of dichloromethane (methylene chloride). Remember, the bottom layer is the more dense liquid. Shake

gently at first since dichloromethane can form emulsions with organics and water. If you get an emulsion, you can draw off the clear part of the dichloromethane until the emulsion on your first two extractions. On your third extraction, shake the mixture more gently and allow more time for separation. You can also gently swirl the liquid in your separatory funnel. If there are lots of bubbles at the interface, leave that part behind to avoid pulling off excess water. Combine all of your dichloromethane extracts (~45 mL). If you can see water globules floating on the top, you may want to redo a separation in the sep funnel. Next, add enough sodium sulfate so that the separated dichloromethane does not clump. Swirl the flask well to allow the drying agent to absorb the water from the wet dichloromethane. Remember, any water present will on the top of the CH_2Cl_2 and the sodium sulfate will be on the bottom. When the CH_2Cl_2 is dry you should be able to decant it from the sodium sulfate. If you see any suspended particulate matter, then do a gravity filtration.

Measure your volume of dicholoromethane solution in a dry graduated cylinder. Place one fifth in a 50 mL beaker, cover it with some tin foil, and allow the dichloromethane to evaporate over the next week at the back of the hood. Call this fraction A. You will check this with TLC and IR in the next lab. This 1/5 fraction has all of the volatile oil components steam distilled from the cloves (perhaps eugenol esters). Make sure your flask is identified with your initials or name using a Sharpie pen.

Take the remaining 4/5 of your dichloromethane solution and add it to your 125 mL separatory funnel. Extract it with 3 x 10 mL of 5% aqueous NaOH solution. Dry (Na_2SO_4) and save the dichloromethane solution to see if any esters of eugenol or other volatile oil material remains after you have extracted the eugenol. Decant the dried dichloromethane solution into a clean, dry, tared 50 mL beaker. Label it with a Sharpie, cover the top with a small piece of tin foil and place in the hood to evaporate over the next week. This fraction has any volatile oil material not extracted into the aqueous base solution. Call this fraction B. You will check this with TLC and IR in the next lab.

Acidify the aqueous NaOH extracts to a pH < 3 with concentrated HCl (drop wise addition, use litmus paper to check the pH by touching the paper with the tip of a pipet or glass rod). Extract the HCl solution with 3 x 8 mL of dichloromethane. Dry the combined extracts with sodium sulfate, as before. Either rotovap off the dichloromethane, or let it evaporate from a 50 mL beaker, as with the other solutions over the next week. Make sure your clean, dry flask is identified, and tared. Calculate a percent recovery of eugenol from the cloves. Call this fraction C. You will check this with TLC and IR in the next lab.

Analyze your different fractions (A, B and C) using TLC. Develop 2 different TLC plates with the three fractions. Use 2:1 dichloromethane/hexane and 1:2 dichloromethane/hexane. Which solvent system works better? Take an IR of each of the fractions (if you can) and run an H NMR, C NMR and GC-MS on the eugenol fraction (C).

Combine all of your discarded aqueous layers and neutralize them with sodium carbonate or HCl, as needed. Dilute them with water and wash them down the drain. Discard any residual dichloromethane in a halogenated waste bottle. Allow the sodium sulfate to dry in the hood and then place it in a nonhazardous solid waste container. Dump you wet cloves on some paper towels in the hood, let them dry until the next lab and then place them in a large beaker for disposal.

