

NAME _____

ID # _____

INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

9:05 – 9:55 am, December 13, 2010

Exam 4

This exam is open book and open note. You are permitted to use any written materials you have brought as aids on this exam. You may also use a simple calculator. Other than this, please do not use any other electronic devices (cell phones, computers, recording devices, etc.) during the exam.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

Feel free to remove the corner staple if this helps you analyze the spectra; you will have the opportunity to re-staple your exam at the end. The exam in this packet is designed to take 30 minutes to complete. You will be given 50 minutes total to finish the test. This exam contains two problems, which are split into parts. Many of these parts can be answered independently. *Do not get stuck* on one part and then assume that you will be unable to answer the rest of the question—move on. In addition, partial credit will be given for incorrect but still plausible answers, so *guess* on problems you cannot answer perfectly.

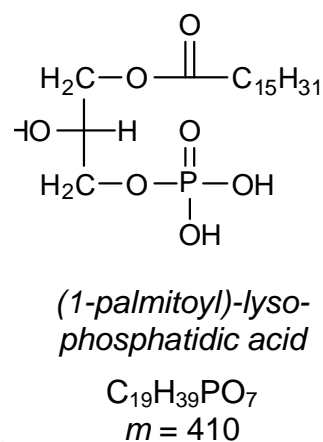
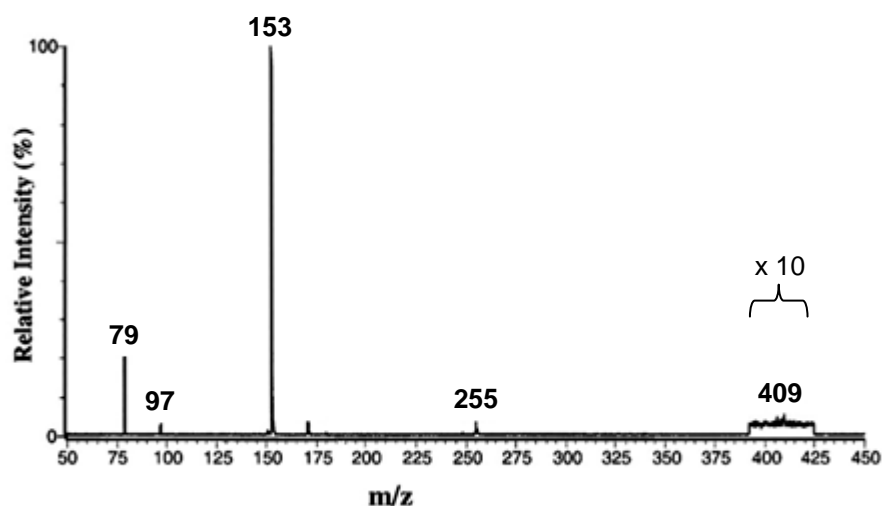
At the end of the 50 minute exam period you will be asked to return your exam to the proctor. Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded. This packet should contain XX pages, including this one. Please check to make sure that your packet contains XX pages before beginning your exam.

NAME _____

Scoring: 1. _____ / 50 2. _____ / 50

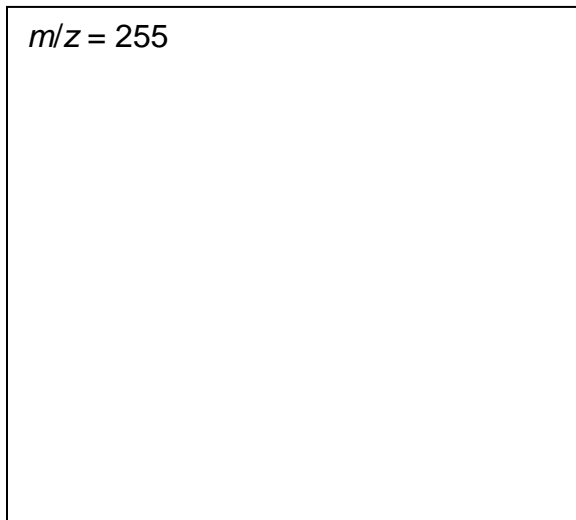
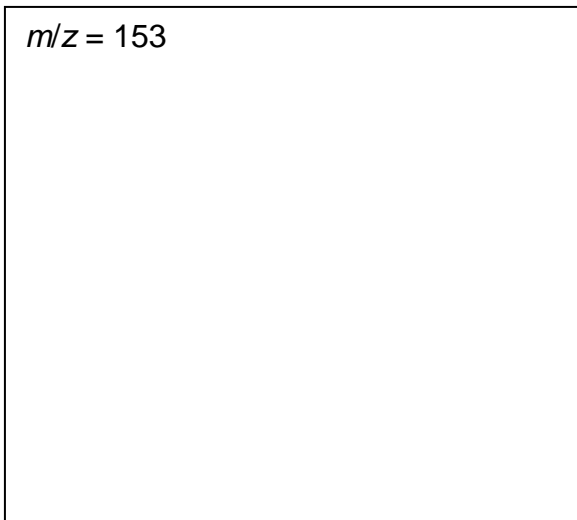
Total Score: _____ / 100

