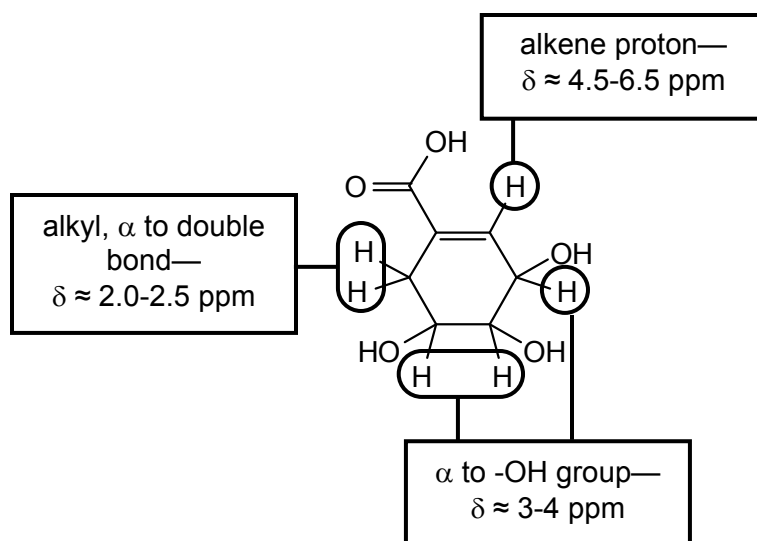


### Exam 1 Answer Key

Exam 1 Mean: 67  
Exam 1 Median: 67  
Exam 1 St. Dev.: 17

1. Shikimic acid has some characteristic types of protons that should appear at distinct chemical shift values. From this info, we can conclusively assign one proton—H<sub>2</sub>, at  $\delta = 6.38$  ppm—but we'll need to look closer to assign anything else. It probably helped at this point to go through the multiplets and calculate coupling constants for each:



$\delta$ (ppm)	Coupling constants $J$ (Hz)
6.38	$J_1 = 1.5$ Hz $J_2 = 2.4$ Hz $J_3 = 4.4$ Hz
4.34	$J_1 = J_2 = 4.4$ Hz (+ some small ones?)
3.93	$J_1 = 5.6$ Hz $J_2 = 7.6$ Hz $J_3 = 9.2$ Hz

$\delta$ (ppm)	Coupling constants $J$ (Hz)
3.65	$J_1 = 4.4$ Hz $J_2 = 9.2$ Hz
2.71	$J_1 = 5.6$ Hz $J_2 = 17.9$ Hz (+ some small ones?)
2.14	$J_1 = 1.5$ Hz $J_2 = 2.4$ Hz $J_3 = 7.6$ Hz $J_4 = 17.9$ Hz

Important to keep in mind: In a complex multiplet, the distance between peaks 1 and 2 is  $J_1$ , and between peaks 1 and 3 is  $J_2$ . If the distance between peaks 1 and 4 is not  $J_1 + J_2$ , then it is  $J_3$ . However, if the distance between peaks 1 and 4 is is  $J_1 + J_2$ , then  $J_3$  is the distance between peaks 1 and 5. Both cases occurred here. At  $\delta = 3.93$  ppm, the distance between peaks 1 and 4 is not  $J_1 + J_2$ , so it is  $J_3$ . By contrast, at  $\delta = 6.38$  ppm,  $J_3$  is the distance between peaks 1 and 5.

There are lots of coupling constants with different magnitudes. A couple stand out. The largest one, 17.9 Hz, must be the geminal  $^2J$  between  $H_{6ax}$  and  $H_{6eq}$ —there are no other possible partners. Those two protons have one other coupling partner in common at  $\delta = 3.93$  ppm with medium-sized ( $J = 5.6$  and  $7.6$  Hz) coupling constants. I'm going to guess that those are vicinal  $^3J$ s, and that  $\delta(H_5) = 3.93$  ppm. For that proton we only have one  $J$  left (9.2 Hz), which is probably a  $^3J$  to  $H_4$  at  $\delta = 3.65$ . That leaves us with  $H_3$  having the only unassigned  $\delta = 4.34$  ppm.

