

EXP. 57A
EXTRACTION AND CHARACTERIZATION
OF ESSENTIAL OILS FROM SPICES

EXPERIMENTAL OBJECTIVES: To extract the essential oils from various spices by steam distillation and characterize the structures using spectroscopy data.

READINGS: Pages 502 - 506 from the laboratory textbook, as indicated in the syllabus.

ADVANCE PREPARATION (one week earlier)

Your lab instructor will assign one of the following spices to each group:

- a) Cinnamon
- b) Cumin
- c) Caraway

1. Weigh 2 g of the spice and crack it into smaller pieces. There is no need to grind it into a powder or a paste, just smaller pieces.
2. Place the cracked spice into an erlenmeyer flask and add 15 mL water. Swirl a few times.
3. Seal the flask with parafilm or aluminum foil and allow it to stand in the drawer for a week.

PROCEDURE

1. Open the flask containing the spice mixture and boil the contents for about 5 min, being careful to control frothing and foaming.
2. Allow the spice bits to settle and pour 5 mL of the supernatant into a 10 mL round-bottom flask with a spin vane in it.
3. Assemble a distillation apparatus as shown in fig. 18.3, page 753 of your textbook. Use a sand bath instead of the aluminum block.
4. Begin the steam distillation by following the procedure described on page 505 of your textbook under the heading **Steam Distillation** (about mid page).
5. As the reservoir of the Hickman Head fills up with distillate, draw it out with a pasteur pipette and collect it into a graduated cylinder. At the same time, add more of the spice solution to the round-bottom flask to maintain a level of liquid of about half to two thirds of the flask volume. Do not fill the flask to the neck.
6. Continue the distillation process in this fashion until you have collected about 10 mL of distillate.
7. Transfer the distillate to a centrifuge tube and extract the essential oil with methylene chloride as described on page 505 of your textbook under the heading **Extraction of the Essential Oil**.

8. Combine and dry the organic extracts using anhydrous sodium sulfate.
9. Transfer the organic extract to a small erlenmeyer flask or beaker (about 10 mL in size), place it into a hot water bath (at about 80° celsius), place a wooden stick inside the solution, and proceed to evaporate the solvent until all the methylene chloride has been removed from the sample.
10. The boiling point of methylene chloride is about 40°. To make sure all the methylene chloride has evaporated, monitor the temperature inside the spice solution until it reaches about 80°. At the same time make sure you're not losing substantial amounts of your product through evaporation (which you should not, because the boiling point of your product is likely above 200°).
11. It is important to evaporate all the methylene chloride because otherwise it will show a strong peak in the NMR spectrum that will interfere with the peaks from your product. **The chemical shift of methylene chloride is about 5.3 ppm.** Any peaks in this region whose integral is not a multiple of those of the other peaks in the spectrum might be due to residual methylene chloride. A similar reasoning applies to chloroform (a contaminant in deuterated chloroform), whose chemical shift is about 7.2 ppm. For a list of NMR solvent chemical shifts see http://www.sdsnmr.com/cs_table.html
12. Record the percent recovery of your essential oil relative to the amount of spice originally weighed. Record an IR spectrum and submit a sample to your instructor for NMR analysis.
13. NMR ANALYSIS: Refer to the recitation notes for exp. 57A. Decide which of the structures shown on page 502 of your textbook best matches your NMR spectrum. Verify that the IR pattern agrees with your choice of structure, and report your conclusion along with your rationale

NICE WEBSITE FOR ORDERING SPICES, TEAS, OILS, AND OTHER RELATED ITEMS

San Francisco Herb Co.: <http://sfherb.com>

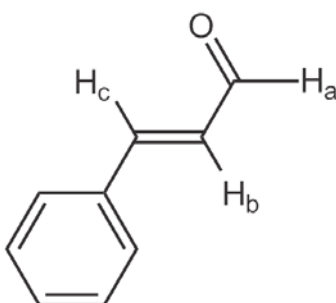
PREDICTING A $^1\text{H-NMR}$ SPECTRUM FROM THE STRUCTURE

USEFUL READINGS

Refer to your organic chemistry lecture textbook (L.G. Wade Jr. *Organic Chemistry*, 6th ed.), chapter 13 (p. 559) and appendices 1A, 1B, and 1C (p. 1243). Your lab textbook also has a useful discussion in Technique 26, p. 868-899, including some useful spectra that you can compare your structures to.