1. The negative-ion-mode electrospray ionization (ESI) mass spectrum of (1-palmitoyl)-lysophosphatidic acid is shown below. The ESI experiment was run with a relatively high pressure of inert gas in the ionization region to promote fragmentation.

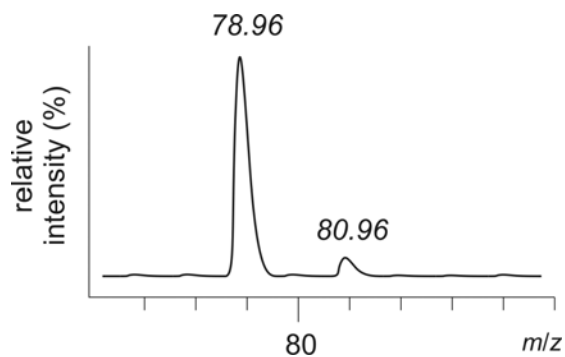


- a. What is the structure of the “parent”, $m/z = 409$ ion?

- b. Draw chemical structures that describe the $m/z = 153$ and $m/z = 255$ fragments below.



- c. A closeup of the $m/z = 75$ to 85 region of the spectrum is shown at right. It shows that, in addition to the $m/z = 79$ peak, there is a small but measurable peak at $m/z = 81$, but no peak at $m/z = 80$.



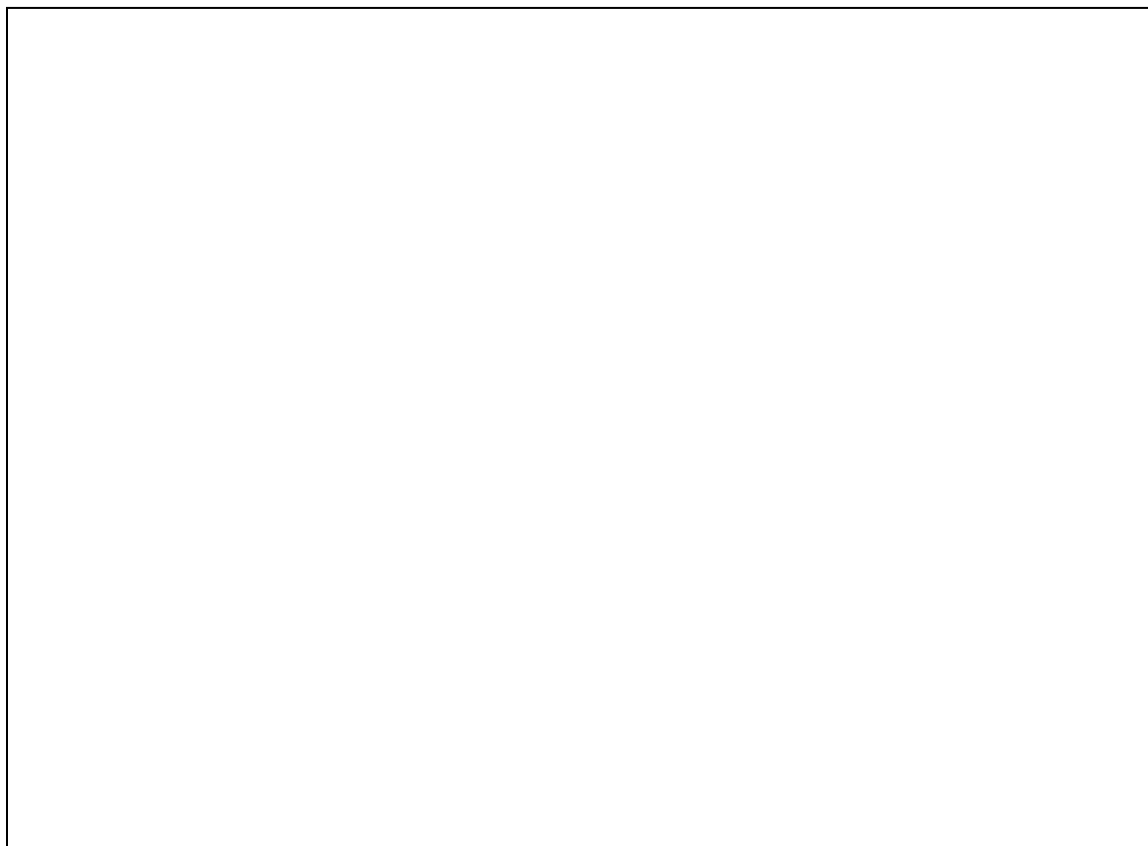
To within 0.2%, what intensities would you expect at $m/z = 80$ and 81 , relative to the intensity at $m/z = 79$?

