

Jackrel, S.L. and T.C. Morton. 2017. Inducible Phenotypic Plasticity in Plants regulates Aquatic Ecosystem Functioning.

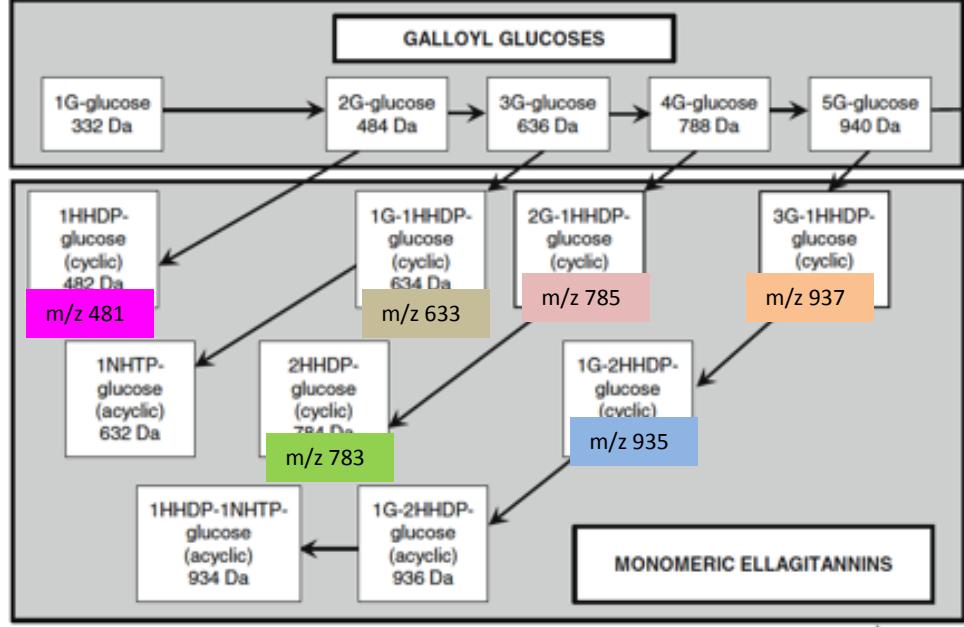
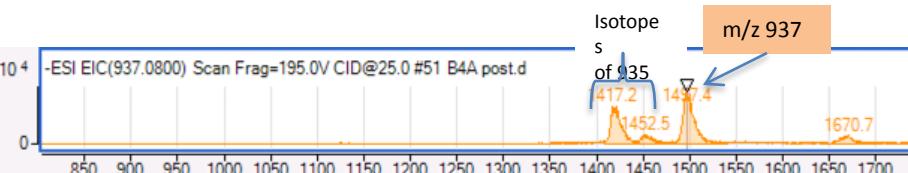
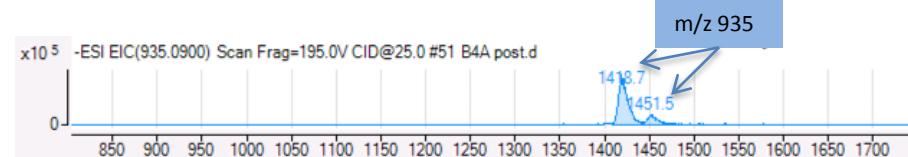
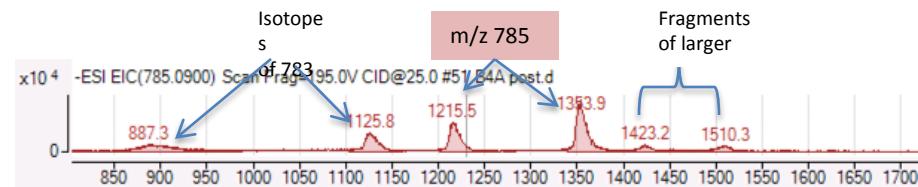
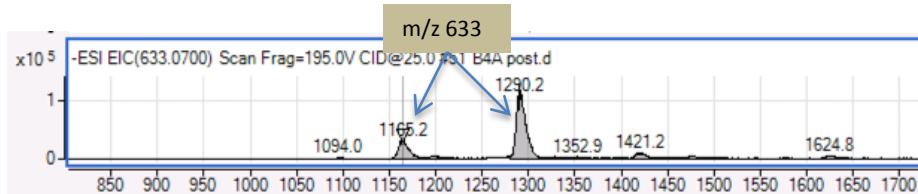
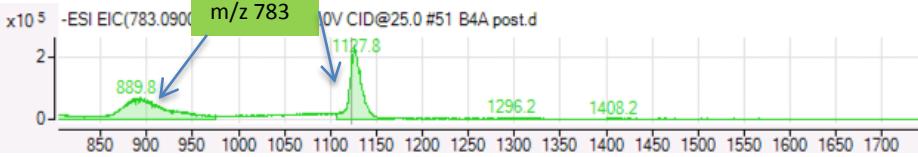
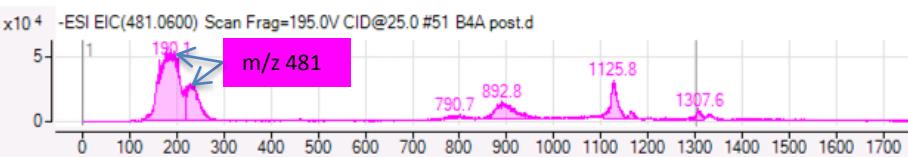
# Notes on Secondary Metabolite Identification