REFER TO THE STRUCTURES PRESENTED ON p. 502 OF YOUR LAB TEXTBOOK

Structure A

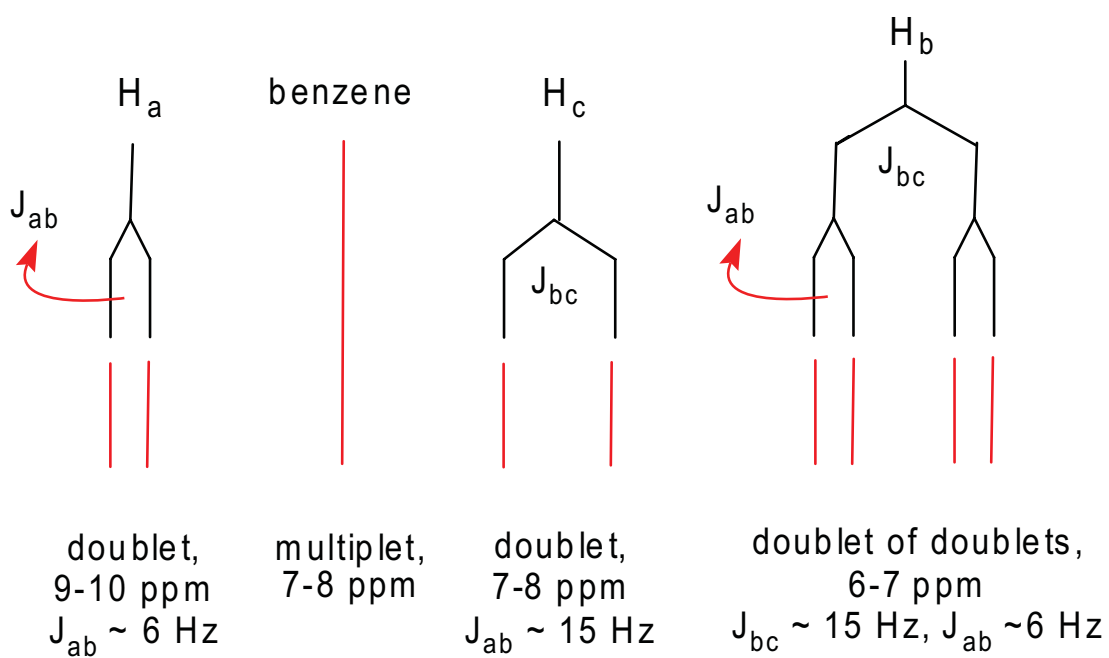
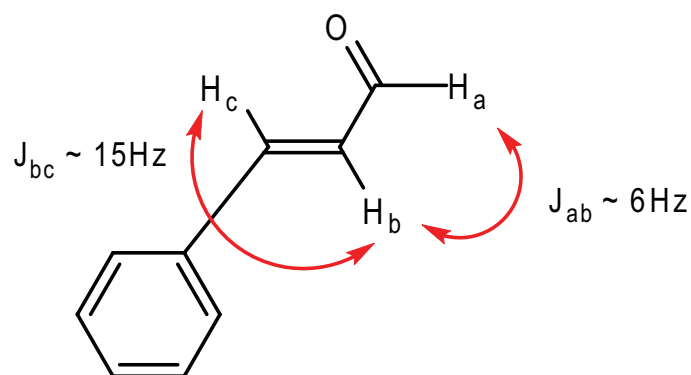


Each proton NMR signal is split into two by each nonequivalent neighboring proton. The size of the splitting (separation between the two peaks) is determined by the coupling constant J between the two neighbors. The coupling constant for two neighboring hydrogens connected through single bonds, such as H_a and H_b is J_{ab} , and its average value is about 6 Hz (Wade, p. 583). The coupling constant for two neighboring protons connected through a pi-bond and *trans* to each other, such as H_b and H_c is J_{bc} , and its average value is about 15 Hz. Finally, when they are *cis* to each other (not the case in the above structure), the coupling constant average would be about 10 Hz.