For $I_{79} = 100\%$,

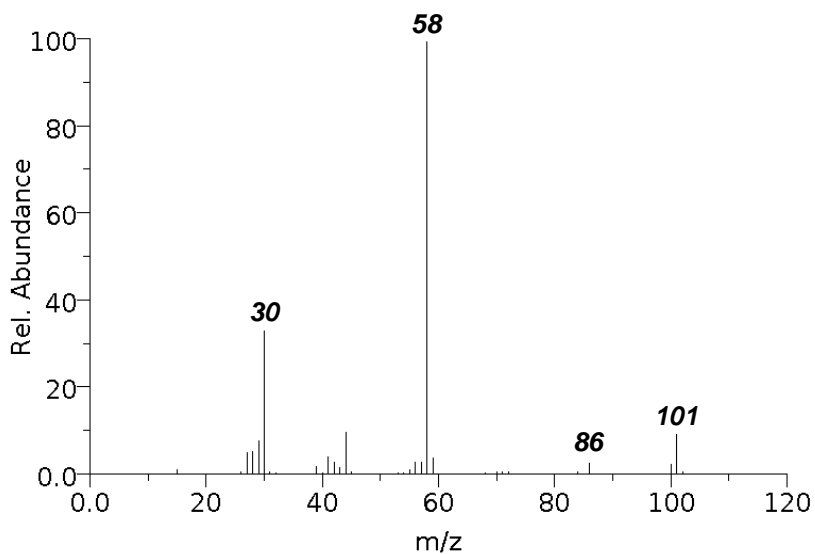
$I_{80} =$ %

$I_{81} =$ %

- d. Briefly describe a mass spectrometry experiment on (1-palmitoyl)-lysophosphatidic acid that might help illustrate the chemical structure of the $\text{-C}_{15}\text{H}_{31}$ group.



2. The electron-ionization (EI) mass spectrum of an unknown organic substance is shown at right. High-resolution MS analysis of the $m/z = 101$ parent indicates that the unknown has chemical formula $\text{C}_6\text{H}_{15}\text{N}$.



- a. What is the chemical structure of the unknown?



- b. Draw mechanisms (using “electron pushing”) that describe the formation of $m/z = 58$ and $m/z = 30$ fragment (daughter) ions from your $m/z = 101$ parent ion. *Hint:* The $m/z = 30$ fragment requires a McLafferty-like rearrangement of the parent.

mechanism for $m/z = 58$ fragment



mechanism for $m/z = 30$ fragment



- c. If the mass spectrum of this unknown were obtained via atmospheric pressure photoionization (APPI) instead of EI, would there be

more or **less** or **the same amount of** fragmentation?
(Circle one.)

What would the parent ion m/z be in this case?

- d. If the mass spectrum of this unknown were obtained via chemical ionization (CI) using CH_4 as the reagent gas instead of via EI, would there be

more or **less** or **the same amount of** fragmentation?
(Circle one.)

What would the parent ion m/z be in this case?