An Introduction to Mass Spectrometry

Masses of Common Isotopes

Carbon $^{12}C = 12.000000$

Hydrogen $^{1}H = 1.007825$

Nitrogen $^{14}N = 14.003050$

Oxygen $^{16}O = 15.994914$

CO MW = 27.994914

N_2 MW = 28.006100

$CH_2=CH_2$ MW = 28.031300

Resolution of Masses

	CO	N_2	$CH_2=CH_2$
	27.994914	28.006100	28.031300
Resolution			
1/100	28	28	28
1/1,000	28.0	28.0	28.0
1/10,000	27.99	28.01	28.03

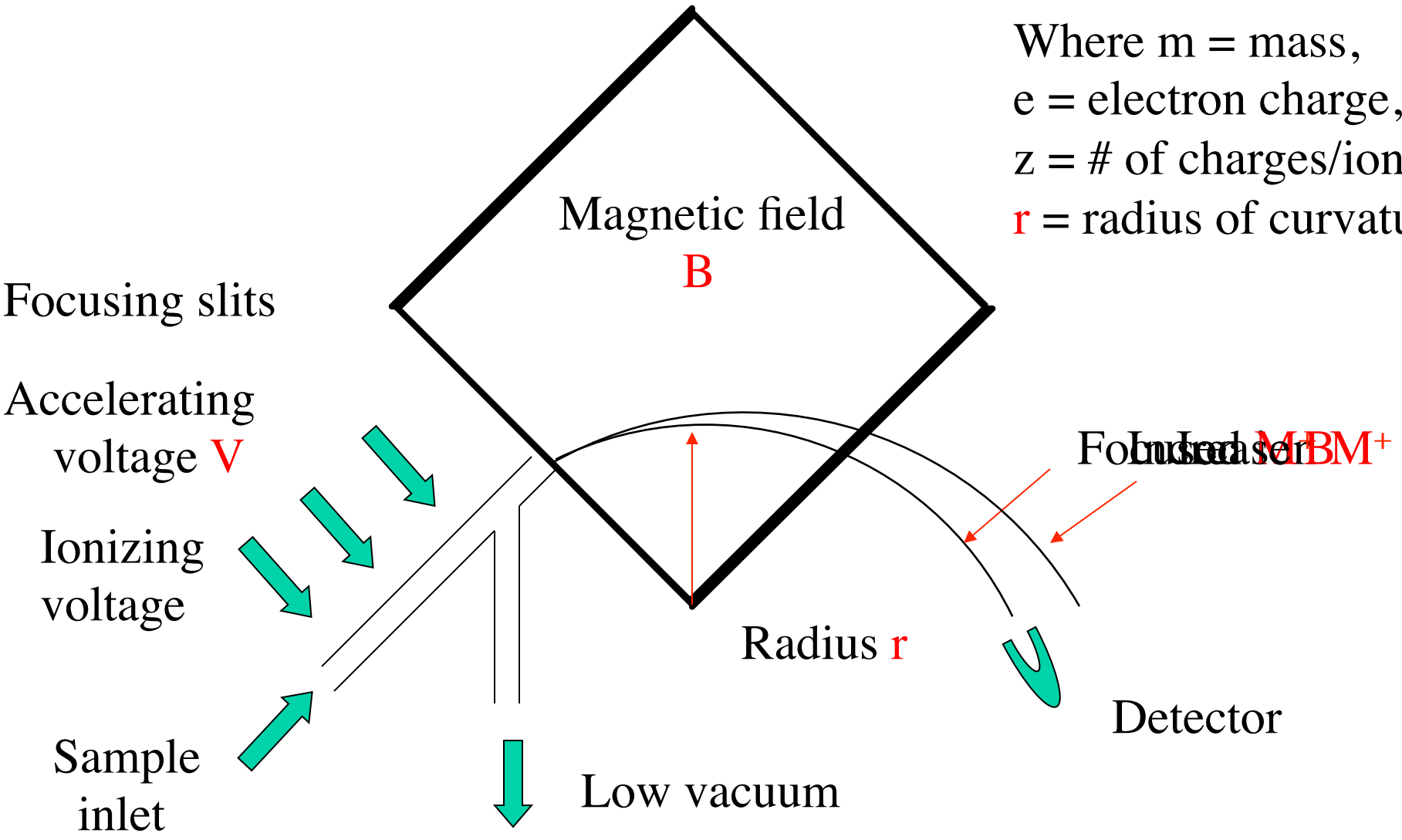
Natural Abundance of Common Elements

Hydrogen	$^{1}H = 99.985\%$	$^{2}H = 0.015\%$	
Carbon	$^{12}C = 98.90\%$	$^{13}C = 1.10\%$	
Nitrogen	$^{14}N = 99.63\%$	$^{15}N = 0.37\%$	
Oxygen	$^{16}O = 99.762\%$	$^{17}O = 0.038\%$	$^{18}O = 0.200\%$
Sulfur	$^{32}S = 95.02\%$	$^{33}S = 0.75\%$	
	$^{34}S = 4.21\%$	$^{36}S = 0.02\%$	
Chlorine	$^{35}Cl = 75.77\%$	$^{37}Cl = 24.23\%$	
Bromine	$^{79}Br = 50.69\%$	$^{81}Br = 49.31\%$	

The Mass Spectrometer

$m/z = B^2r^2e/2V$

Where m = mass,
e = electron charge,
z = # of charges/ion
r = radius of curvature

