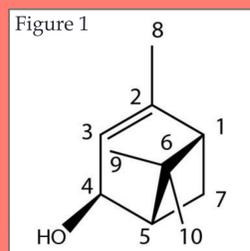


^1H and ^{13}C NMR Assignments for (S)-cis-verbenol

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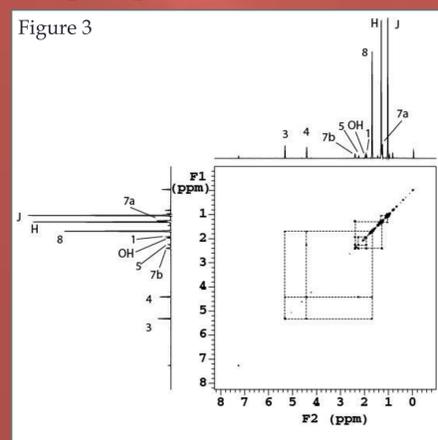
(S)-cis-Verbenol, formally (1S,cis)-4,6,6-Trimethyl-bicyclo(3.1.1)hept-3-en-2-ol, has a M_w of 152.24g/mol. Industrial uses include: pine beetle pheromone, perfume, flavoring, and "green pesticides".

^1H NMR 1D Analysis:

The ^1H NMR spectrum was recorded at 800MHz (^1H) using a spectral width of 7396.45 Hz and 16384 complex points. We can identify the ^1H resonance at 5.36 ppm (A) as the proton attached to C3 based on canonical values for vinylic ^1H resonances. The ^1H resonance at 4.46 ppm (B) is consistent with a proton bound to a COH moiety, and we assign that resonance as H4. The resonance at 2.05 ppm (E) corresponds to the hydroxyl proton. The resonance at 1.73 ppm (G) is assigned to the methyl group at C8. This resonance has a curious fine-structure triplet with very small J -value due to a long range coupling to the protons at positions 1 and 3 (thus a pseudo-triplet). The resonances at 1.30 ppm (I) and 2.44 ppm (C) are assigned based on the Karplus Equation (cis vs. gauche 3° -coupling) to protons 7a and 7b. First we examine the doublet at 1.30 ppm which we designate as 7a. We see minimal coupling to protons bound to adjacent carbons atoms, hence the observed doublet structure of the resonance. Vicinal protons coupling constants are known to depend on the torsional angle between the participating ^1H nuclei (Karplus equation). If the relative angle between the two protons is between 85° and 95° , we expect that a coupling constant close to zero to result. We will designate this proton as 7a because we addressed it first. Next we examine the multiplet at 2.44 ppm, which we designate as 7b. The fine structure of this resonance occurs due to coupling to the protons at 2.88 ppm and 1.95 ppm respectively. According to the Karplus equation this would mean that the proton C would be cis to the two other protons it couples with. We also observe that the resonance at 2.88 ppm (D) would correspond to C5 due to the inductive effect of the hydroxyl group (downfield shift). This leaves the resonance at 1.95 ppm (F) to be the proton attached to C1. Resonances at 1.07 ppm (J) and 1.35 ppm (H) cannot be resolved using this spectrum alone.

COSY ANALYSIS:

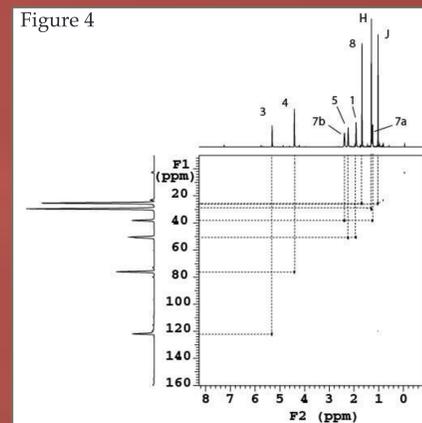
The COSY spectrum was recorded on an 800MHz (^1H) spectrometer using a spectral width of 7396.45 Hz with 1024 complex points in the direct (F2) dimension and a spectral



width of 7396.45 Hz and 512 points in the indirect (F1) dimension. Review of Figure 3 reveals correlations between resonances corresponding to: protons 3 and 8; protons 3 and 4; protons 4 and 8; protons 4 and 5; protons 7b and 7a; protons 7b and 1; protons 7b and 5; and protons 5 and 1. Observation of these correlations improves our confidence in the tentative assignments.

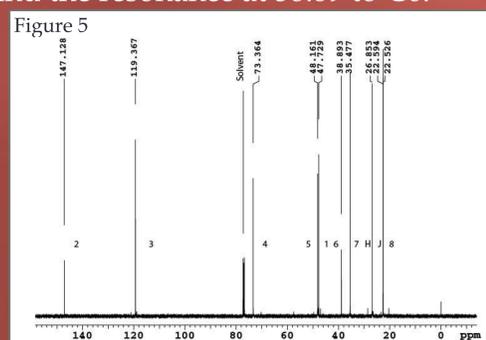
HMOC Analysis:

The HMOC spectrum was obtained on a 800MHz (^1H) spectrometer with a spectral width of 7396.45 Hz and 1024 complex points in the direct (F2) dimension, and a spectral width of 48250 Hz and 512 complex points in the indirect (F1) dimension. We use this spectrum to assign the carbon resonances using correlations from the directly bound proton resonances. We see that 7a and b both have correlations to the same carbon at 35.47 ppm. We can also assign carbons 1, 3, 4, 5, and 8 and 5 using the correlations to the respective proton resonances. We put C1 at 47.72 ppm and C3 at 119.37 ppm, C4 at 73.36 ppm C5 at 48.16 ppm, and C8 at 22.53. This also verifies that E corresponds to the hydroxyl group because it has no correlation to a carbon peak. The spectra also shows two carbons without any correlation, which are the quaternary carbons at positions C2 and C6.