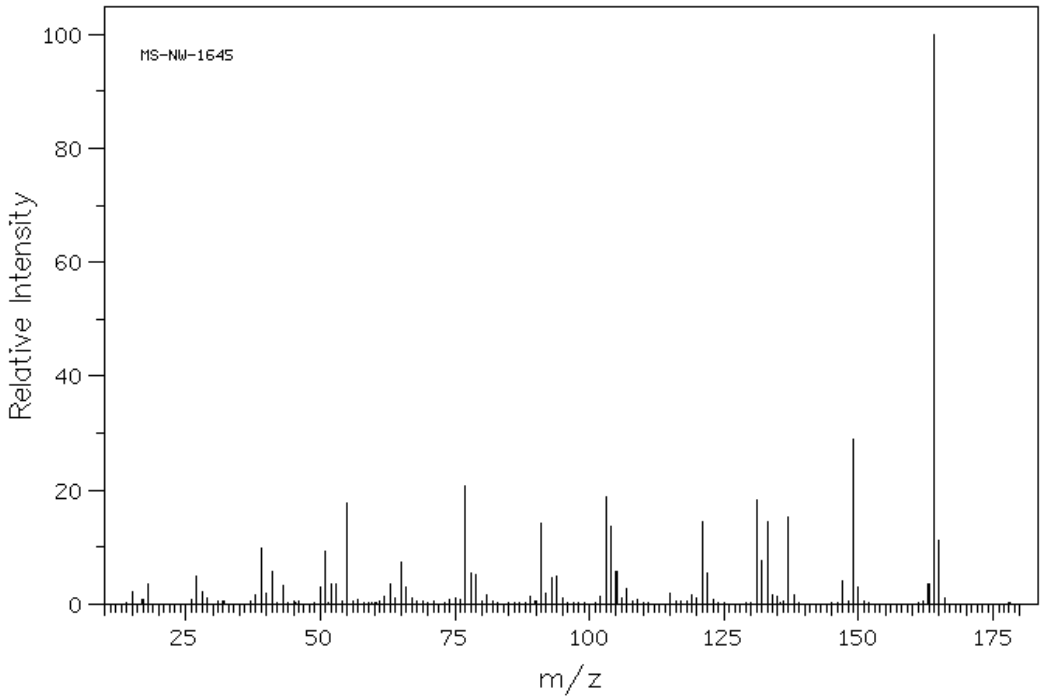
Necessary materials:
Steam distillation glassware, ring stands, Keck clamps, cloves, water, dichloromethane, 5% NaOH, concentrated HCl, sodium sulfate (drying agent), TLC slides, TLC solvents (1:2 hexane/dichloromethane and 2:1 hexane/dichloromethane), spotting capillaries, several small beakers (50 mL should work), NMR tube, NMR solvent ($CDCl_3$), IR plates, tin foil, 100 mL graduated cylinder.

You will repeat the eugenal extraction using a Soxhlet extractor for comparison.

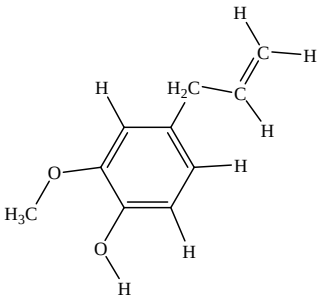
Eugenol Spectra

Mass Spec – explain as many of the MS peaks that seem explainable.