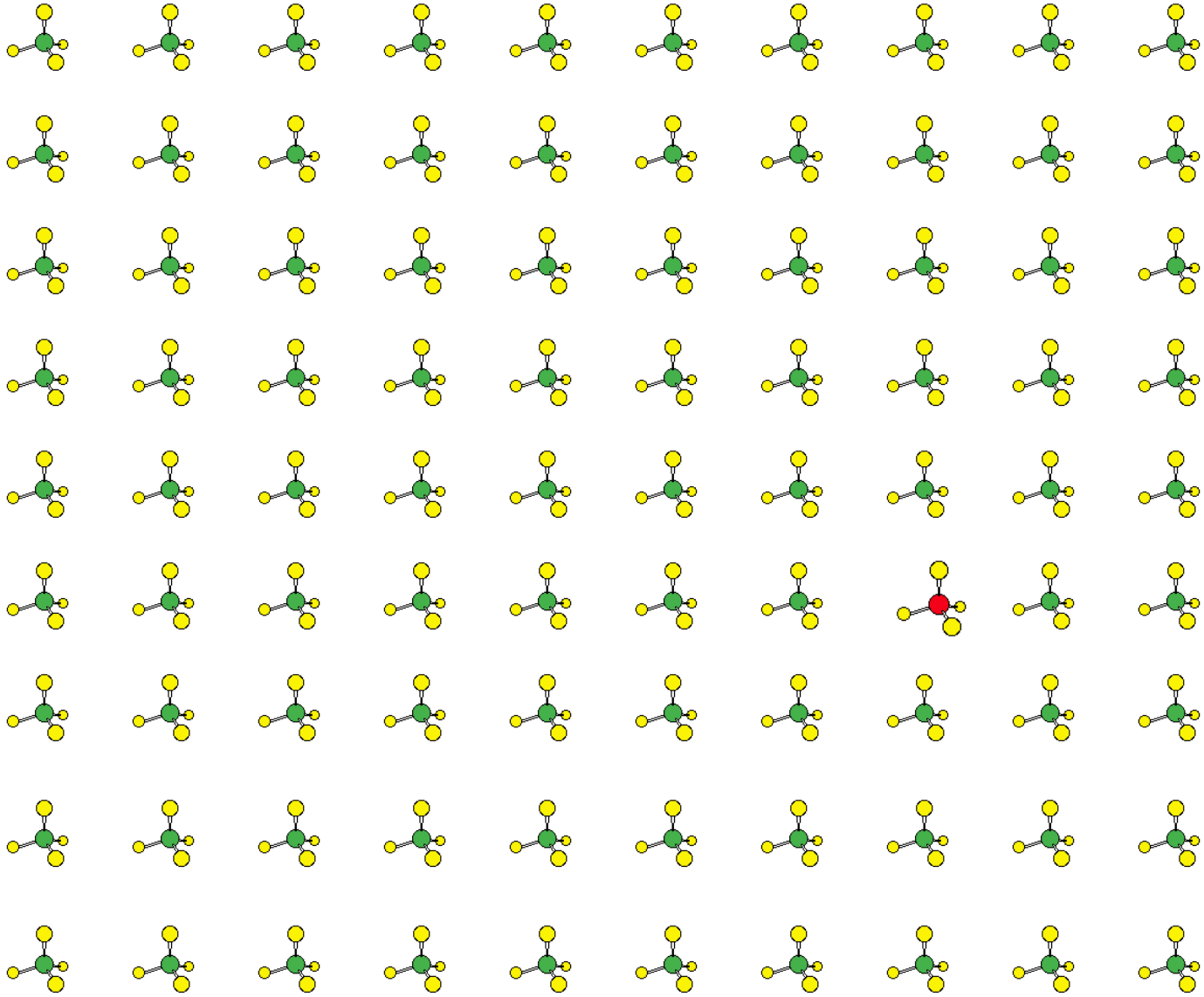


For carbon,

One in ~90 atoms of carbon is C-13

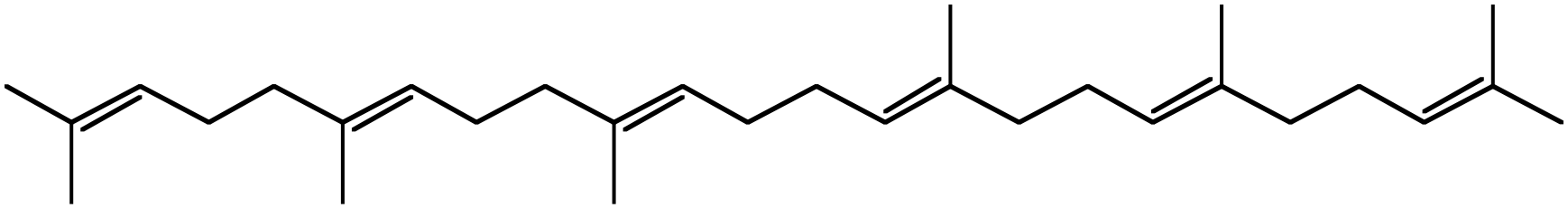
For every 90 molecules of methane ...

only one molecule contains C-13

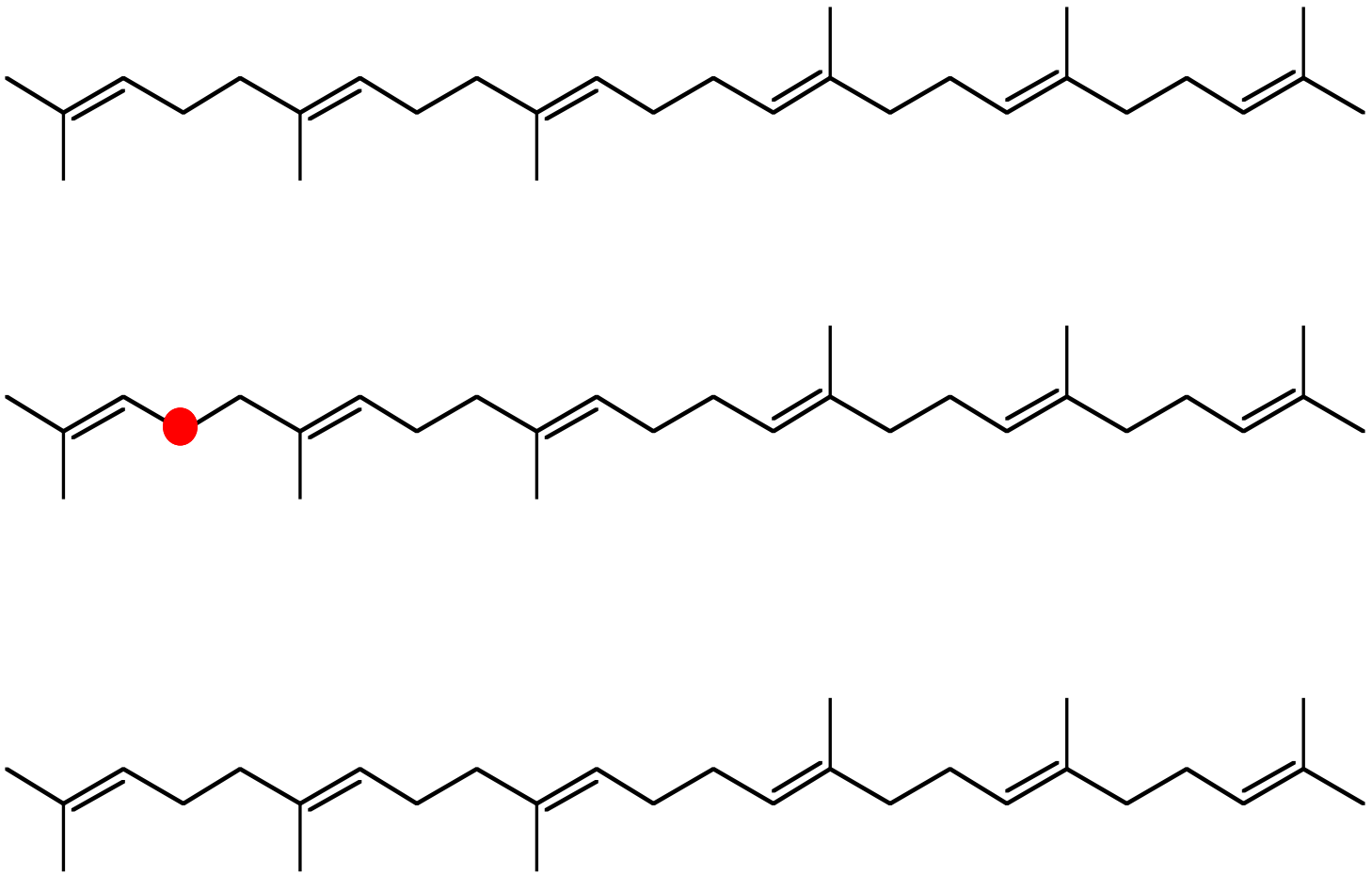


Where's Waldo?

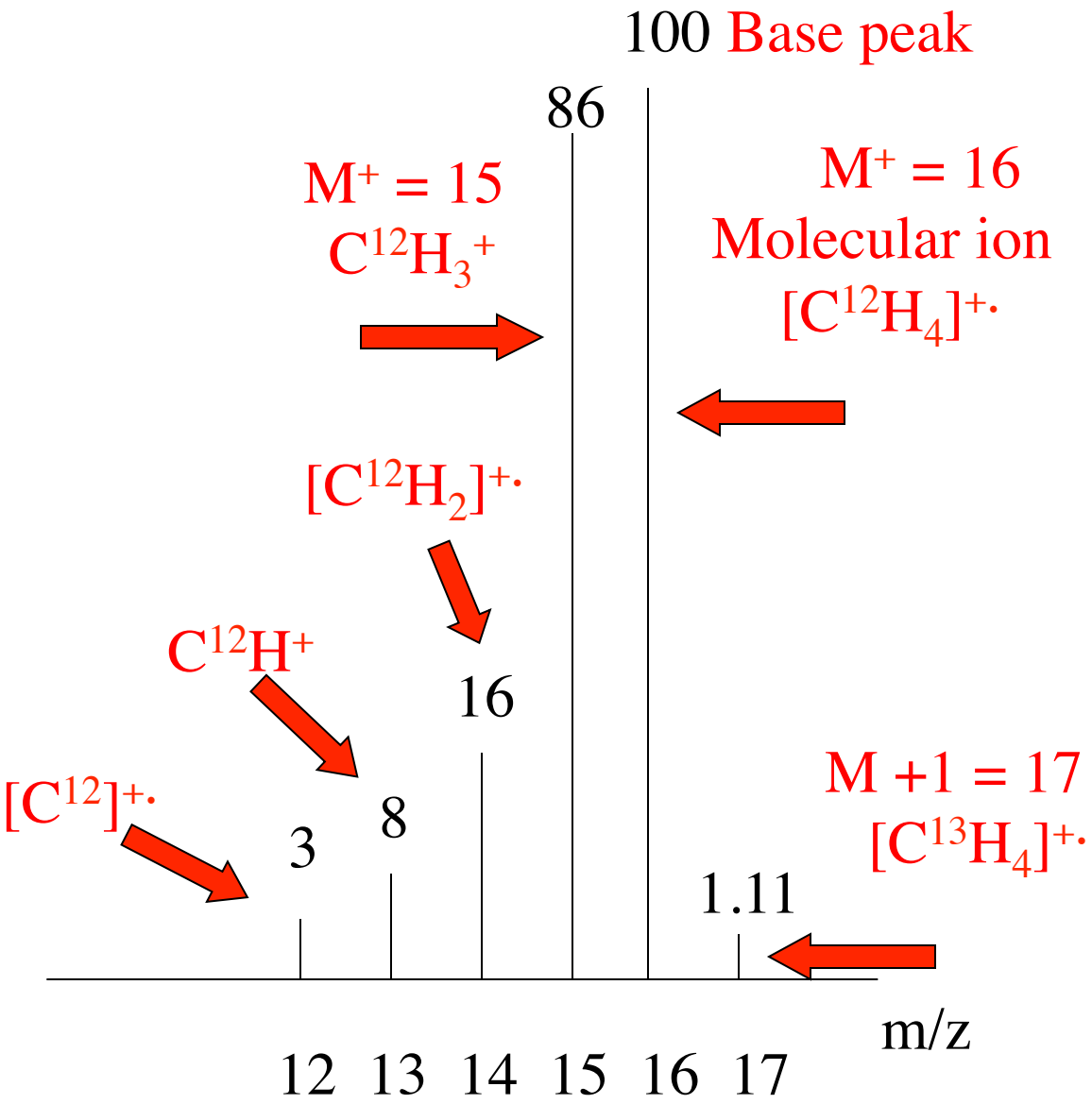
… or for the C_{30} triterpene squalene

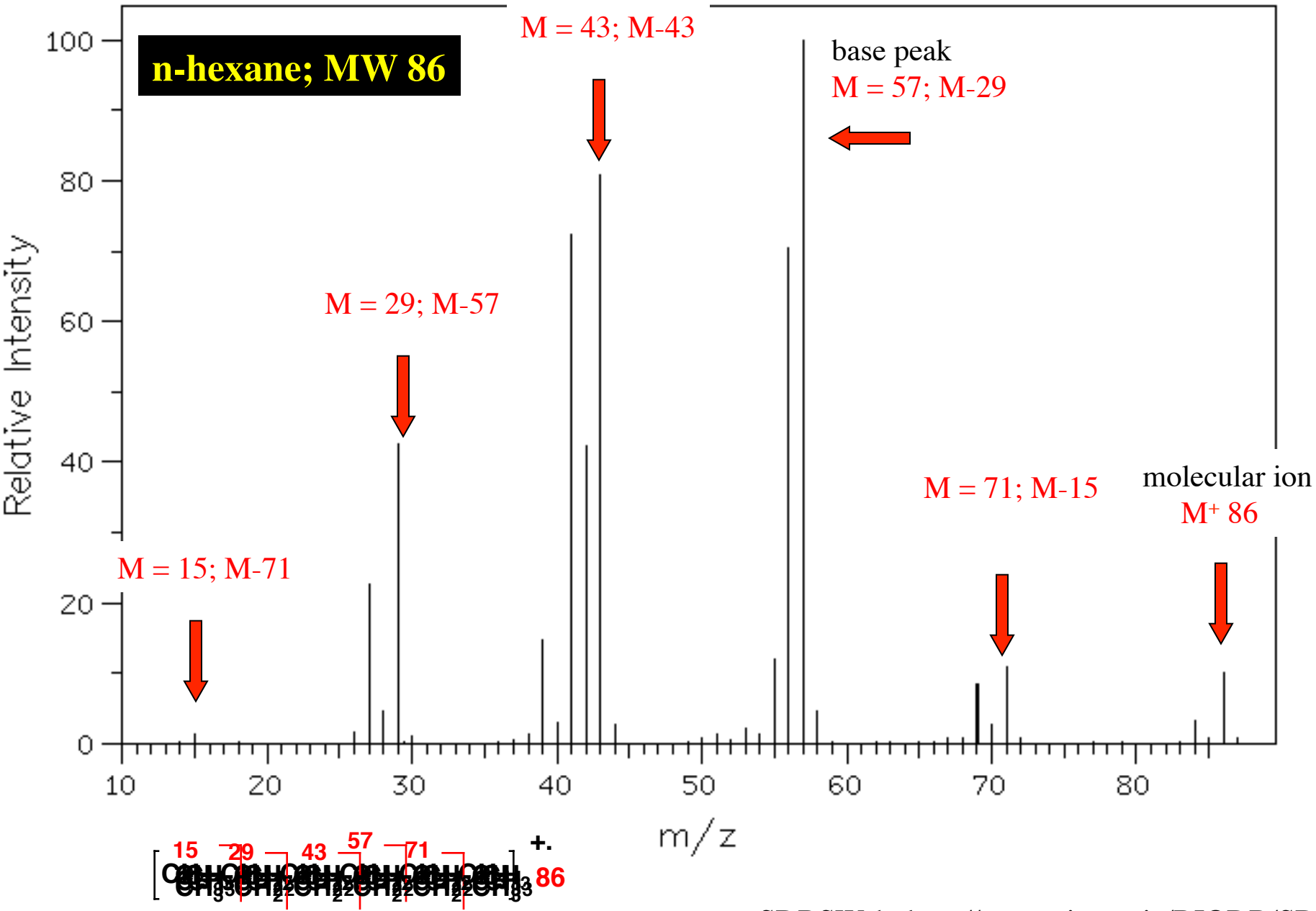


one carbon in 3 molecules is C-13



The Mass Spectrum of Methane

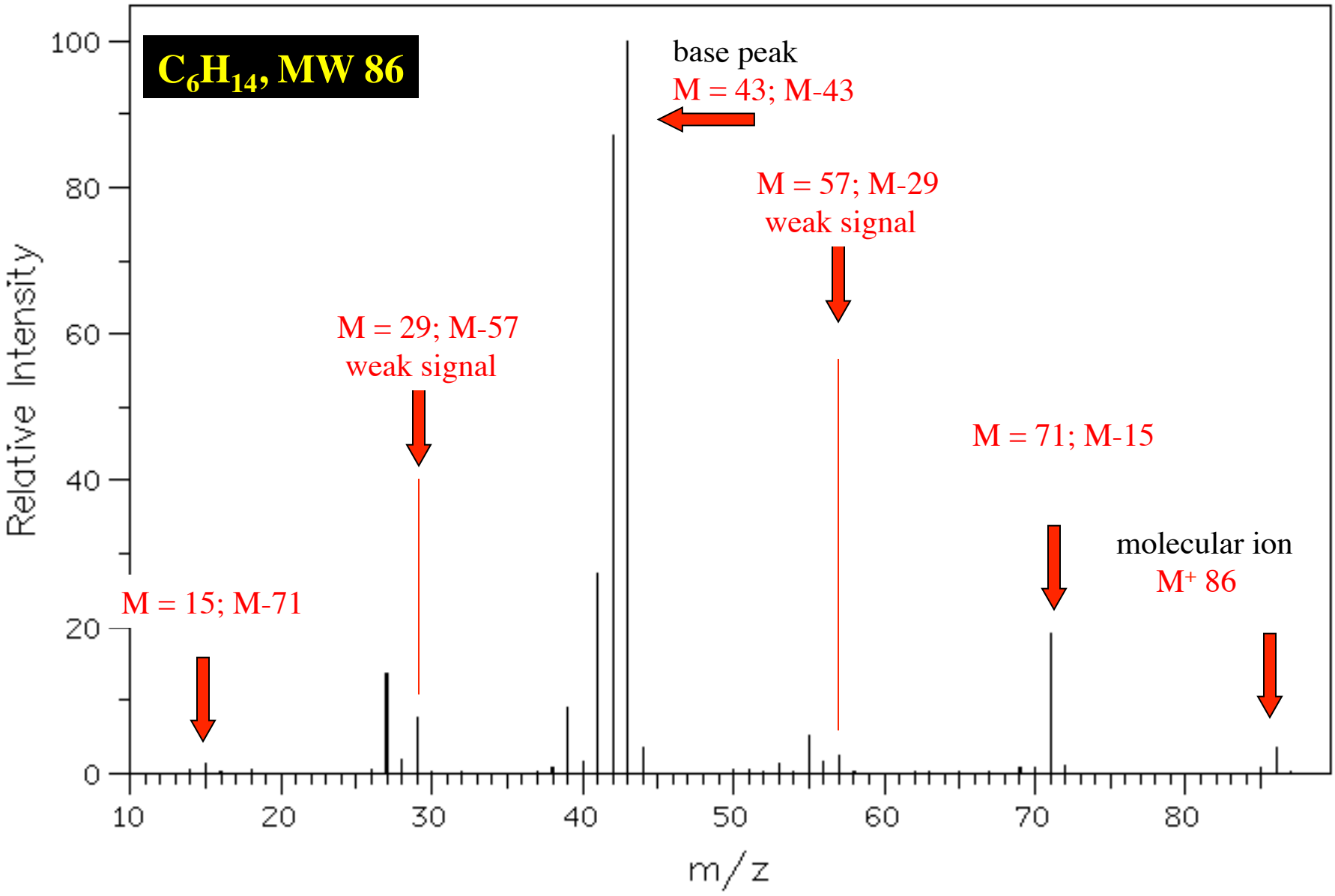




SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/

There are five constitutional isomers of C_6H_{14}

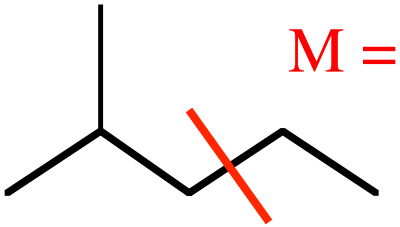
Which one of the remaining four has
the following mass spectrum?



SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/

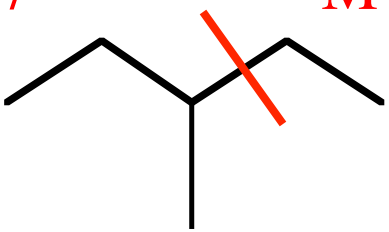
The Four Remaining Hexanes

M = 57 M = 29



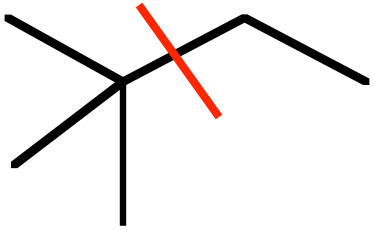
2-methylpentane

M = 57 M = 29

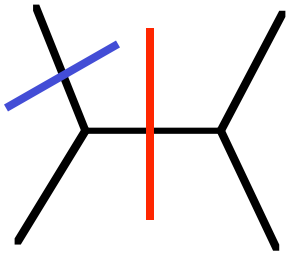


3-methylpentane

M = 57 M = 29



2,2-dimethylbutane

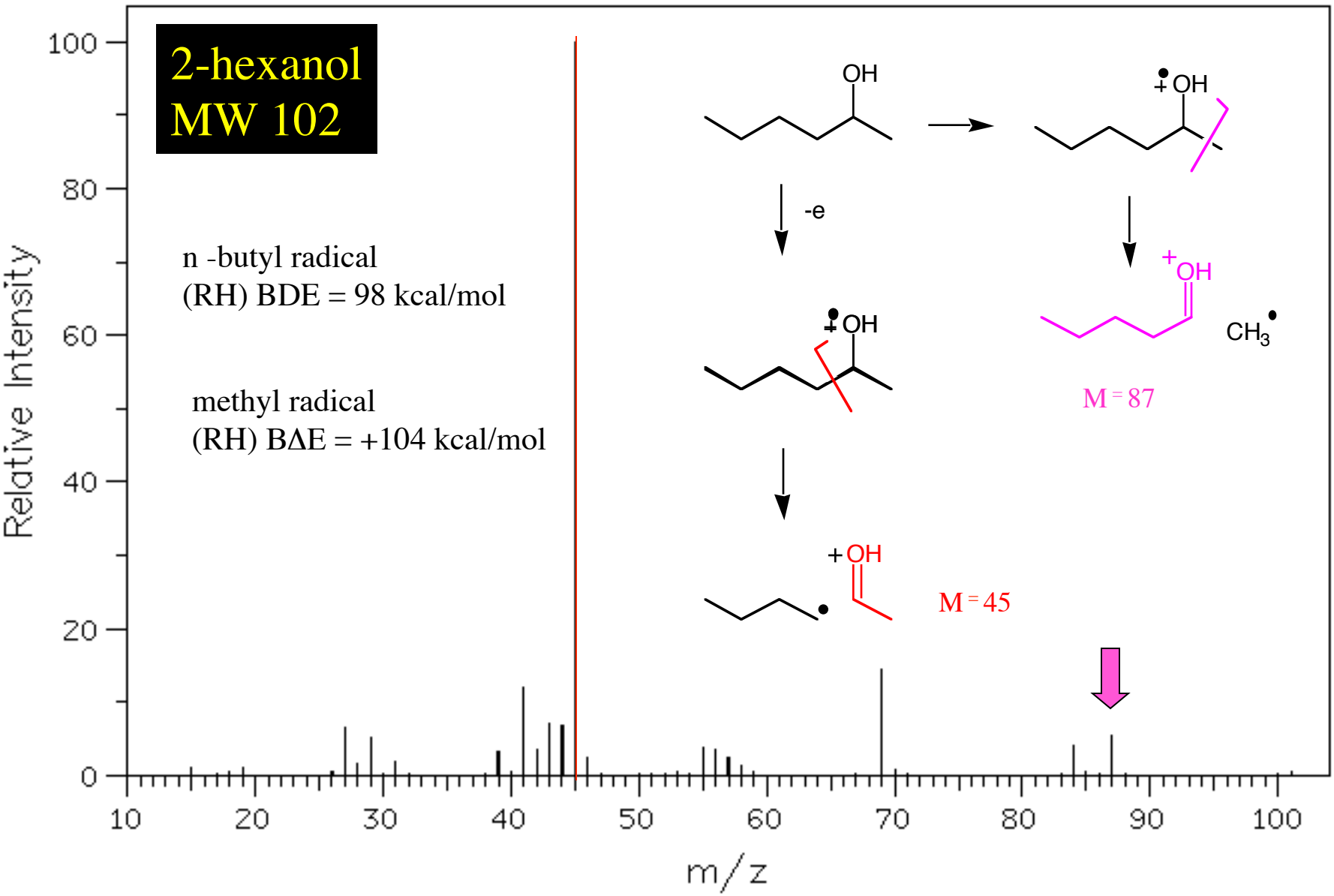


M = 43

M = 71

M = 15

2,3-dimethylbutane



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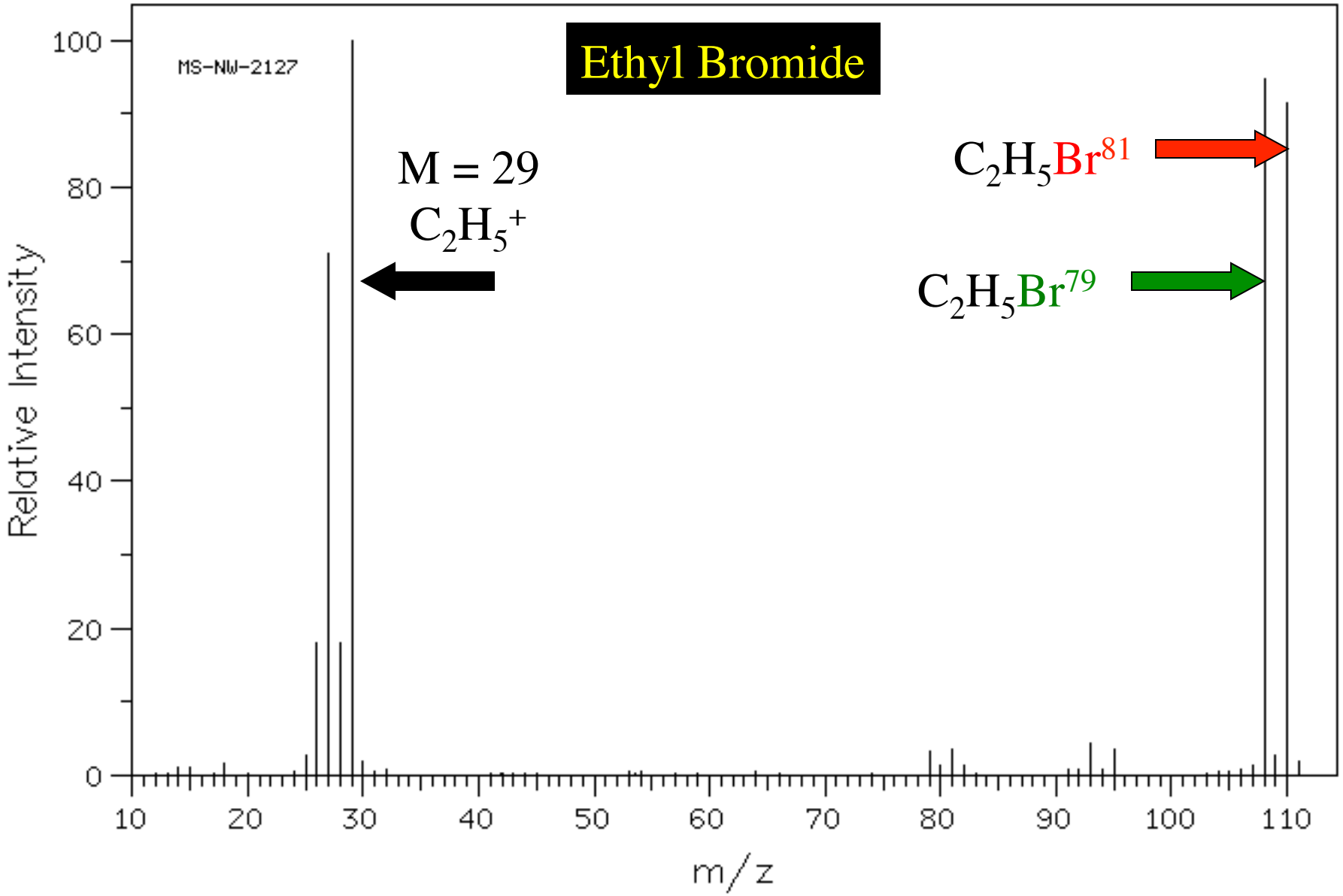

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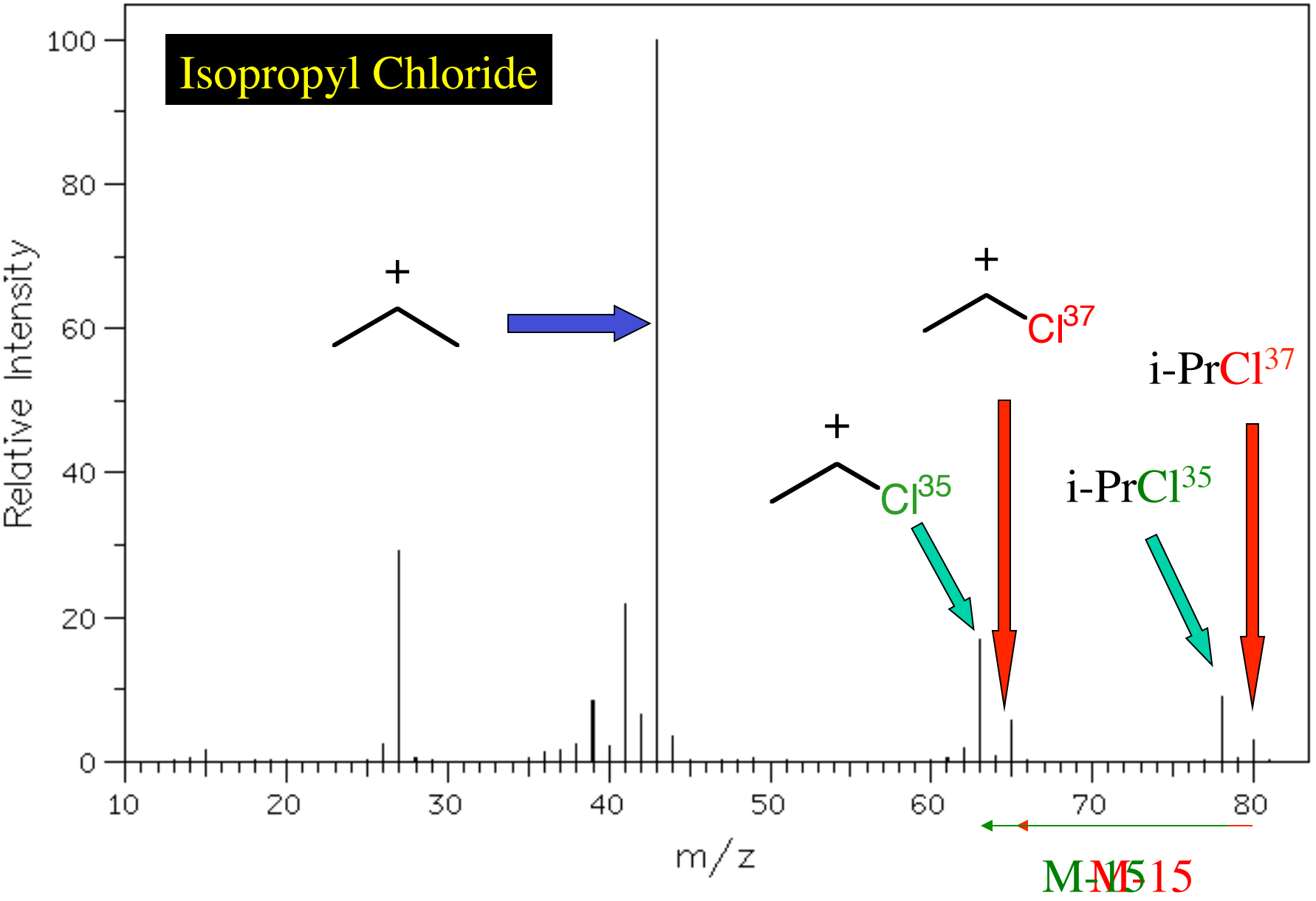
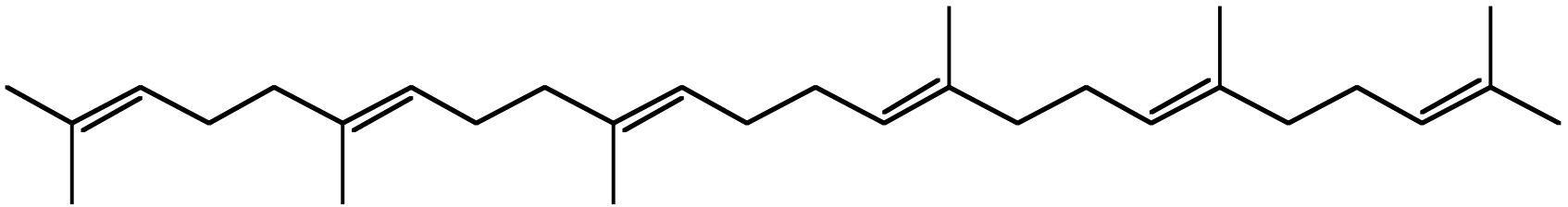


SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/

Back to squalene ($C_{30}H_{50}$)

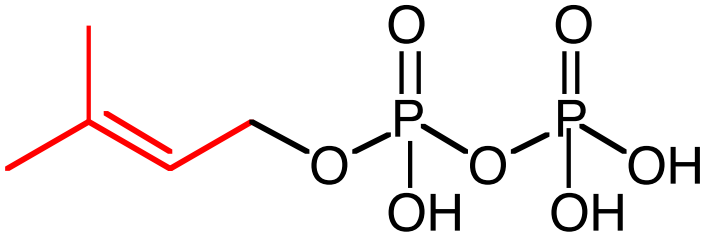


or

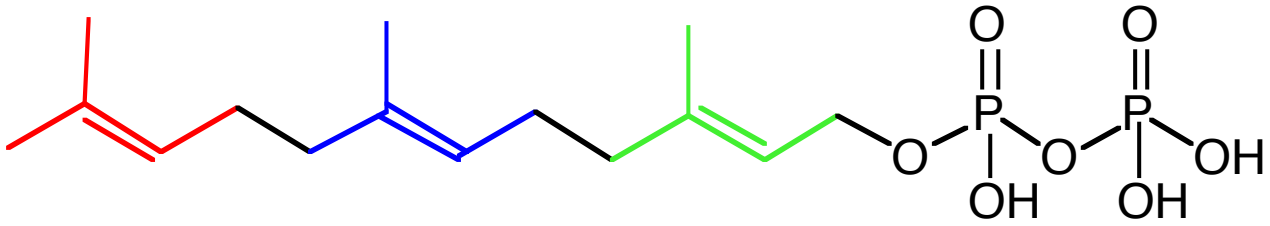
(6*E*, 10*E*, 14*E*, 18*E*)-
2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene

On the Mechanism of the Biosynthesis of Squalene

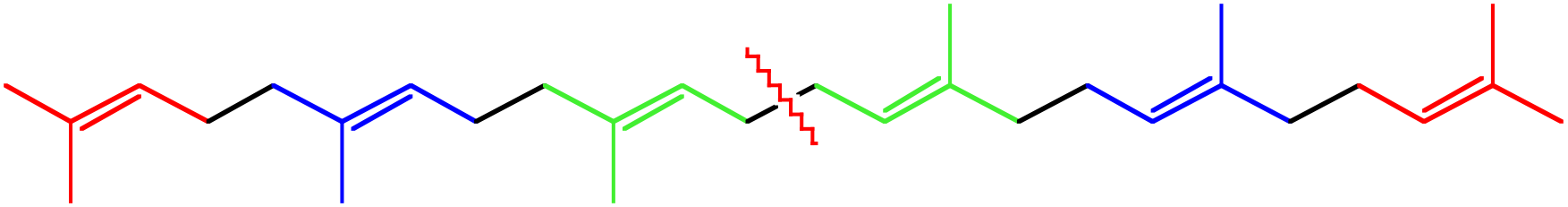
3 CH_3CO_2H



Pentenylpyrophosphate

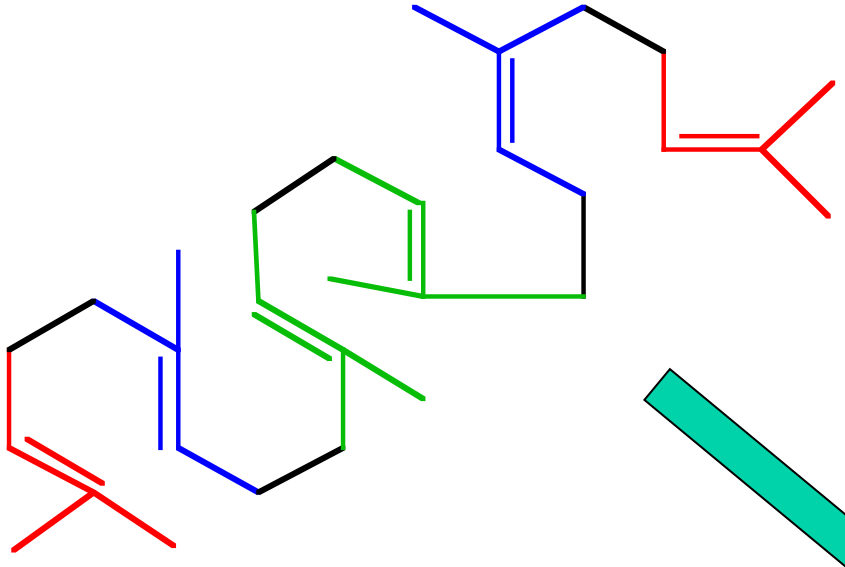


Farnesylpyrophosphate

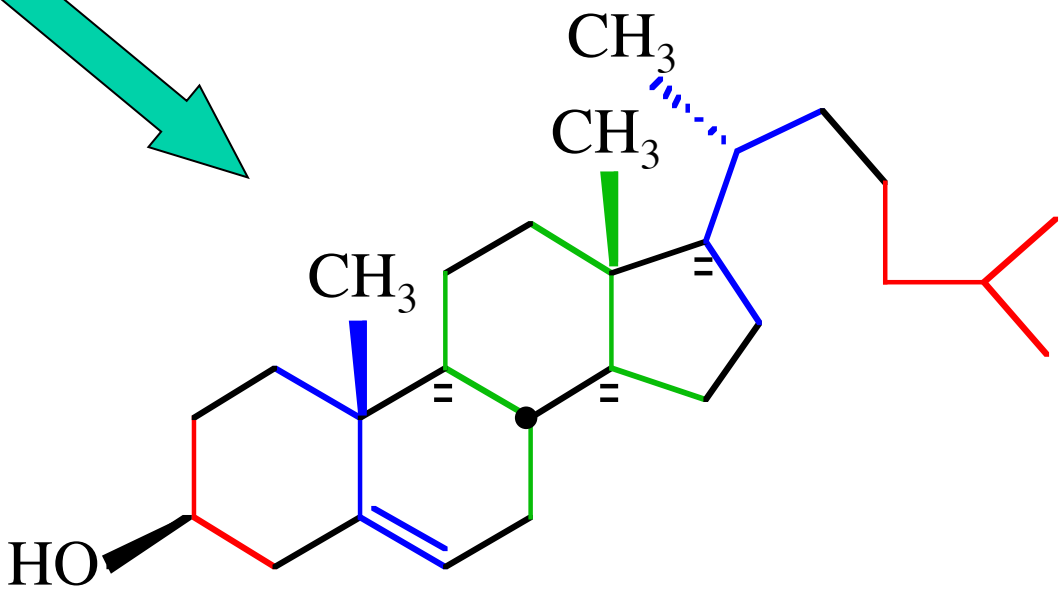


Squalene

On the Biochemical Conversion of Squalene to Cholesterol

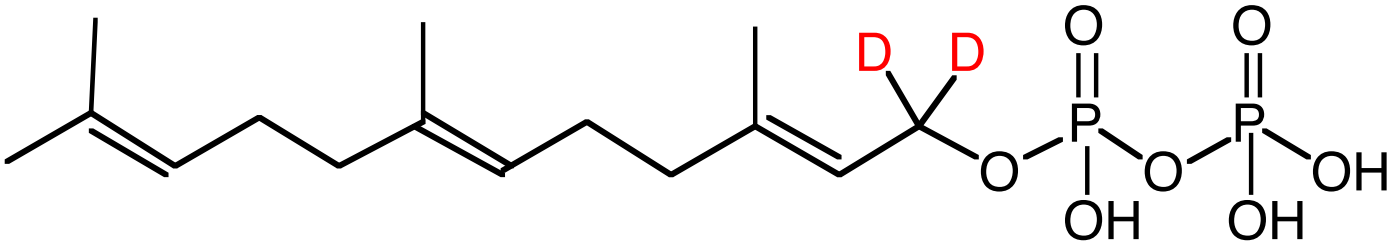


Squalene C_{30}

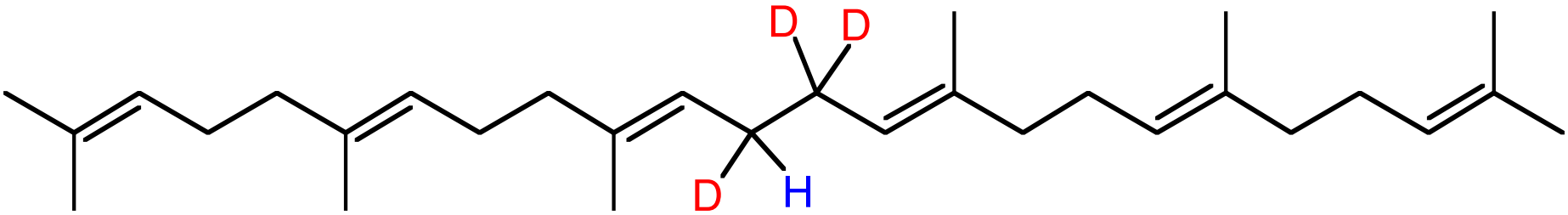


Cholesterol C_{27}

A Deuterium Labeling Experiment on the Biosynthesis of Squalene

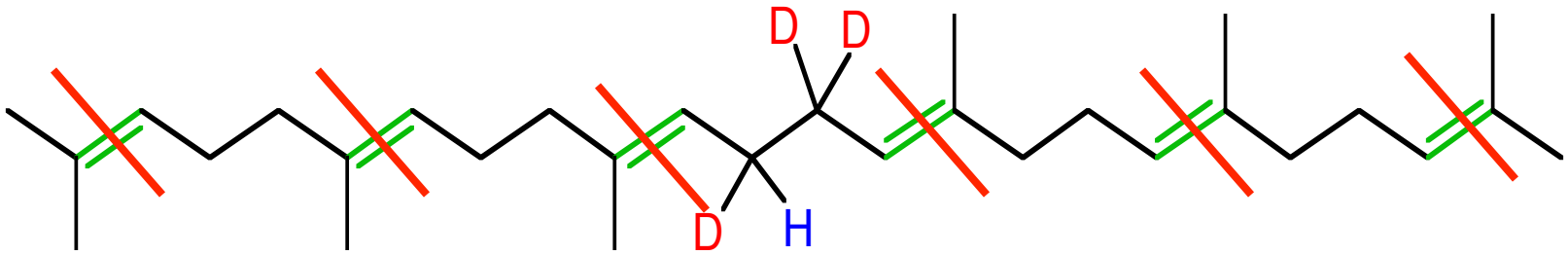


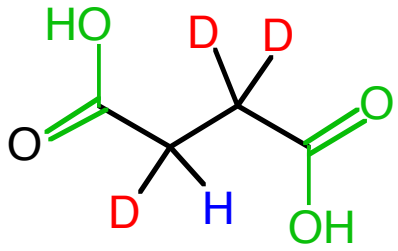
Farnesylpyrophosphate - d_2

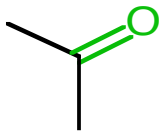


Squalene - d_3

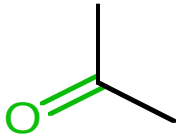
Oxidative Ozonolysis of Deuterium Labeled Squalene