Tim Morton

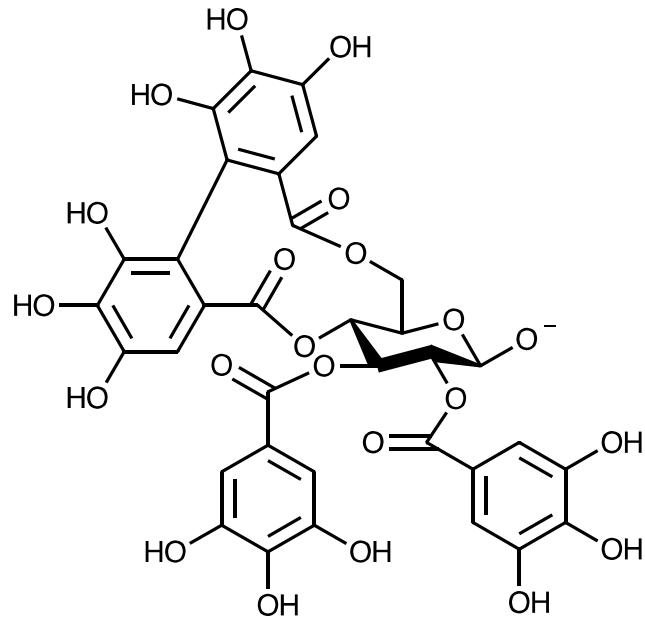
Department of Ecology & Evolution,  
University of Chicago

Contact authors for raw mass spectra files: [tmorton@uchicago.edu](mailto:tmorton@uchicago.edu) , [sjackrel@umich.edu](mailto:sjackrel@umich.edu)