This means we can almost complete the chart:

$\delta$ (ppm)	Name of proton ( $H_n$ )	Coupling constants $J$ (Hz)	Assign coupling constants $J(H_m, H_n)$
6.38	$H_2$	$J_1 = 1.5$ Hz $J_2 = 2.4$ Hz $J_3 = 4.4$ Hz	$J(H_2, H_3)$
4.34	$H_3$	$J_1 = 4.4$ Hz $J_2 = 4.4$ Hz	$J(H_2, H_3)$ $J(H_3, H_4)$
3.93	$H_5$	$J_1 = 5.6$ Hz $J_2 = 7.6$ Hz $J_3 = 9.2$ Hz	$J(H_5, H_{6??})$ $J(H_5, H_{6??})$ $J(H_4, H_5)$
3.65	$H_4$	$J_1 = 4.4$ Hz $J_2 = 9.2$ Hz	$J(H_3, H_4)$ $J(H_4, H_5)$
2.71	$H_{6??}$	$J_1 = 5.6$ Hz $J_2 = 17.9$ Hz	$J(H_5, H_{6??})$ $J(H_{6??}, H_{6??})$
2.14	$H_{6??}$	$J_1 = 1.5$ Hz $J_2 = 2.4$ Hz $J_3 = 7.6$ Hz $J_4 = 17.9$ Hz	$J(H_5, H_{6??})$ $J(H_{6??}, H_{6??})$

The only things that still aren't clear are (1) which H<sub>6</sub> is equatorial and which is axial, and (2) what the tiny coupling constants correspond to. The H<sub>6</sub> question is the easier of the two. The coupling constant  $J(\text{H}_5/\text{H}_{6\text{ax}})$ , with  $\phi = 180^\circ$ , should be larger than  $J(\text{H}_5/\text{H}_{6\text{eq}})$ , with  $\phi = 30^\circ$ . Also, the Pretsch book states that equatorial H's are downfield of axial ones. This means that  $\delta(\text{H}_{6\text{ax}}) = 2.14$  ppm, and  $\delta(\text{H}_{6\text{eq}}) = 2.71$  ppm.

The small coupling constants are a little trickier. Two of them must be long-range allylic coupling between H<sub>2</sub> and the two H<sub>6</sub> protons. But there must be a third long-range coupling too; H<sub>6ax</sub> has two unexplained J's, and only one of them can be that allylic coupling. Pretsch says that the largest allylic coupling occurs when the allylic H is parallel with the pi-orbital system, and that is true for H<sub>6ax</sub>; this would suggest that  $J(\text{H}_2, \text{H}_{6\text{ax}}) = 2.4$  Hz, and that  $J(\text{H}_2, \text{H}_{6\text{eq}}) = 1.5$  Hz. (In principle you can't see the 1.5 Hz coupling in H<sub>6eq</sub> because the peak's too blobby.) So what is the fourth coupling constant for H<sub>6ax</sub>? I think it's a <sup>5</sup>J with H<sub>3</sub>, the other broad multiplet that might hide a small J. So,

$\delta$ (ppm)	Name of proton (H <sub>n</sub> )	Coupling constants J (Hz)	Assign coupling constants $J(\text{H}_m, \text{H}_n)$
6.38	H <sub>2</sub>	$J_1 = 1.5$ Hz $J_2 = 2.4$ Hz $J_3 = 4.4$ Hz	$J(\text{H}_2, \text{H}_{6\text{eq}})$ $J(\text{H}_2, \text{H}_{6\text{ax}})$ $J(\text{H}_2, \text{H}_3)$
4.34	H <sub>3</sub>	$J_1 = 4.4$ Hz $J_2 = 4.4$ Hz	$J(\text{H}_2, \text{H}_3)$ $J(\text{H}_3, \text{H}_4)$
3.93	H <sub>5</sub>	$J_1 = 5.6$ Hz $J_2 = 7.6$ Hz $J_3 = 9.2$ Hz	$J(\text{H}_5, \text{H}_{6\text{eq}})$ $J(\text{H}_5, \text{H}_{6\text{ax}})$ $J(\text{H}_4, \text{H}_5)$
3.65	H <sub>4</sub>	$J_1 = 4.4$ Hz $J_2 = 9.2$ Hz	$J(\text{H}_3, \text{H}_4)$ $J(\text{H}_4, \text{H}_5)$
2.71	H <sub>6eq</sub>	$J_1 = 5.6$ Hz $J_2 = 17.9$ Hz	$J(\text{H}_5, \text{H}_{6\text{eq}})$ $J(\text{H}_{6\text{eq}}, \text{H}_{6\text{ax}})$
2.14	H <sub>6ax</sub>	$J_1 = 1.5$ Hz $J_2 = 2.4$ Hz $J_3 = 7.6$ Hz $J_4 = 17.9$ Hz	$J(\text{H}_3, \text{H}_{6\text{ax}})$ $J(\text{H}_2, \text{H}_{6\text{ax}})$ $J(\text{H}_5, \text{H}_{6\text{ax}})$ $J(\text{H}_{6\text{eq}}, \text{H}_{6\text{ax}})$

**Rubric:**

3 points each proton name.

3 points partial (out of 6) for  $[H_{6ax} + H_{6eq}]$  for switching them or being indeterminate.

