A note about exam keys: The answers presented here may be significantly longer than expected from a student taking the exam. An exam key serves not only to reveal what was expected, but to instruct you as well. Some questions may have more than one answer, even if only one answer is presented here.

To see the projected course grade cutoffs, consult the grading scale on the Chem 14C course web page. The final grade cutoffs cannot be determined until after the final exam has been graded.


2. Uric acid is highly soluble. *Uric acid has many polar bonds and few nonpolar bonds. It also has many hydrogen bond donors and hydrogen bond acceptors.*

3. Many other answers are possible. *In this example, a hydrogen bond donor site was removed by converting an N–H bond into an N–CH₃ bond.*

4. (a) \( pK_a = 15 \)

(b) Proton A is more acidic than proton B because the conjugate base formed by the removal of proton B enjoys less resonance stabilization than the conjugate base formed by removal of proton A from uric acid. Less stable conjugate base = stronger conjugate base = weaker acid. However, the change isn't so much as to make proton B as weakly acidic as methane (\( pK_a \approx 50 \)).

5. It is mostly ionized (\( K_{eq} > 1 \)). *An acid-base equilibrium favors the weakest acid, which in this case is carbonic acid.*

6. (a) Resonance, conjugation, and aromaticity (all resulting from p-orbital overlap) are all favorable molecular properties because of these give the molecule increased electron delocalization and increased stability.

(b) If colchicine rings A and C lie in the same plane, colchicine gains more electron delocalization, more conjugation, and more stability.

7. (a) 21 conjugated atoms

(b) Six \( sp^2 \) oxygen atoms
8. Colchicine's nitrogen atom is $sp^2$ because this hybridization has the $p$ orbital necessary to allow the lone pair to be conjugated with the carbonyl $pi$ bond.

9. Colchicine's A ring is aromatic.

Colchicine's B ring is not aromatic because it does not have a closed $p$-orbital loop.

Colchicine's C ring is aromatic.

10. *All other resonance contributors violate at least one resonance contributor preference rule.*

11. Don't forget partial $pi$ bonds formed by oxygen lone pair delocalization.

12. (a) *Priorities: $N > C=C > CH_2 > H$*

(b) Cannot determine. *The molecule is chiral and therefore optically active, but based only on the structure we cannot determine if the optical activity is dextrorotatory or levorotatory.*

13. The colchicine structure shown at the top of exam page 2 has one enantiomer and zero diastereomers.
14. Cannot determine. The information given at the start of the exam states the enantiomer shown is useful to treat gout, but we cannot make any conclusions about the biological activity of its enantiomer.

15. **Lipid**: A molecule of biological origin that is soluble in solvents of low polarity and insoluble in solvents of high polarity. * Taken from the Illustrated Glossary of Organic Chemistry at the course web site. 

16. Any fatty acid containing an even number of carbons and one, nonconjugated, cis alkene is acceptable. Oleic acid is a typical example.

![Oleic acid](image)

17. (a) α-helix, β-sheet and (random) coil.

(b) Nitrogen

(c) C=O

18. **Mass spectrum**: m/z = 143 (M): *Molecular weight (lowest mass isotopes) = 143 amu*  
*Odd number of nitrogen atoms*  
m/z = 144 (M+1): 9.62% / 1.107% = 8.69 *Eight or nine carbon atoms*  
m/z = 145 (M+2): Less than 1% so no sulfur, chlorine, or bromine

**Formula (C₈):** 143 - 96 (C₈) = 47 amu for oxygens, nitrogens, and hydrogens.

<table>
<thead>
<tr>
<th>Oxygens</th>
<th>Nitrogens</th>
<th>47 - O - N = H</th>
<th>Formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>47 - 0 - 14</td>
<td>C₈H₃₃N</td>
<td>Violates H-rule</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>47 - 16 - 14</td>
<td>C₈H₁₇NO</td>
<td>Reasonable</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>47 - 32 - 14</td>
<td>C₈HNO₂</td>
<td>¹H-NMR has more than one signal</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>47 - 0 - 42</td>
<td>C₈H₃N₃</td>
<td>Does not fit ¹H-NMR integrals</td>
</tr>
</tbody>
</table>

**Formula (C₉):** 143 - 108 (C₉) = 35 amu for oxygens, nitrogens, and hydrogens.

<table>
<thead>
<tr>
<th>Oxygens</th>
<th>Nitrogens</th>
<th>35 - O - N = H</th>
<th>Formula</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>35 - 0 - 14</td>
<td>C₉H₂₃N</td>
<td>Does not fit ¹H-NMR integrals</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>35 - 16 - 15</td>
<td>C₉H₂NO</td>
<td>Does not fit ¹H-NMR integrals</td>
</tr>
</tbody>
</table>

**DBE:** 8 - (17/2) + 1/2 + 1 = 1 DBE  *One ring or one pi bond*

**IR:**  
Zone 1: Alcohol O–H: Absent - no peak.  
Amine/amide N–H: Absent - no peak.  
≡C–H: Absent - no peak.

Zone 2: Aryl/vinyl C–H: Absent - no peaks > 3000 cm⁻¹.  
Aldehyde C–H: Absent - no peak ~ 2700 cm⁻¹.  
Carboxylic acid O–H: Absent - not broad enough; not enough oxygens.
Zone 3: C≡C: Absent - no peak; not enough DBE.
    C≡N: Absent - no peak; not enough DBE.