At the same time that we also consider the probable chemical shift (δ) values. For an aldehyde proton such as H_a , the average chemical shift is about 9-10 ppm. For vinylic protons such as H_b and H_c the average chemical shift is about 6-7 ppm. We expect H_b to be closer to 7 because of the effect of the carbonyl group, and we expect H_c to be even higher, maybe greater than 7, because of the effect of the benzene ring. Finally, the protons in the benzene ring itself have an average chemical shift of about 7-8 ppm. Thus there might be overlap between H_c and the benzene ring signals.

We typically don't try to predict the pattern of benzene ring protons because it can follow complex factors whose study is beyond the scope of this course. Therefore we will simply accept that they will appear somewhere between 7-8 ppm, but can never be sure about the degree of complexity or the shape of the multiplet.

On the following page we have the predicted proton NMR spectrum according to the above guidelines. In reality, a spectrum may or may not appear as predicted, but the predicted pattern is a starting point towards the elucidation of the structure and eventual assignment of the signals actually observed.



Predicted Spectrum (by decreasing chemical shift):

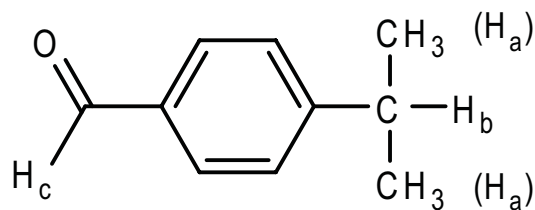
Ha: 9-10 ppm, doublet, $J_{ab} \sim 6\text{ Hz}$

Benzene cluster: 7-8 ppm, multiplet

Hc: 7-8 ppm, doublet, $J_{bc} \sim 15\text{ Hz}$

Hb: 6-7 ppm, doublet of doublets, $J_{bc} \sim 15\text{ Hz}$, $J_{ab} \sim 6\text{ Hz}$

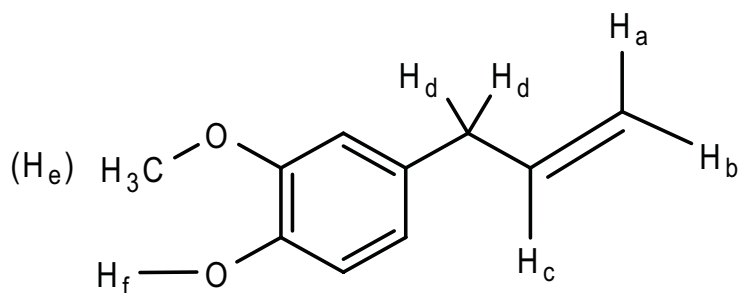
Structure B



Structure B hardly requires any discussion. Once again, we simply expect a multiplet around 7-8 ppm integrating to 4 hydrogens for the **benzene ring**. We also expect the **aldehyde proton** around 9-10 ppm, except that this time it's going to be a singlet because there are no adjacent protons.

The only other group present is the **isopropyl group**. Thus we expect to see the *isopropyl group pattern* (refer to p. 581 in the Wade textbook, 6th ed.). The methyl group doublet will probably appear between 1-2 ppm (alkane region), whereas the septet, or multiplet, will be deshielded by the benzene ring, appearing around 2-3 ppm (benzyl group region). Since the benzene ring contains an electron withdrawing group at the *para*-position (the aldehyde group), we expect further deshielding of the benzyl protons H_b to where they might appear closer to 3 ppm.

