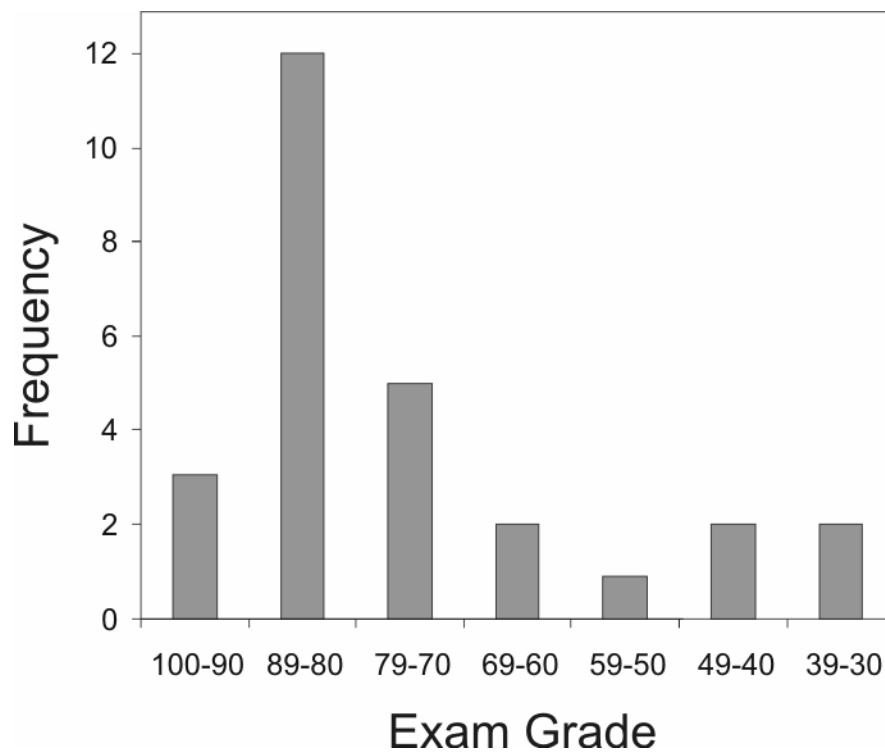


**Final Exam
Answer Key**

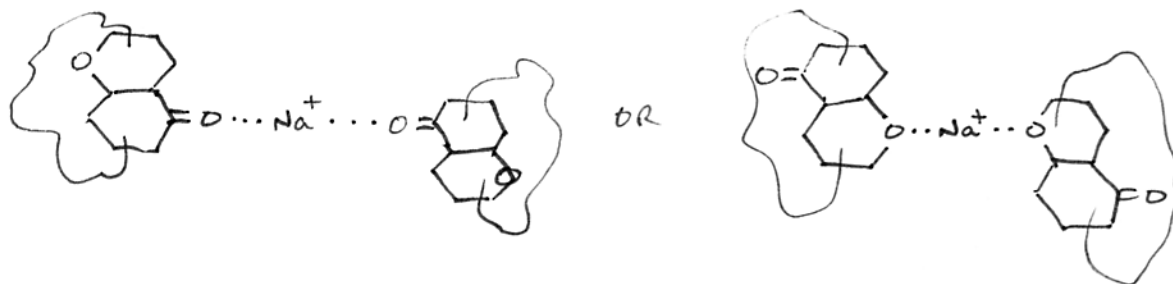
Final Mean: 75
Final Median: 82
Final St. Dev.: 17



FINAL EXAM SOLUTIONS

1. a) IN ADDITION TO H^+ , INJECTION MIXTURE ALSO CONTAINS Na^+ , SO, ONE MIGHT EXPECT THAT, IN ADDITION TO $[M+H]^+$, $[M+Na]^+$ WOULD ALSO BE FORMED. $m/z(M+Na)^+ = 309.2$.