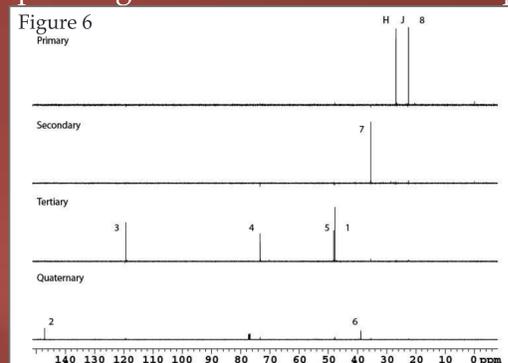
^{13}C 1D Analysis:

The spectrum was obtained on a 500 MHz (^{13}C) spectrometer using a spectral width of 31250 Hz with 32768 complex points. Review of this spectrum allows us to assign the quaternary resonances corresponding to C2 and C6 by inspection. Specifically, the resonance of C2 would be expected to be significantly farther downfield than that of C6, due to the sp^2 hybridization at C6. Thus we assign the resonance at 147.13 ppm to C2 and the resonance at 38.89 to C6.



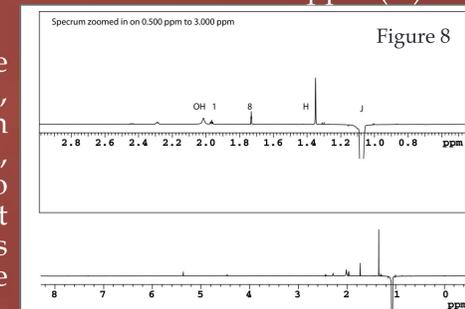
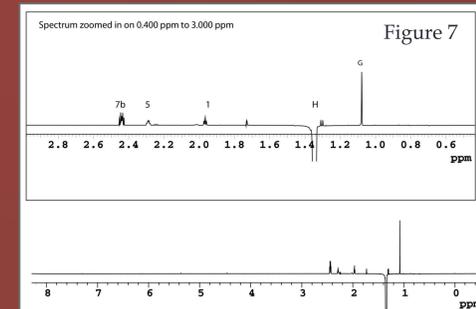
^{13}C DEPT Analysis:

The DEPT spectra were recorded on a 500MHz (^1H) spectrometer with a spectral width of 31250 and 32768 complex points. These spectra confirm our previous assignments: resonances corresponding to C8, C9, and C10 are all methyl groups (primary); the resonance corresponding to C7 is from a methylene group (secondary); the resonances corresponding to C1, C2, C4, and C5 are from methine groups (tertiary); and the resonances corresponding to C2 and C6 are from quaternary carbon moieties.



1D NOESY Analysis:

The 1D NOESY Spectra were obtained on a 800 MHz (^1H) spectrometer using 7022.47 Hz and 16384 complex points. Data were recorded using 256 transients. By inspection of the spectra for the resonances found at 1.07 ppm and 1.34 ppm respectively we are able to assign positions H and J. Figure 7 shows NOE correlation from the resonance at 1.34 ppm (H) and 2.44 ppm (7b). Figure 8 shows an NOE correlation between the resonance at 1.07 ppm (J) and 2.05 ppm (OH). Consideration of a 3D model of the molecule reveals that of the two methyl groups attached to the C6 position, one methyl group (9) is clearly closer to proton 7b and that the other methyl group (10) is much closer to the hydroxyl group. Based on the NOE analysis, we can now assign resonance H to position 10 and J to position 9. After review of F figure 4 we can assign the methyl carbon 9 at 22.59 ppm and carbon 10 at 26.85 ppm respectively.



Results and Conclusions:

Using the experiments shown we were able to assign all of the resonances of (S)-cis-Verbenol. Most of the proton resonances could be assigned from the ^1H 1D NMR spectrum. Assignment of the methyl group resonances required the use of the selective 1D NOE experiment. The ^{13}C assignments were assigned based on the assigned ^1H resonances using the HMOC experiment and direct inspection of the 1D ^{13}C experiment (C2 and C6). The DEPT and 2D COSY experiments provided critical assignment confirmation.

Proton Assignments (ppm):

| 1 | 3 | 4 | 5 | 7a | 7b | 8 | 9 | 10 | OH |
|------|------|------|------|------|------|------|------|------|------|
| 1.95 | 5.36 | 4.46 | 2.88 | 1.30 | 2.44 | 1.73 | 1.34 | 1.07 | 2.05 |

Carbon Assignments (ppm):

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-------|--------|--------|-------|-------|-------|-------|-------|-------|-------|
| 47.72 | 147.13 | 119.37 | 73.36 | 48.16 | 38.89 | 35.72 | 22.53 | 22.59 | 26.85 |

References and Acknowledgements:

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