    Looks good for ketone; $^{13}$C-NMR confirms.
    No 2700 cm$^{-1}$ peak for aldehyde.
    Not enough oxygen for ester, carboxylic acid.
    1716 cm$^{-1}$ too high for amide; $^{13}$C-NMR confirms no amide.

Zone 5: Benzene ring: Absent - not enough DBE.
    Alkene: Absent - not enough DBE for C=O plus C=C.

$^1$H-NMR:

<table>
<thead>
<tr>
<th>Chemical shift</th>
<th>Splitting</th>
<th>Integral</th>
<th># H</th>
<th>Implications</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.52 ppm</td>
<td>singlet</td>
<td>1.0</td>
<td>2 H</td>
<td>CH$_2$ or 2 x CH</td>
</tr>
<tr>
<td>2.64 ppm</td>
<td>quartet</td>
<td>2.0</td>
<td>4 H</td>
<td>2 x CH$_2$ in CH$_2$CH$_3$, 2 x CH$_2$ in CH$_2$CH$_2$CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4 x CH in CHCH$_3$, 4 x CH in CH$_2$CHCH, 4 x CH in CH(Ch)$_3$</td>
</tr>
<tr>
<td>2.45 ppm</td>
<td>quartet</td>
<td>1.0</td>
<td>2 H</td>
<td>CH$_2$ in CH$_3$CH$_3$, CH$_2$ in CH$_3$CH$_2$CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 x CH in CHCH$_3$, 2 x CH in CH$_2$CHCH, 2 x CH in CH(Ch)$_3$</td>
</tr>
<tr>
<td>1.06 ppm</td>
<td>triplet</td>
<td>1.5</td>
<td>3 H</td>
<td>CH$_3$ in CH$_3$CH$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3 x CH in CHCH$_2$, 3 x CH in CHCHCH</td>
</tr>
<tr>
<td>1.02 ppm</td>
<td>triplet</td>
<td>3.0</td>
<td>6 H</td>
<td>2 x CH$_3$ in CH$_3$CH$_2$, 3 x CH$_2$ in CH$_3$CH$_2$, 3 x CH$_2$ in CHCH$_2$CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6 x CH in CHCH$_2$, 6 x CH in CHCHCH, 6 x CH in CHCHCH</td>
</tr>
</tbody>
</table>

Totals 8.5 17 H CH$_3$ + (2 x CH$_2$) + CH$_3$ + CH$_3$ + (2 x CH$_3$) = C$_7$H$_{17}$

$^{13}$C-NMR: 203.9 ppm singlet = ketone C=O. There are six signals in the $^{13}$C-NMR spectrum versus eight carbons in the formula, so two of the carbons are equivalent to other carbons (the molecule has some symmetry).

Atom check: C$_8$H$_{17}$NO - C$_7$H$_{17}$ ($^1$H-NMR) - CO (ketone C=O; IR and $^{13}$C-NMR) = N. Because this nitrogen is not accounted for by the $^1$H-NMR (there is no N–H peak in zone 1) and because there is no amide (the C=O stretching frequency is too high), this nitrogen is part of a tertiary amine (R$_3$N).

DBE check: One (calculated for C$_8$H$_{17}$NO) - one (C=O) = all DBE used.

Pieces: CH$_2$ CH$_3$ in CH$_3$CH$_2$ C=O
        2 x CH$_2$ in CH$_3$CH$_3$, 2 x CH$_3$ in CH$_3$CH$_2$ N (R$_3$N)

Assembly: We begin as always with the $^1$H-NMR splitting patterns. These tell us that 2 x CH$_2$ in CH$_3$CH$_3$ and 2 x CH$_3$ in CH$_3$CH$_2$ combine to form 2 x CH$_3$CH$_2$. In addition, the remaining methylene group and methyl group combine to form another ethyl group.

CH$_2$ CH$_3$CH$_2$ C=O
2 x CH$_3$CH$_3$, N (R$_3$N)
The ethyl groups cannot merge to form butane (CH$_3$CH$_2$CH$_2$CH$_3$), because this violates the one-molecule rule. The two equivalent ethyl groups cannot be bonded to the carbonyl group (giving 3-pentanone); this is another one-molecule rule violation. Therefore the two equivalent ethyl groups must be bonded to the nitrogen atom.

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_3\text{CH}_2 & \quad \text{C}=\text{O} \\
& & \quad \text{N}($\text{CH}_2\text{CH}_3$)$_2$
\end{align*}
\]

The N($\text{CH}_2\text{CH}_3$)$_2$ piece cannot be bonded to the remaining ethyl group (causing a one-molecule rule violation) or to the carbonyl (forming an amide; ruled out by both the IR and $^{13}$C-NMR). Therefore the N($\text{CH}_2\text{CH}_3$)$_2$ piece must be bonded to the CH$_2$ group.

\[
\begin{align*}
\text{CH}_2\text{N}($\text{CH}_2\text{CH}_3$)$_2$ & \quad \text{CH}_3\text{CH}_2 & \quad \text{C}=\text{O}
\end{align*}
\]

These pieces can only be assembled in one way: