Mass Spec

$M^{\cdot+} = 196$ Give possible formulas that may include CHO only

Rule 13 CH = 13 units

$$13 \overline{)\,196}\quad 15$$

13

66

65

1 ⟸ additional hydrogens

$$15 \times CH + 1H \rightarrow C_{15}H_{15} + H \rightarrow C_{15}H_{16}$$

	MW	units unsat
$C_{15}H_{16}$	196	8
$C_{14}H_{28}$	196	1
$C_{14}H_{12}O$	196	4
~~$C_{13}H_8O_2$~~	~~196~~	~~10~~
~~$C_{12}H_4O_3$~~	~~196~~	~~11~~
$C_{11}H_{16}O_3$	196	4
$C_{10}H_{12}O_4$	196	5

Equivalents

C = 12H

O = CH_4

$M^{\cdot+} = 142$ may contain $CHOCl$

monoisotopic masses use most abundant isotope

$H = 1$ $Cl = 35$

$C = 12$

$N = 14$

$O = 16$

$13 \overline{)142}$ R 12

$C_{10}H_{10+12} = C_{10}H_{22}$

$^{12}C = 12H$

$^{16}O = CH_4$

$^{35}Cl = C_2H_{11}$

$C_{10}H_{22}$

$C_9H_{18}O$

$C_8H_{11}Cl$

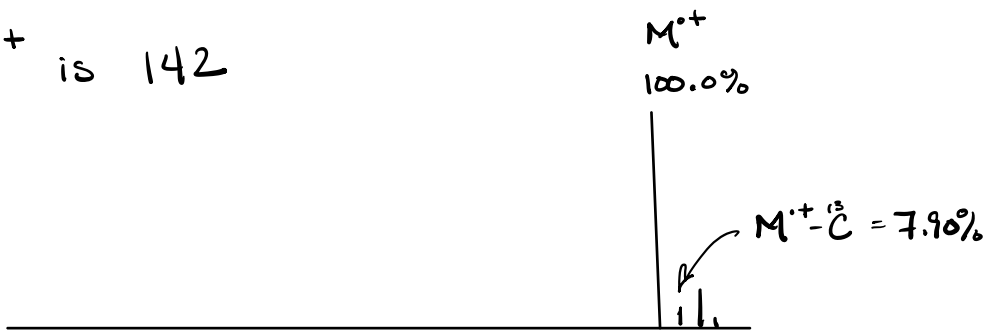
C_7H_7OCl

$C_8H_{14}O_2$

~~C_6Cl_2~~ $C_5H_{12}Cl_2$

$C = 12H$

$M^{\cdot+}$ is 142



How to use % abundance to find # of Carbons in formula

$$\frac{\left[\dfrac{M^{\cdot+}\text{-}{}^{13}C \text{ \% abundance}}{M^{\cdot+} \text{ \% abundance}} \times 100\right]}{1.1\% \text{ (natural } {}^{13}C/{}^{12}C \text{ abundance)}} = \#C \text{ in formula}$$

$$\frac{\left[\dfrac{7.9\%}{100.0\%} \times 100\right]}{1.1} = 7.1 \approx 7.0 \text{ Carbons}$$

$$\boxed{C_7H_7OCl}$$

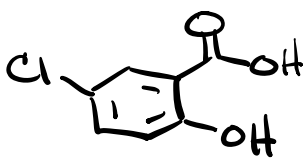
m/z ratio

$C_5H_{10}O_2^{\bullet+}$	102
C_3H_8	44
C_3H_7Cl	78
C_3H_7F	62
C_3H_7Br	122

All even !

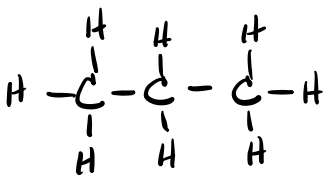
^{19}F

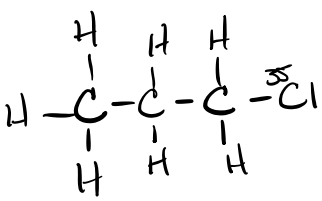
^{79}Br

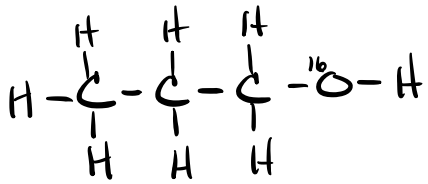


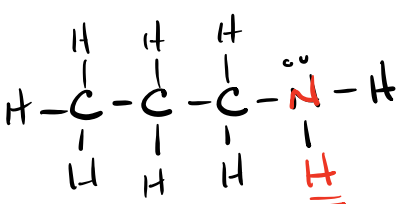
$C_7H_5ClO_3$ 172

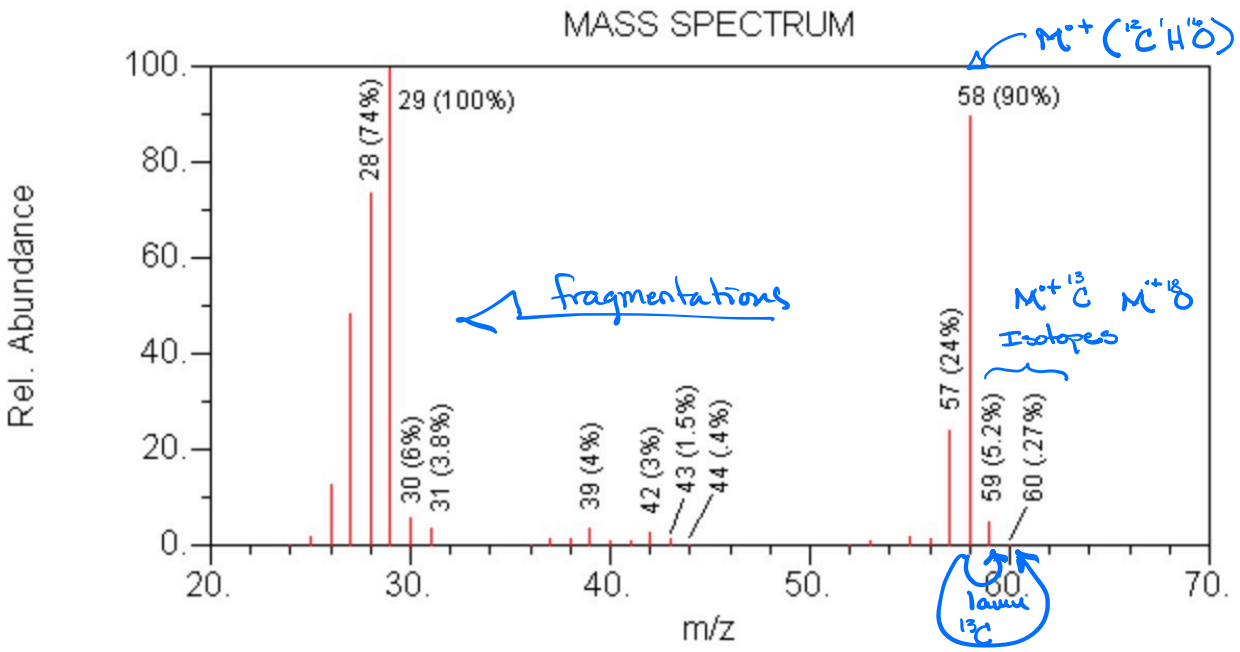
^{14}N  $C_4H_{11}N$ 73 odd

 44

 78

 60

 57



^{12}C vs ^{13}C — 1 amu

^{16}O ^{18}O — 2 amu

$^{13}C = 1.1\%$

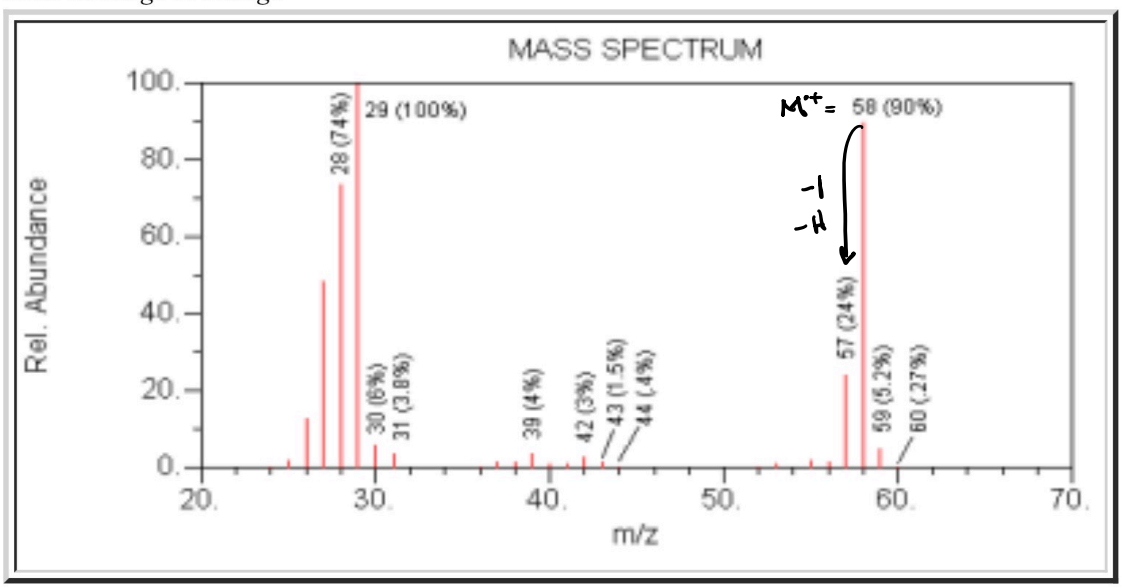
$$\#C = \frac{\left\{\frac{M^{\bullet+} - {}^{13}C \text{ \% abundance}}{M^{\bullet+} \text{ \% abundance}} \times 100\right\}}{1.1} = \frac{\left(\frac{5.2}{90}\right) \times 100}{1.1} = 5$$

1.1 ← % of $^{13}C/^{12}C$

$$\#O = \frac{\left\{\frac{M^{\bullet+} - {}^{18}O \text{ \% abundance}}{M^{\bullet+} \text{ \% abundance}} \times 100\right\}}{0.2} = \frac{\left(\frac{0.27}{90}\right) \times 100}{0.2} = 1.5$$

0.2 ← % $^{18}O/^{16}O$

Click on image to enlarge



- **a)** butanal — C_4H_8O 72
- **b)** propanal — C_3H_6O 58 — Loss of 1 = aldehyde
- **c)** 2-propenal — C_3H_4O 56
- **d)** methoxy-ethene — C_3H_6O 58
- **e)** ethanediol — $C_2H_6O_2$ 62

M/z = 58

α - fragmentation

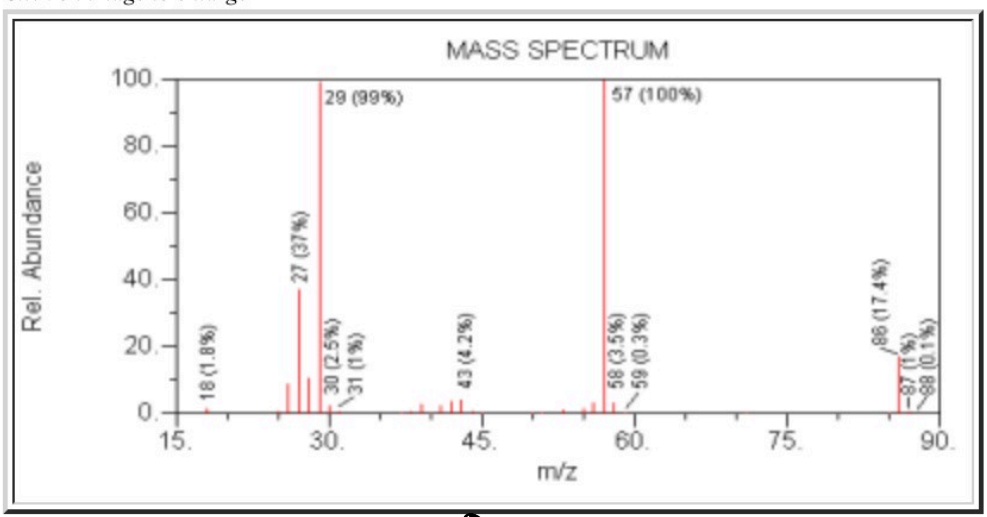
Loss 1

M/z = 57

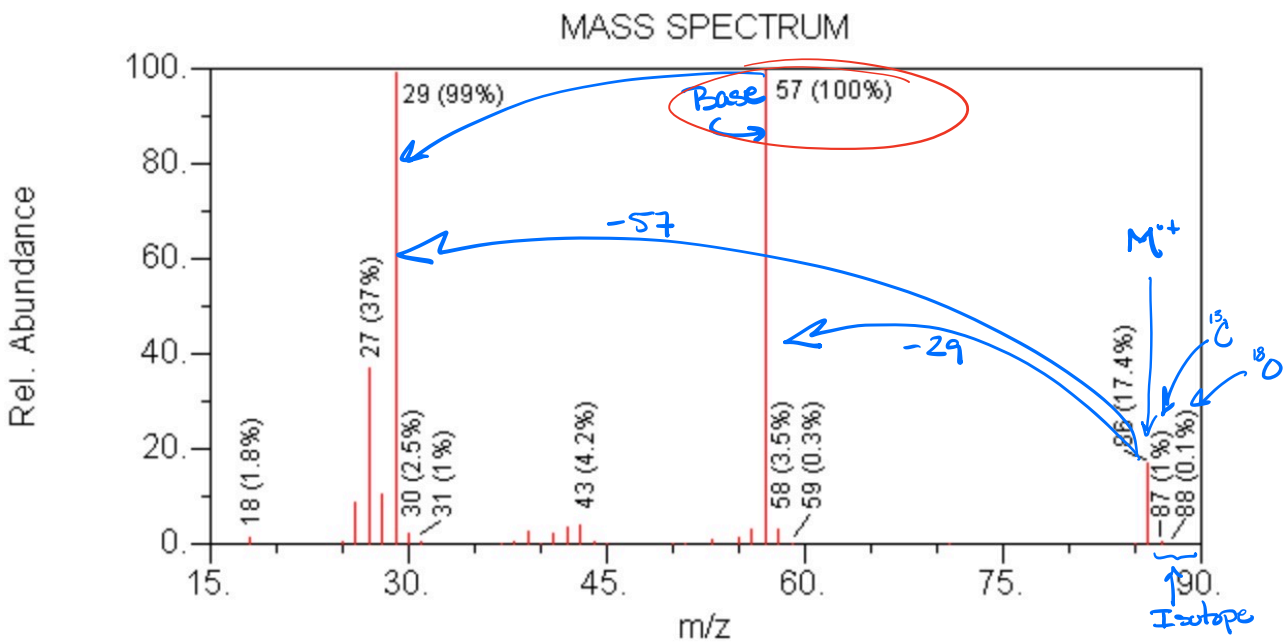
5. ***For this same spectrum, choose the compound that the spectrum represents.***

Hint

Click on image to enlarge



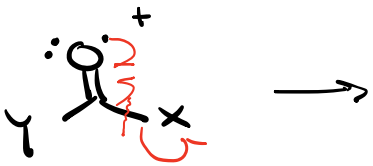
- ○ **a)** 4-heptanone — $C_7H_{14}O$ 114
- ○ **b)** 3-methyl-2-butanone — $C_5H_{10}O$ 86
- ● **c)** 3-pentanone — $C_5H_{10}O$ 86
- ○ **d)** 2-butanone — C_4H_8O 72
- ○ **e)** 2-pentanone — $C_5H_{10}O$ 86

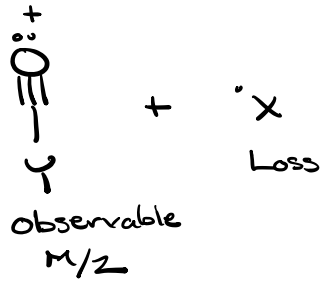


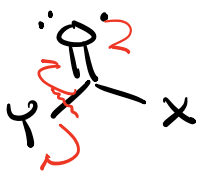
$$\#C = \left[\frac{1\%}{17.4\%} \times 100\right] \div 1.1 = 5 \text{ carbons} \checkmark$$

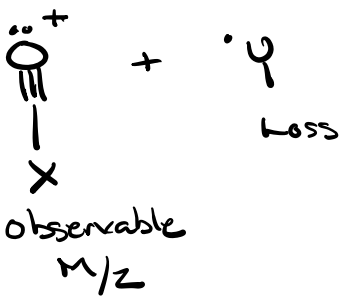
(^{13}C over 1%; M^{+} under 17.4%; % ^{13}C/^{12}C over 1.1)