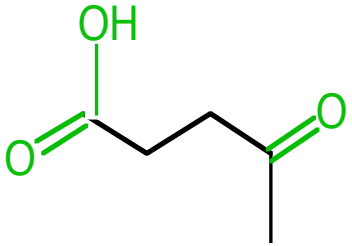


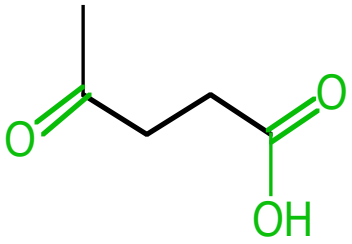


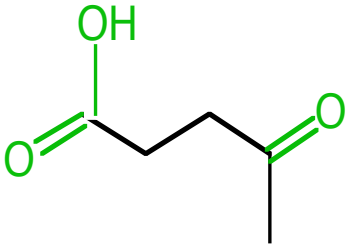


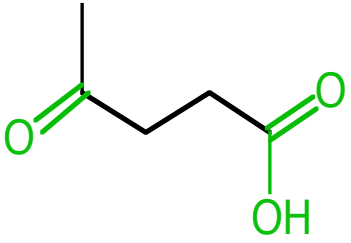
and





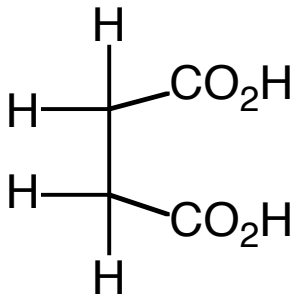




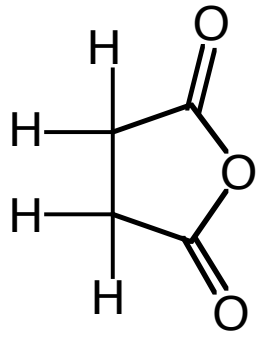


succinic acid- d_3

Formation of Succinic Anhydride

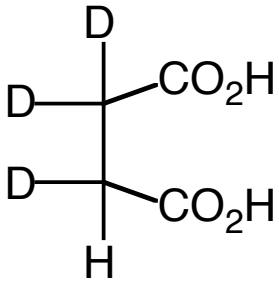


-H_2O

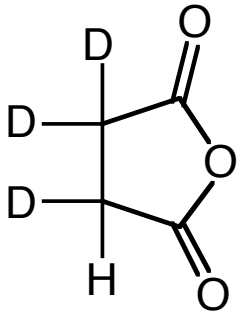


Succinic acid

Succinic anhydride

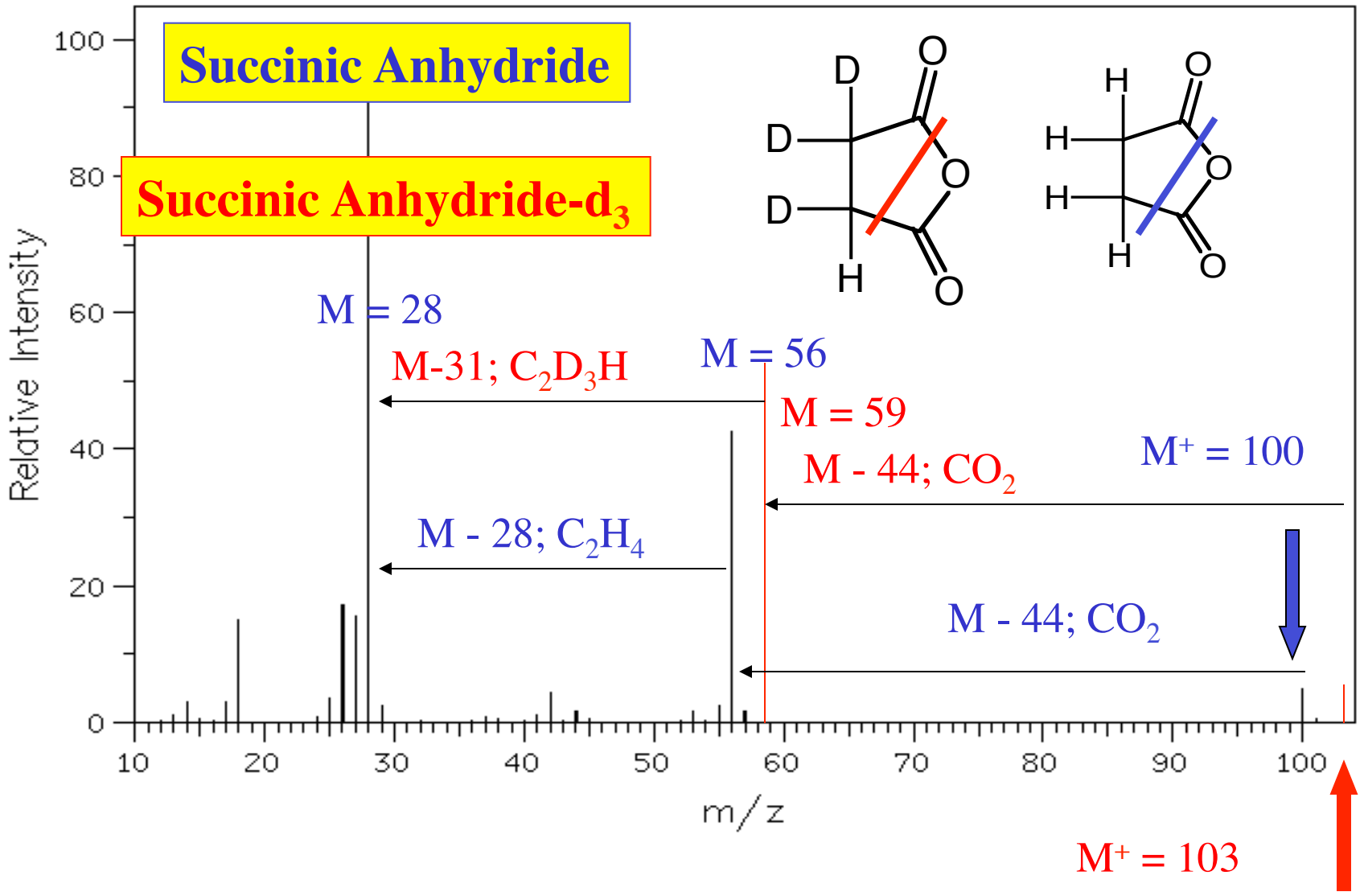


-H_2O



Succinic acid - d_3

Succinic anhydride - d_3


Succinic Anhydride
Succinic Anhydride-d3
M = 28
M-31; C2D3H
M = 56
M = 59
M - 44; CO2
M+ = 100
M - 28; C2H4
M - 44; CO2
M+ = 103
Relative Intensity
m/z
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
D
D
D
H
O
O
O
H
H
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The End