Structure C

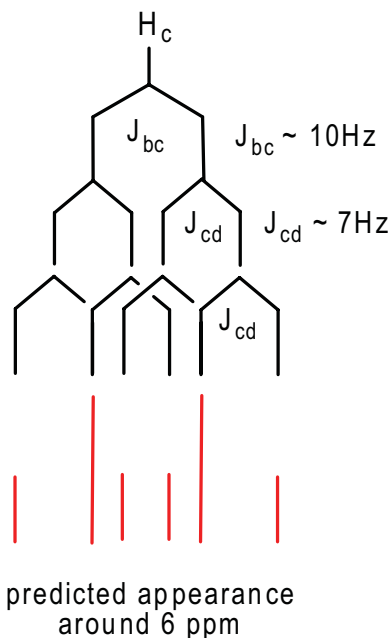


Structure C is a little more challenging. When we face this situation we try to predict the easiest patterns first. Once again, our **benzene cluster** will be around 7-8 ppm, except that now we expect it to integrate to only 3 hydrogens, since the benzene ring is trisubstituted. Likewise, the **methyl protons** (H_e) will appear as a singlet around 3-4 ppm, which is the region assigned to ethers, and they are further deshielded by the benzene ring. H_f is the next easiest to predict. It will be a single multiplet, but hydrogen bonding signals such as alcohol protons can fluctuate in a wide range of chemical shift values, maybe between 3-6 ppm, and they could appear either as sharp or broad signals. It will obviously integrate to 1 hydrogen.

H_d protons only have one neighbor (H_c) to couple with. They are deshielded by the benzene ring and the double bond, so we expect them to appear in the allylic region, which is normally around 2 ppm (table 13.3, p. 568 in Wade), but shifted downfield to maybe 3-4 ppm. We expect it to be a doublet integrating to 2 hydrogens, with a coupling constant J_{dc} of about 7 Hz.

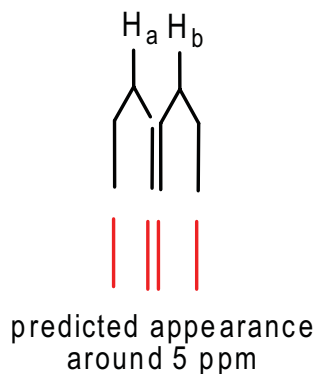
Protons, H_a, H_b, and H_c, are even more challenging. For one thing they are all vinylic protons that will appear close together, but coupled to their neighbors with different coupling constants.

H_c will probably appear separate from H_a and H_b further downfield because it's closer to the benzene ring. Its signal will be split once by H_b with a coupling constant of about 10 Hz because they are *cis* to each other. Then it will be split twice by H_d because there are two of them, with coupling constant of about 7 Hz. Thus we can predict a pattern such as the following:



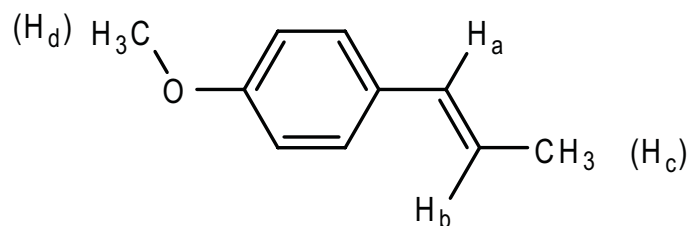
However, be warned that there might be complicating effects such as long range coupling to far away protons, and others not uncommon in this type of spectrum. This can distort the appearance of the predicted pattern. Nonetheless, H_c will appear as a complex multiplet around 6 ppm integrating to 1 hydrogen.

H_a and H_b are nonequivalent (one is *cis* to H_c while the other is *trans*) but will probably appear very close together, perhaps around 5 ppm. The coupling constant between the two is very small -about 2 Hz- since they are geminal (see p. 583 of Wade). Thus, we might predict a kind of triplet such as might be the following:



However, once again, there might be complicating effects that may distort the appearance of the predicted pattern. Nonetheless, this cluster will appear as a multiplet around 5 ppm integrating to 1 hydrogen as well.