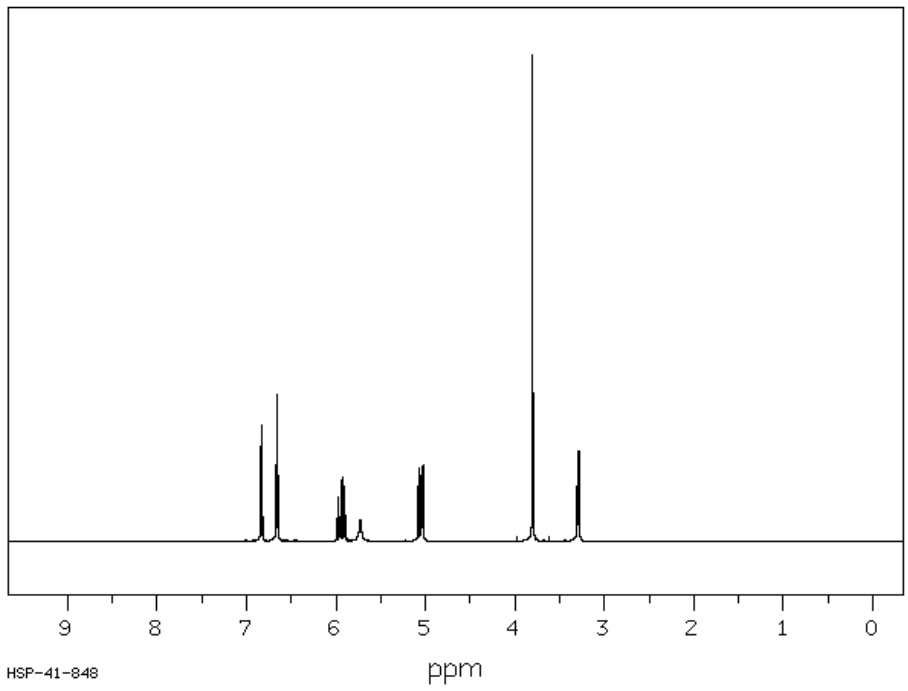
55.0	17	
65.0	7	
77.0	20	
78.0	5	
79.0	5	
91.0	14	
103.0	18	
104.0	13	
105.0	5	
121.0	14	
122.0	5	
131.0	18	
132.0	7	
133.0	14	
137.0	15	
149.0	28	
164.0	100	= MW
165.0	11	
166.0	1	



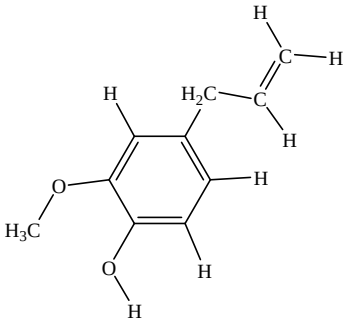
Proton NMR – as best you can match the protons to the chemical shifts



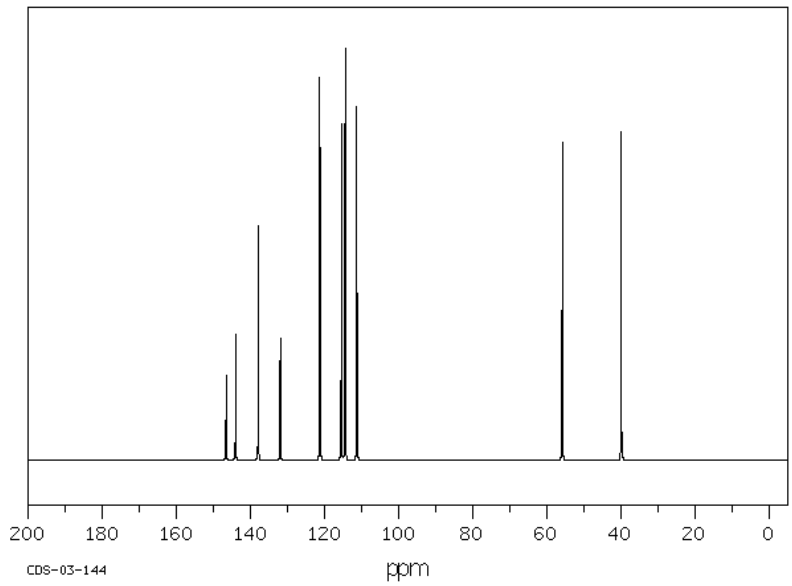
proton	shift
A	6.83
B	6.66
C	6.65
D	5.93
E	5.73
F	5.06
G	5.04
J	3.80
K	3.21



Carbon NMR – as much as possible match the carbon chemical shifts to the carbon atoms



shift
147
144
138
131
121
115
114
111
56
40



IR – match each wavenumber with a functional group feature in the eugenol molecule

IR (cm^{-1})
3520
3080, 3060
2980-2850
1610-1450
1270
1230