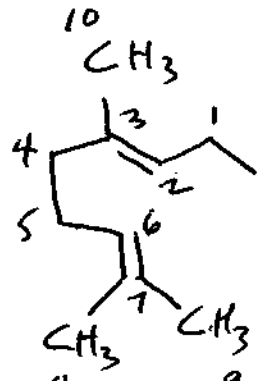
Problem Set #7 Answers

Chapt 10 #5:



Geraniol

$C_{10}H_{18}O$

(i) DEPT-135

2 olefinic CH's at ~125 ppm

3 CH_2's

3 CH_3's

8 c's — Molecule has 10 c's + no symmetry
∴ peaks for C-3 & C-7 do not show up in DEPT.

So only 8 c's show up, unless care is taken, since long T_1's & O nOe for C-3 & C-7 mean that they have low intensity (discussed in class).

They occur at 137 & 131 ppm (range not shown in ^{13}C onP 563)

COSY interpretation

Starting point: H's on C-1 should be a doublet at ~ 4 ppm.

(ii) – strong correlation to multiplet at 5.5 ppm

∴ C-2 H is at ~ 5.5.

(iii) – also, there is a correlation to a CH_3 at ~ 1.5 ppm (^4J coupling). This must be C-10 H's.

(iv) the other olefinic H (on C-6) must be at ~ 5.1 ppm it shows a strong correlation to the multiplet at ~ 2.0 ppm ∴ H's on C-5 must be at ~ 2.0 ppm

(v) there is also a correlation to the two methyls at ~ 1.6 ppm (some overlap here)

– these must be C8 + C9.

(vi) looks like H's on C-4 overlap with those on C-5 (∵ both are allylic). at ~ 2 ppm

∴ all H's assigned !

HETCOR of Geraniol

(6)

^1H assignment	δ	^{13}C
H-1's (2H)	4.2	60
H-2	5.5	~ 123.
H-4 (2H)	2.0	~ 40
H-5 (2H)	2.0	~ 28 (shielded by cis-CH_3)
H-6 (1H)	5.1.	124
C-9, C-9 (CH_3's)	1.6	16 & 18
C-10	1.5 - 1.6	26

∴ Some ambiguity in CH_3 assignments remains!

Problem Set #7 Answers

Chapter 10 #7: $C_6H_{12}O_2$ ∴ # sites of unsat'n $= 7 - \frac{12}{2} = 1$.

Looks like $-\overset{O}{\overset{\|}{C}}-OH$ present.
(∵ of IR and 12 ppm in ^1H NMR).

^1H NMR integration info:

1 : 1 : 1 : 1 : 1 : 6 & 1 H at 12 ppm

∴ all 12 H's accounted for!

^1H NMR – High field region
– looks like $(CH_3)-CH_2$
∴ triplet (3 H)

and $(CH_3)-CH$
∴ doublet (2 H)

also $-\overset{O}{\overset{\|}{C}}-OH$

∴ We have accounted for 5 C's.
10 H's
2 O's.

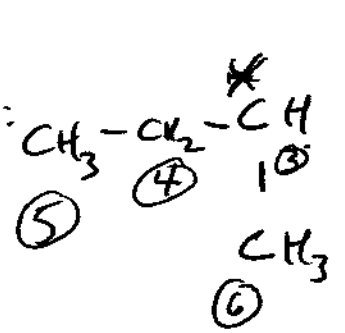
Looking at ^{13}C-^{1}H HETCOR.

- note that $-\overset{\overset{O}{\|}}{C}-O-H$ resonance is missing (around 170 ppm)

- but there are 2 cases with non-equivalent H's on the same C

∴ must have 2 CH_2's adjacent to a stereogenic centre!!

Possible structure:



Use Appendix #6 to calculate ^{1}H shift for H's on C②: Results: Predicted Shift

is 0.23 + 1.55 + 0.47

= 2.25 ppm

observed is 2.1 → 2.4 ppm

∴ Good Fit!!

Spectral Analysis

J_{AB} must occur 4 times as follows:

719.92	713.67	655.58	647.49
704.85	698.59	640.50	632.41
15.07	15.08	15.08	15.08

$\therefore {}^2J = 15.08$ Hz. (J_{AB}).

other couplings

(i) "left" multiplet

719.92	704.85
713.67	698.59
6.25	6.26

$\therefore {}^3J \simeq 6.25$ Hz.

(ii) "right" multiplet

655.58	640.50
647.49	632.41
8.09	8.09

otta ${}^3J \simeq 8.09$ Hz.