$m/z = 595.4$ IS A BIT UNUSUAL. CLEARLY, IT'S SOMETHING CLOSE TO TWICE THE PARENT MASS. BUT IT STILL MUST BE MADE OF $\frac{2}{m}$ OR $\frac{3}{m}$. ANSWER IS NONCOVALENT DIMER W/ ONE Na^+ ION:



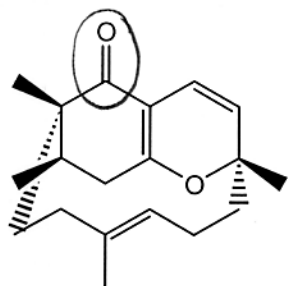
OR, IN OTHER TERMS, $[2M+Na]^+$, $m/z = 595.4$.

5 POINTS EACH. 309.2: ALL OR NOTHING, ANY DRAWING W/ $M+Na$ ACCEPTABLE.

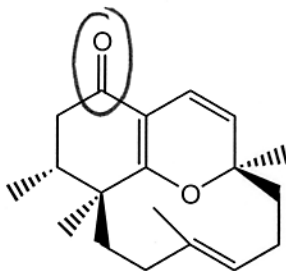
595.4: 5 POINTS FOR ANY NONCOVALENT $2M+Na$ COMPLEX.

2 POINTS FOR COVALENT $[2M]$ PRODUCT (WOULD NOT OCCUR IN ESI).


b) A BIT ODD; ~~IN~~ IN THIS COMPOUND ALKENE STRETCHES ($1607, 1640 \text{ cm}^{-1}$) ARE VERY STRONG, BUT CARBONYL STRETCH (1688 cm^{-1}) IS WEAK. (ORDINARILY, CARBONYL STRETCHES ARE PROMINENT.) SO,



2



3

3 POINTS FOR EITHER ONE,
2 MORE FOR BOTH.
(5 POINTS TOTAL.)
ANYTHING THAT INCLUDES CARBONYL IS FINE. (e.g., )

c) THE MEAT OF THIS PROBLEM. ACCOUNTING-WISE, STRUCTURE HAS 26 PROTONS, AND SUM OF INTEGRALS IS ~ 27 , SO THERE IS A LITTLE BIT OF SPURIOUS SIGNAL SOMEWHERE; HOWEVER, WE'RE NOT ASSIGNING THE ENTIRE MOLECULE, SO THIS MAY BE OKAY.

~~THE~~ ^1H SPECTRUM HAS THREE REGIONS TO IT:

4-7 ppm: ALKENE, 3 RESONANCES;

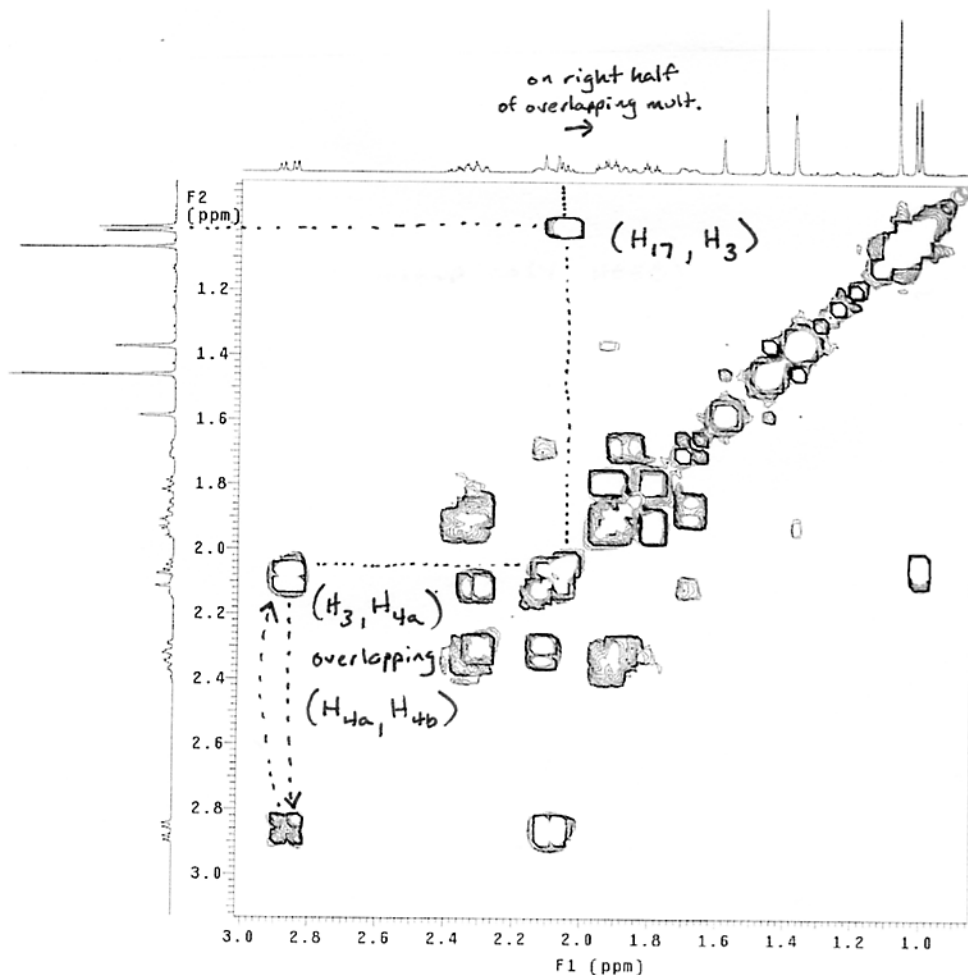
1.5-3 ppm: ALKANE, LOTS OF OVERLAPPING RESONANCES;

1-1.5 ppm: METHYL, $4 \times 3\text{H}$ RESONANCES.

THESE MAKE SENSE BASED ON EITHER STRUCTURE 2 OR 3 - BOTH HAVE THREE ALKENE PROTONS ($\text{H}_7, \text{H}_8, \text{H}_{12}$) AND BOTH HAVE FOUR METHYL GROUPS ($\text{H}_{16}, \text{H}_{17}, \text{H}_{18}, \text{H}_{19}$).

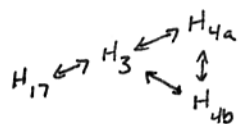
ASSIGNING $H_{17} \rightarrow H_3 \rightarrow H_{4a}, H_{4b}$:

OF THE FOUR METHYL GROUPS, ONE IS SPLIT INTO A DOUBLET (THE REST ARE SINGLETS). THIS RESONANCE MUST BE H_{17} , WHICH IS COUPLED TO H_3 . ~~THE REST ARE SINGLETS~~ CAN ALREADY MEASURE $J(H_3, H_{17}) = 7 \text{ Hz}$, WHICH SOUNDS TOTALLY REASONABLE. THE COSY NMR SHOWS THAT THE DOUBLET ($\delta = 1.02 \text{ ppm}$) EXHIBITS ONLY ONE CROSSPEAK; THE CLOSE-UP COSY SHOWS THAT THIS CROSSPEAK LINES UP WITH THE RIGHT HALF OF THE OVERLAPPING MULTI-MULTIPLY @ 2.0-2.2 ppm.



IN 1-D SPECTRUM (CLOSEUP) OF THIS MULTIPLY, YOU ARE GIVEN THE HINT THAT THIS RIGHT HALF IS A QUINTET OF DOUBLETS (WHERE THE "DOUBLETS" J IS VERY SMALL). THIS MAKES SENSE - H_3 HAS 5 COUPLING PARTNERS ($3 \times H_{17}, H_{4a}, H_{4b}$), AND A QUINT. OF DOUBLETS HAS 5 J'S (4 OF WHICH ARE IDENTICAL). FINALLY, THE QUINTET PART HAS $J = 7 \text{ Hz}$, JUST LIKE H_{17} . THIS MEANS THAT $J(H_3, H_{4a}) = 7 \text{ Hz}$, AND $J(H_3, H_{4b}) = 1 \text{ Hz}$. (NATURALLY, H_{4a} & H_{4b} COULD BE SWITCHED; ~~I~~ I DEFINE THEM ARBITRARILY HERE.) SO, ~~THE COSY SPECTRUM~~ $\delta(H_3) = 2.07 \text{ ppm}$ (THE CENTER OF THE QUINTET).

IN THE COSY, $\delta = 2.07 \text{ ppm}$ MATCHES UP WITH ONLY ONE OTHER RESONANCE - THE dd @ 2.86 ppm. ONE OF THE COUPLING CONSTANTS HERE IS 6.5 Hz, VERY CLOSE TO 7 Hz. SO THIS MULTIPLY REPRESENTS H_{4a} (BASED ON OUR ARBITRARY DEFN ABOVE). THE MULTIPLY ALSO HAS A LARGE $J = 20 \text{ Hz}$ (!) WHICH MUST BE $J(H_{4a}, H_{4b})$. THERE'S ONLY ONE OTHER MULTIPLY THAT HAS THIS LARGE A J: THE DOUBLET @ 2.10 ppm, WHERE THE J READS 18.5 Hz, BUT ONE OF THE LABELS IS A BIT OFF CENTER. ACTUALLY, IF YOU LOOK CLOSE, THE DOUBLET REALLY LOOKS LIKE A dd WITH A 1 Hz $J(H_3, H_{4b})$. SO, TO CONCLUDE:

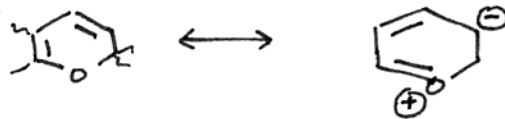


$\delta(H_3) = 2.07$	$J(H_3, H_{17}) = 7 \text{ Hz}$
$\delta(H_{4a}) = 2.86$	$J(H_3, H_{4a}) = 7 \text{ Hz}$
$\delta(H_{4b}) = 2.10$	$J(H_3, H_{4b}) = 1 \text{ Hz}$
$\delta(H_{17}) = 1.02$	$J(H_{4a}, H_{4b}) = 20 \text{ Hz}$

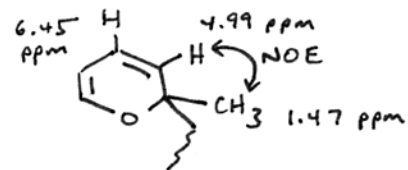
ASSIGNING H_7, H_8, H_{12} (& H_{19})

ALKENE REGION HAS ONLY THREE PROTONS, AND THE COSY SHOWS THAT TWO ARE COUPLED TO EACH OTHER AND NOTHING ELSE (H_7 & H_8 , ● @ 4.99 & 6.45 ppm, $J_{H_7, H_8} = 10.5$ Hz; CANNOT ASSIGN WHICH IS H_7 & WHICH IS H_8 YET). REMAINING RESONANCE MUST BE H_{12} ($\delta = 5.15$ ppm).

SO WHICH IS H_7 & WHICH IS H_8 ? MIGHT GUESS BASED ON CHEMICAL SHIFT ALONE. SINCE RESONANCE OF OXYGEN LONE PAIRS PUTS e^- DENSITY ON H_8 ,



YOU MIGHT EXPECT $\delta(H_8)$ TO BE UPFIELD OF $\delta(H_7)$. BETTER EVIDENCE THAN THIS - NOE. IRRADIATION OF $\delta = 4.99$ Hz RESONANCE GIVES POSITIVE NOE TO THE OTHER ALKENE (EXPECTED) AND A METHYL GROUP, PROBABLY H_{19} . IRRADIATION OF THIS METHYL GROUP @ $\delta = 1.47$ SHOWS NOE ONLY TO $\delta = 4.99$ ppm AND NOT $\delta = 6.45$ ppm. BEST EXPLANATION FOR THIS IS



SO, TO SUM UP: $\delta(H_7) = 6.45$ ppm $J(H_7, H_8) = 10.5$ Hz
 $\delta(H_8) = 4.99$ ppm
 $\delta(H_{12}) = 5.15$ ppm
 $\delta(H_{19}) = 1.47$ ppm

ASSIGNING H₁₆ & H₁₈:

THE LAST TWO METHYL GROUPS ARE BEST ASSIGNED BY NOE. H₁₆ IS RIGHT NEXT TO H₁₇, SO YOU'D EXPECT NOE'S BETWEEN THESE TWO. SURE ENOUGH, IRRADIATION OF $\delta = 1.02$ ppm (H₁₇) SHOWS POSITIVE NOE'S TO ~~H₃~~ H₃, H_{4b}, AND THE SINGLET AT $\delta = 1.07$ ppm. (INCIDENTALLY, THIS SHOWS THAT H_{4b} IS ON THE SAME ~~FACE~~ FACE AS H₁₇, THOUGH THIS ISN'T ASKED FOR.) LIKEWISE, IRRADIATION AT $\delta = 1.07$ ppm SHOWS NOE AT $\delta = 1.02$ (H₁₇). SO $\delta(H_{16}) = 1.07$ ppm. SO, $\delta(H_{18})$ MUST BE 1.38 ppm, THE ~~ONLY~~ ONLY 3H SINGLET LEFT.

$$\text{SO, } \delta(H_{16}) = 1.07 \text{ ppm,}$$

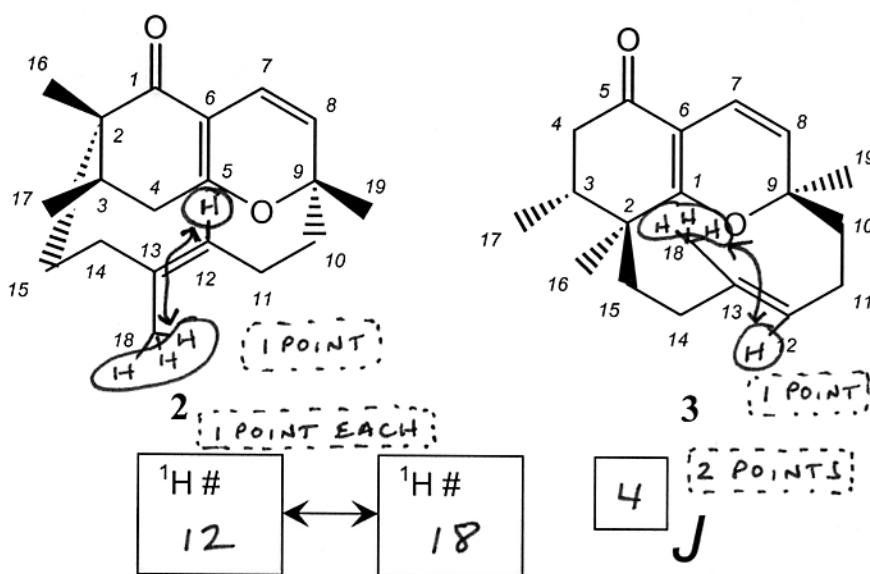
$$\delta(H_{18}) = 1.38 \text{ ppm.}$$

proton	chemical shift (δ , ppm, +/-0.02 ppm)	$^2J_{H,H}/^3J_{H,H}$ coupling constants (Hz, +/-1 Hz)	proton	chemical shift (δ , ppm, +/-0.02 ppm)	$^2J_{H,H}/^3J_{H,H}$ coupling constants (Hz, +/-1 Hz)
H ₃	2.07	$J(H_3, H_{4a}) =$ 7 Hz	H ₈	4.99	see H ₇
		$J(H_3, H_{4b}) =$ 1 Hz	H ₁₂	5.15	complex— please skip
		$J(H_3, H_{17}) =$ 7 Hz	H ₁₆	1.07	no $^{2/3}J_{H,H}$ partners
H _{4a}	2.86	$J(H_{4a}, H_{4b}) =$ 19 Hz	H ₁₇	1.02	see H ₃
H _{4b}	2.10	see H ₃ , H _{4a}	H ₁₈	1.38	no $^{2/3}J_{H,H}$ partners
H ₇	6.45	$J(H_7, H_8) =$ 10.5 Hz	H ₁₉	1.47	no $^{2/3}J_{H,H}$ partners

3 POINTS EACH
BOX.

ANSWERS FOR $\delta(H_{4a})$
AND $\delta(H_{4b})$ CAN
BE SWITCHED. IF
SO, $J(H_3, H_{4a})$ AND
 $J(H_3, H_{4b})$ ALSO
NEED TO BE
SWITCHED.

d) IF YOUR ASSIGNMENT IN THE CHART WAS CORRECT, THIS WAS A GIMME; IF NOT, YOUR ANSWER TO THIS PROBABLY MADE NO SENSE & SHOULD HAVE ENCOURAGED YOU TO RE-EVALUATE THE CHART. THE COUPLING IS BETWEEN H_{12} & H_{18} , AND IN EITHER ~~2~~ $\frac{2}{n}$ OR $\frac{3}{n}$ IS A FOUR-BOND (4J) COUPLING.



6 POINTS
TOTAL.

e) HMQC WAS ACTUALLY VERY HELPFUL IN ASSIGNING SOME ^{13}C RESONANCES. EACH ALKENE PROTON MAPS TO ONE OF THE ALKENE CARBONS:

$$\delta(H_7) \ 6.45 \text{ ppm} \longrightarrow 118 \text{ ppm } (C_7)$$

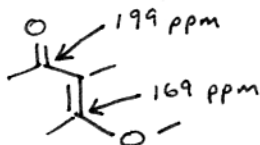
$$\delta(H_8) \ 4.99 \text{ ppm} \longrightarrow 120 \text{ ppm } (C_8)$$

$$\delta(H_{12}) \ 5.15 \text{ ppm} \longrightarrow 125 \text{ ppm } (C_{12})$$

THESE ARE CORRECT FOR BOTH $\frac{2}{n}$ AND $\frac{3}{n}$.

$\delta = 82.9$ IS ONLY sp^3 HETEROATOM CARBON IN ^{13}C SPECTRUM, AND C_9 IS THE ONLY HETEROATOM ~~AND~~ sp^3 CARBON IN $\frac{2}{n}$ AND $\frac{3}{n}$. SO $\delta(C_9) = 82.9 \text{ ppm}$.

FINALLY, THE TWO MOST-DOWNFIELD CARBONS, 198.6 ppm & 169.1 ppm. 199 ppm ~~is~~ WOULD BE CHARACTERISTIC CARBONYL SHIFT, AND 169 ppm ~~is~~ COULD BE HETEROATOM-ALKEENE:



IN 2, THESE ARE C₁ & C₅, AND IN 3 THEY ARE C₅ AND C₁ (REVERSED). SO CHART LOOKS LIKE:

¹³ C chemical shift (δ, ppm)	carbon # (in 2)	carbon # (in 3)
198.6	1	5
169.1	5	1
125.3	12	12
119.8	8	8
118.0	7	7
82.9	9	9

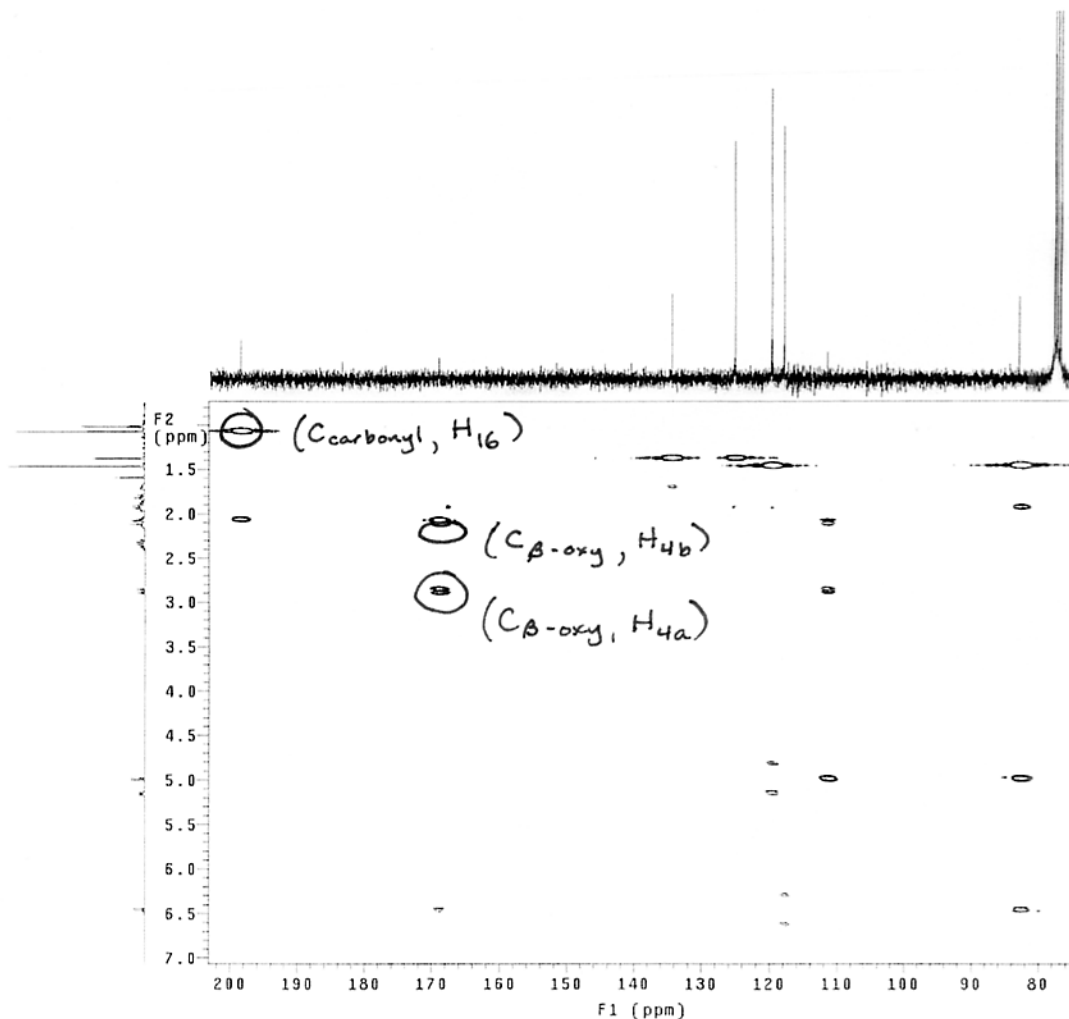
1 POINT EACH BOX.

f) THE PEAKS AT 125, 120 & 118 ppm EACH CORRESPOND TO CARBONS WITH ATTACHED PROTONS. AS A RESULT, THESE CARBONS RELAX MORE EFFICIENTLY AFTER B₁ (RF) EXCITATION, AND THEIR FID RELAXES TO ZERO, DUE TO NOE & VERY EFFICIENT RELAXATION TIMES OF PROTONS. OTHER SHIFTS CORRESPOND TO CARBONS ONLY BOUND TO ~~OTHER~~

CARBONS AND OXYGEN. RELAXATION IS SLOWER, EQUILIBRIUM IS NOT REACHED, AND INTENSITY IS LOWER.

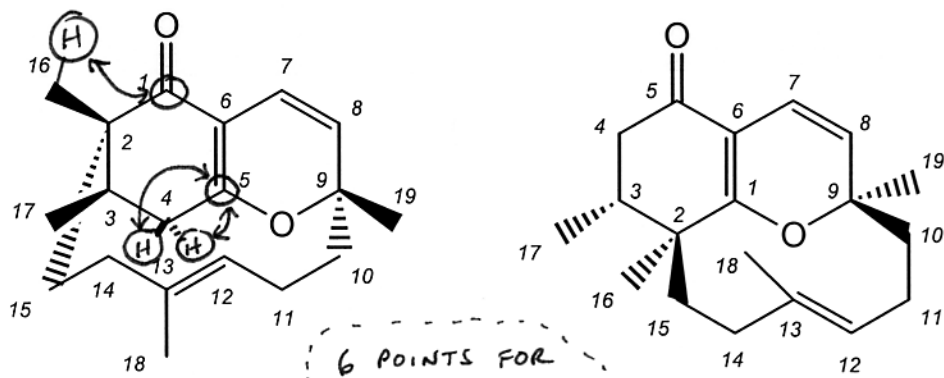
3 POINTS FOR "RELAXATION" RATE DETERMINING INTENSITY;
3 POINTS FOR ATTACHED PROTONS ACCELERATING RELAXATION ~~FOR~~ IN THE CASE OF TALLER PEAKS.

g) THE HMBC SHOWS SOME CHARACTERISTIC CROSSPEAKS THAT LOCATE THE CARBONYL AND β -OXY CARBONS (I.E., THAT ALLOW C_1 & C_5 TO BE ASSIGNED):

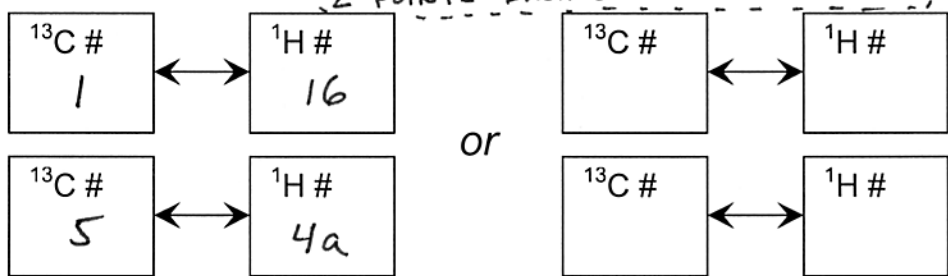


CARBONYL CARBON IS CLOSE TO H_{16} , AND β -OXY CARBON IS CLOSE TO H_{4a} & H_{4b} , ONLY IN 2.

SO,



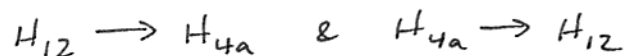
6 POINTS FOR PICKING 2 AS CORRECT.
 1 POINT EACH ARROW.
 (2 POINTS EACH COUPLED PAIR IN BOXES.)



5 \longleftrightarrow 4b \leftarrow ANY TWO OF THESE THREE IS ACCEPTABLE.

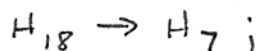
IF ASSIGNMENTS FOR C_1 & C_5 WERE REVERSED IN PART (e), THEN YOU WOULD CONCLUDE THAT 3 WAS CORRECT STRUCTURE ~~AND THAT~~ DUE TO SAME NOE'S. YOU GET FULL CREDIT FOR THIS, IF AND ONLY IF ~~ONLY~~ ASSIGNMENTS FOR C_1 & C_5 ARE SWITCHED IN (e).

h) THERE ARE A COUPLE OF UNIQUE NOE'S:



COULD ONLY REALLY OCCUR FOR $\underline{2}$.

A DECEPTIVE ONE IS



THIS LOOKS SELECTIVE FOR $\underline{3}$ AS DRAWN, BUT ONE MIGHT EASILY IMAGINE THAT UNOBSERVED MACROCYCLIC SEGMENT IN $\underline{2}$ IS FLIPPED, PLACING H_{18} CLOSE TO H_7 :



SO $H_{18} \rightarrow H_7$ ISN'T REALLY INDICATIVE, BUT IT'S CLOSE.

4 POINTS FOR $H_{12} \rightarrow H_{4a}$ OR $H_{4a} \rightarrow H_{12}$.

2 POINTS FOR $H_{18} \rightarrow H_7$.