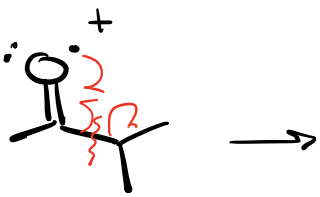
α-Cleavage

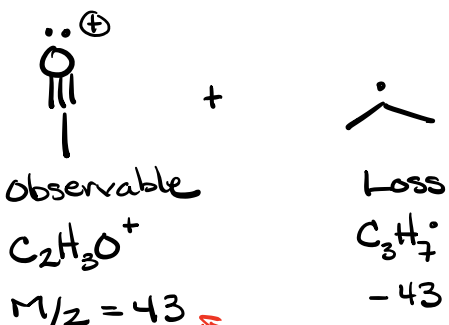




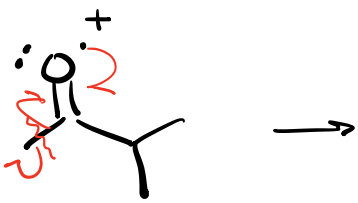


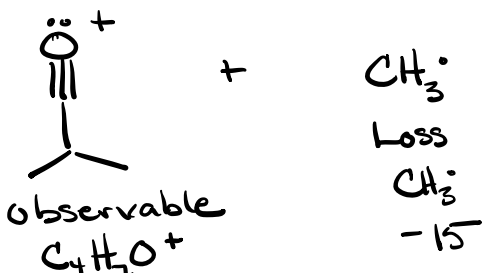




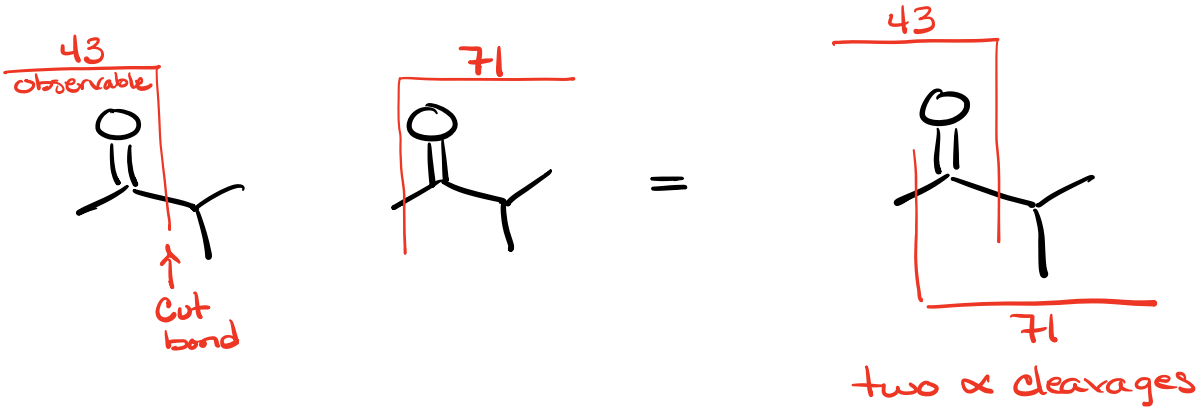


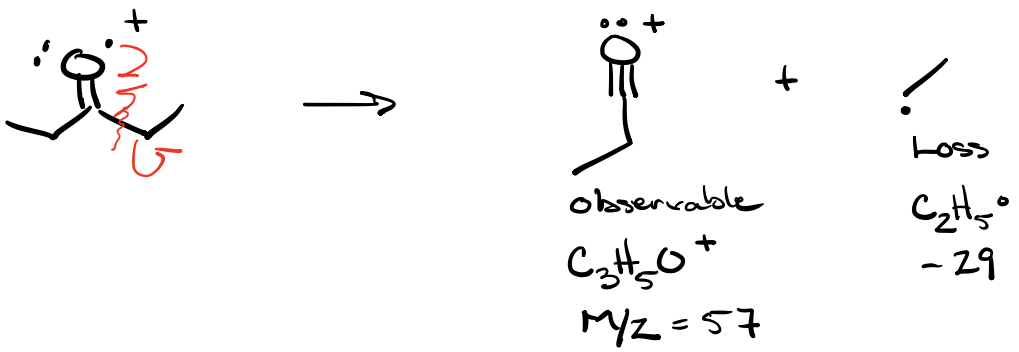
← very tiny in spectrum

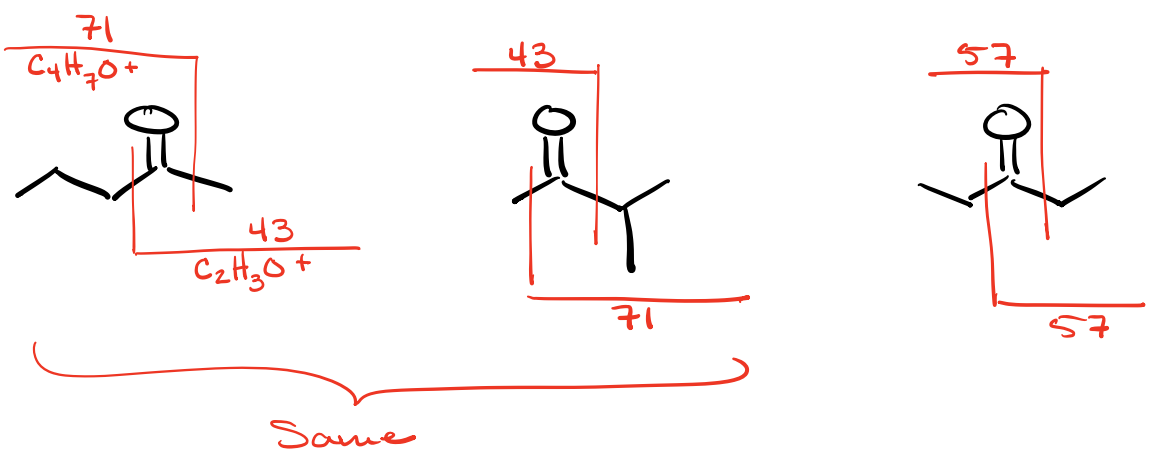




⇐ no 71 in spectrum


43
observable
Cut bond
71
=
43
71
two α cleavages

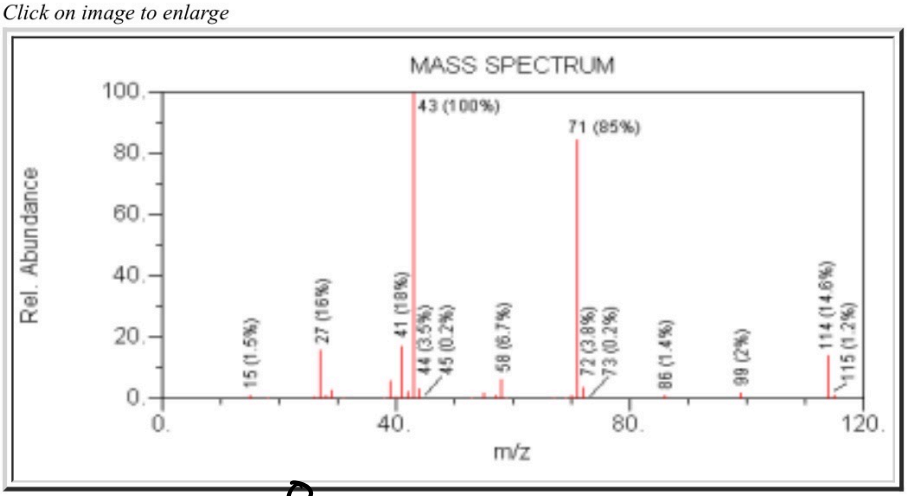

observable
$C_3H_5O^+$
M/Z = 57
Loss
$C_2H_5^\bullet$
-29


71
$C_4H_7O^+$
43
$C_2H_3O^+$
43
71
57
57
Same

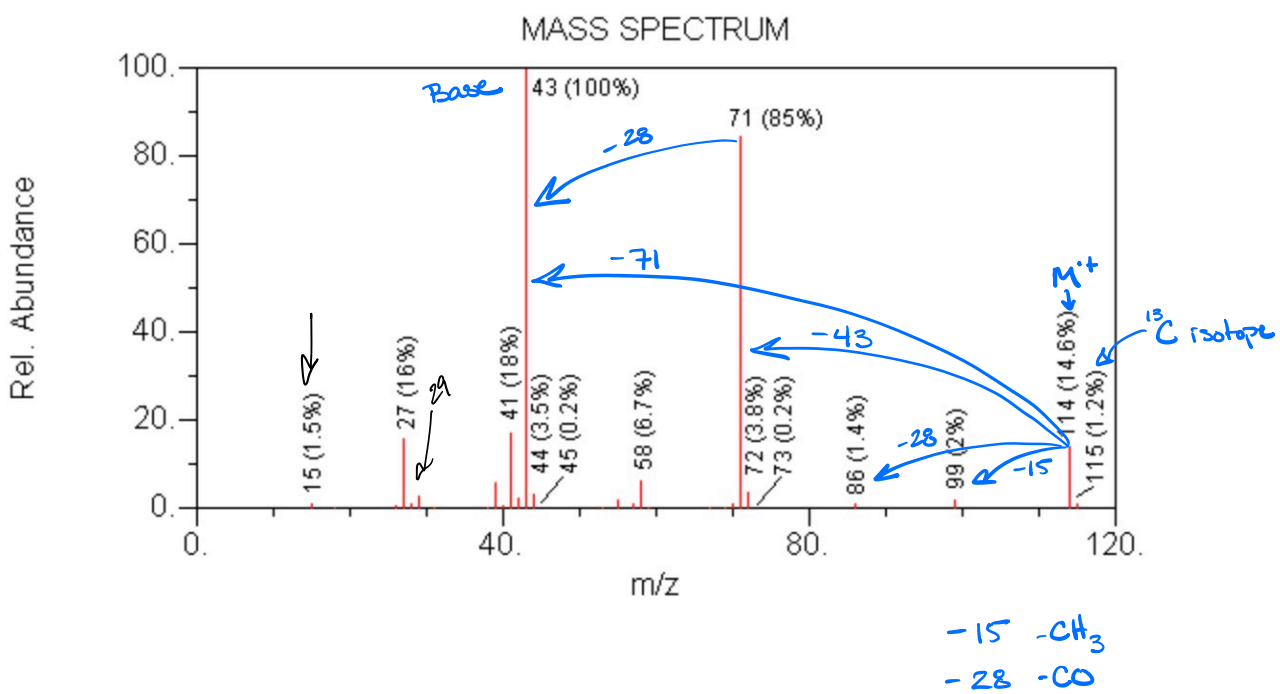
4. ***Choose the compound that this spectrum represents.***

Hint

Click on image to enlarge

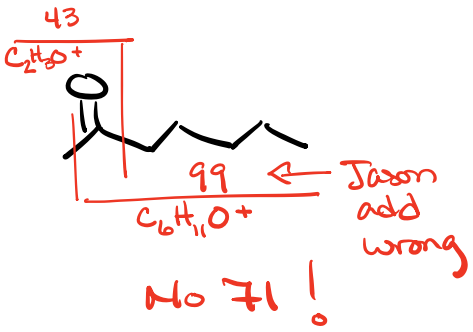


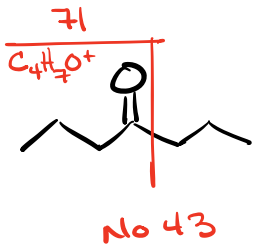
- a) 2-heptanone — $C_7H_{14}O$ 114
- b) 4-heptanone — $C_7H_{14}O$ 114
- c) 3-pentanone — $C_5H_{10}O$ 86
- d) 4-methyl-2-heptanone — $C_8H_{16}O$ 128
- e) 2,4-dimethyl-3-pentanone — $C_7H_{14}O$ 114

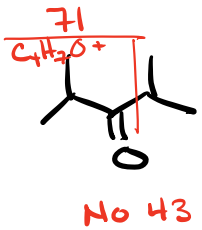


-15 $-CH_3$

-28 $-CO$

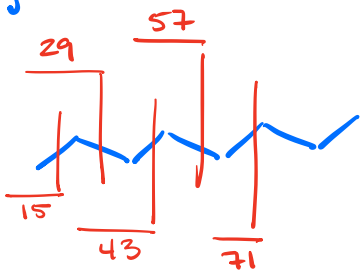






Both Symmetrical & Similar

Alkyl Series



often shows up with straight chain molecules.

Branching throws alkyl series off.

No series present ⇒ molecule probably not straight chain
⇒ more likely branched