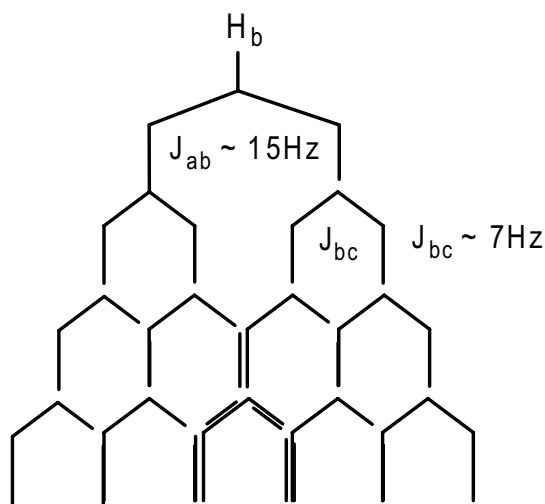
Structure D



At this point you should be able to predict the appearance and chemical shifts of the **methyl groups H_c and H_d** , and of proton **H_a** , based on the previous discussions for the other molecules containing similar types of hydrogens.

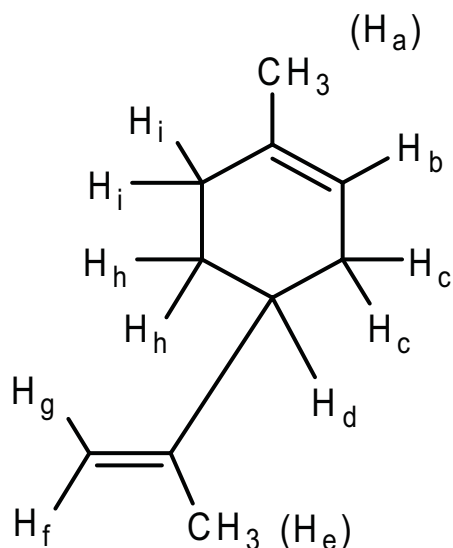
H_a will probably appear as a doublet around 6-7 ppm with J_{ab} of about 15 Hz for *cis* coupling and integrating to 1 hydrogen.

This leaves us with **H_b** . This will probably appear as a multiplet around 6-7 ppm (very close to H_a), split once by H_a with J_{ab} of about 15 Hz, and three times by H_c with J_{bc} of about 7 Hz. Needless to say, it will probably be the most complex multiplet in the spectrum (along with the benzene ring), very close to H_a and integrating to 1 hydrogen. The tree below shows the predicted pattern, but again, we expect that the actual appearance could be distorted due to additional effects.



Multiplet around 6-7 ppm.

Structure E



Let's consider first of all that we have several sets of **allylic protons** here, namely **H_a**, **H_c**, **H_e**, and **H_i**. All of these protons will probably appear close together in the allylic region, 2-3 ppm. However, **the methyl groups H_a and H_e** should stand out as singlets, since technically they don't have neighboring protons on adjacent carbons to couple to. However they could exhibit long range coupling to far away protons and show some fine splitting.

Protons **H_d** and **H_h** might also appear close together and could overlap with the allylic protons, creating a highly complex multiplet. However, the methyl groups should be highly visible and should integrate to a total of 6 hydrogens. Likewise, the integral for the complex multiplet will indicate how many hydrogens it represents. Beyond these remarks we cannot say much more about the pattern of all these protons.

Next we have the vinylic protons, whose typical range is between 5-7 ppm (table 13-3, p. 568, Wade). First we look at the geminal protons **H_f** and **H_g**. They are nonequivalent, since one is *cis* and the other *trans* to the methyl group. They should be singlets, although probably close together, integrating to 1 hydrogen each.

Finally, proton **H_b** will also appear in the vinylic region, but it will be coupled to protons **H_c** and possibly long range coupled to other allylic protons, creating a multiplet which also integrates to 1 hydrogen.