5 points partial (out of 9) for  $[H_3 + H_4 + H_5]$  for switching them or being indeterminate.

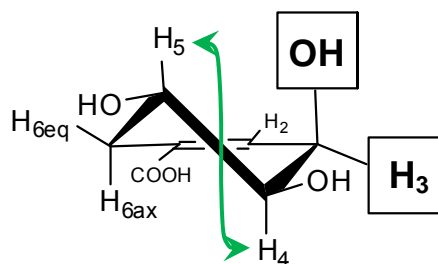
1 point each coupling constant, to within 0.3 Hz.

1 point each coupling assignment.

Full credit for assignments that are incorrect, but are consistent with your answers in first column. (I.e., we won't penalize you twice for incorrect 1<sup>st</sup> column answer.)

Each assignment must be paired with a  $J$  value in column 3--you can't just list them.

2.  $J(H_4, H_5) = 9.2$  Hz is an awful lot larger than  $J(H_3, H_4) = 4.4$  Hz, and that indicates that the geometric relationships between these two pairs of protons are different. We know that the dihedral angle  $\phi(H_4, H_5) = 180^\circ$ , and so we can guess that the dihedral  $\phi(H_3, H_4)$  must be less. This is true only if  $H_3$  is equatorial.



$$J(H_4, H_5) = 9.2 \text{ Hz}$$

**Rubric:**

6 points for filling boxes correctly. *No partial.*

3 points for labeling a coupling relationship and its  $J$  value. Any one will do.

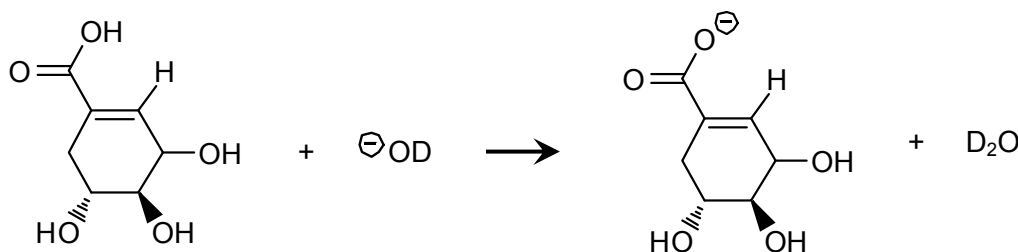
3. In  $D_2O$ , all exchangeable protons—including amine, alcohol and carboxylic acid protons—are exchanged for deuterium atoms, which are silent to  $^1H$  NMR.

**Rubric:**

6 points for correct answer. *No partial.*

*No partial credit for answers that discuss relaxation times, H-bonding or exchange timescales.*

4. In  $NaOD$ , shikimic acid should be deprotonated to its conjugate anion base:



In the anion, H<sub>2</sub> is right next to a negative charge, which should increase the local electron density near the H and shield that atom from the static magnetic field **B**<sub>0</sub>. This will push the resonance **upfield**.

**Rubric:**

4 points for correct answer. *No partial.*

5.

δ (ppm)	Name of carbon
178.1	COOH
138.7	C <sub>1</sub>
133.2	C <sub>2</sub>
74.8	C <sub>3/4/5</sub>

δ (ppm)	Name of carbon
69.5	C <sub>3/4/5</sub>
69.0	C <sub>3/4/5</sub>
35.4	C <sub>6</sub>

The three peaks in the alcohol region are tough to assign specifically. In principle, C<sub>3</sub> could be very different from C<sub>4</sub> and C<sub>5</sub>, but Pretsch has different things to say about those differences. The axial -OH should shift C<sub>3</sub> upfield relative to equatorial -OH, but being adjacent to an alkene shifts it downfield. So I'm not sure we can conclusively assign the δ = 74.8 peak to C<sub>3</sub> (though it seems likely).

**Rubric:**

3 points each carbon name.

*3 points partial (out of 6) for [C<sub>1</sub> + C<sub>2</sub>] for switching them or being indeterminate. Full credit for being determinate for C<sub>3/4/5</sub>.*

6. a. These two carbons have no attached protons, so they relax more slowly. Magnetization transfer is a key mechanism of T<sub>1</sub> relaxation, and this occurs most rapidly from carbon to proton. No nearby protons means incomplete relaxation, which results in the 90° pulse not generating as much **M**<sub>xy</sub> intensity as it could. *Any answer with "slower relaxation" was accepted here.*
- b. These two carbons have no attached protons, so they receive less NOE enhancement during broadband <sup>1</sup>H decoupling. *Any answer that referred to NOE enhancement was accepted here.*

**Rubric:** 5 points each answer. *No partial.*