# Ellagitannin HPLC rules of thumb



# Ellagitannin elution order

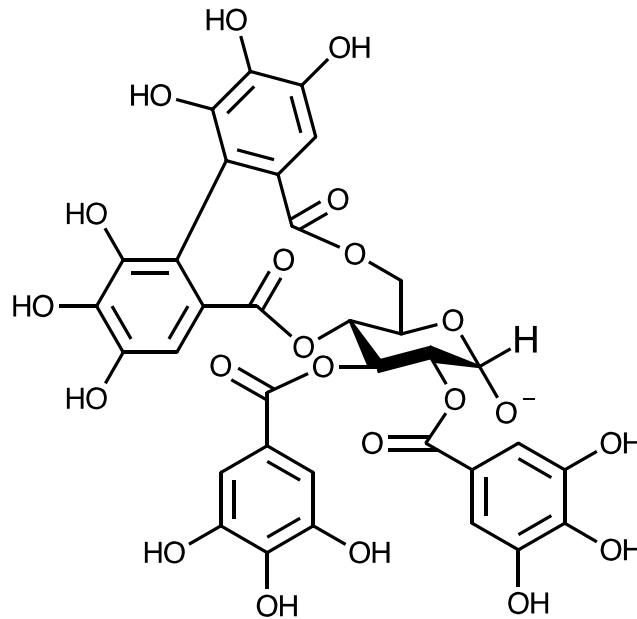


Molecular Formula =  $C_{34}H_{25}O_{22}^-$

Monoisotopic Mass = 785.084 u

tellimagrandin-1 OH beta

20.3 minutes



Molecular Formula =  $C_{34}H_{25}O_{22}^-$

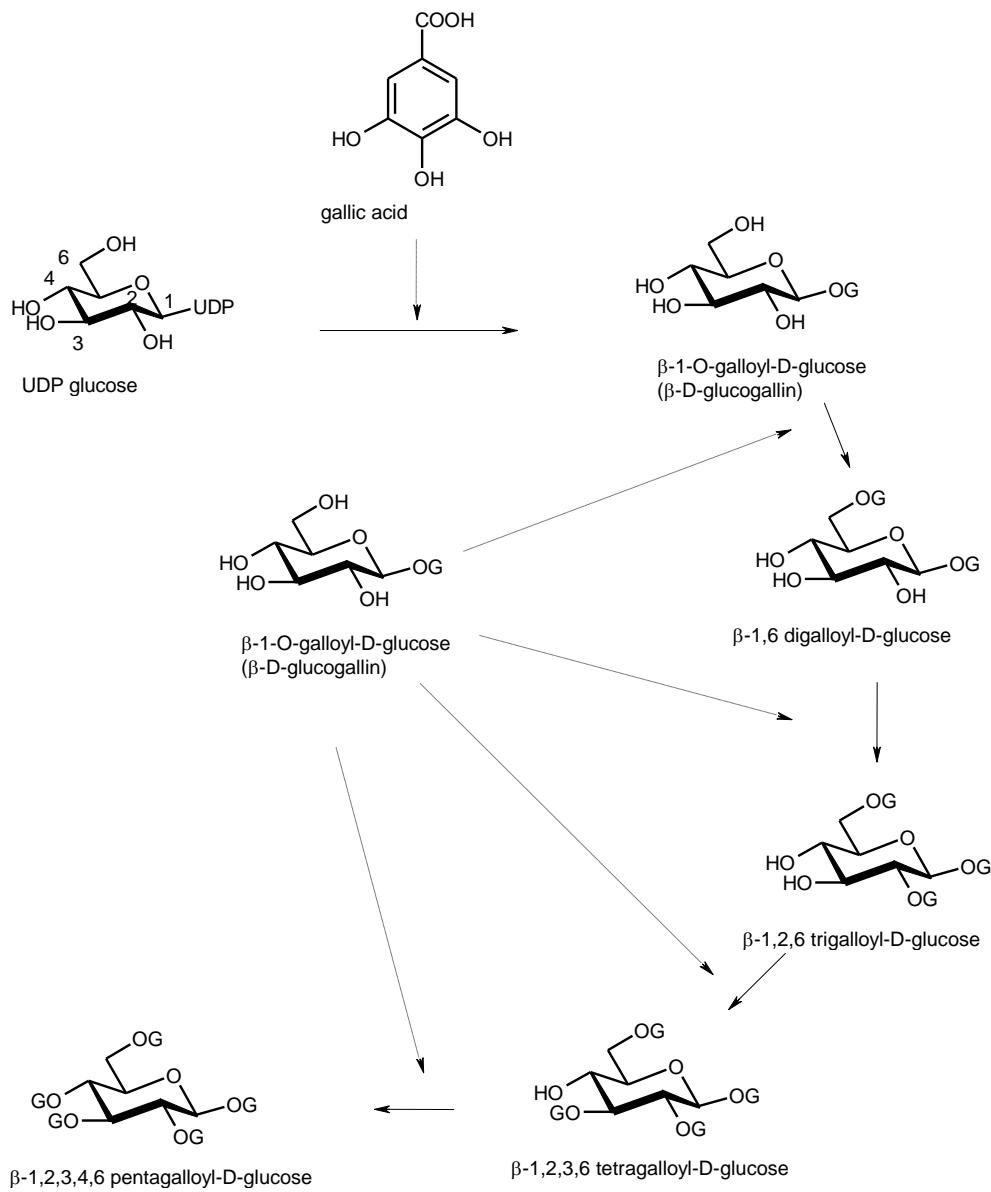
Monoisotopic Mass = 785.084 u

tellimagrandin-1 OH alpha

22.6 minutes

Hydroxyl out of the plane appears more polar

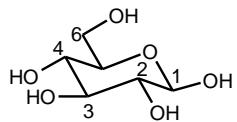
## PGG Penta-galloyl glucose Biosynthesis



$\beta$ -1-O-galloyl-D-glucose is the first product which then serves as the galloyl donor for subsequent reactions.

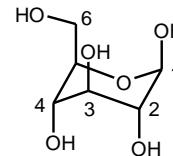
To a lesser extent, any galloyl derivative can serve as the donor. No external energy is needed, this is a high energy bond.

## Glucose conformation



$^4\text{C}_1$  conformation  
glucopyranose

Principal mode of transformation involves this more thermodynamically favorable conformation. First is oxidative C-C coupling of galloyl esters followed by oxidative C-O coupling (not seen in alder).

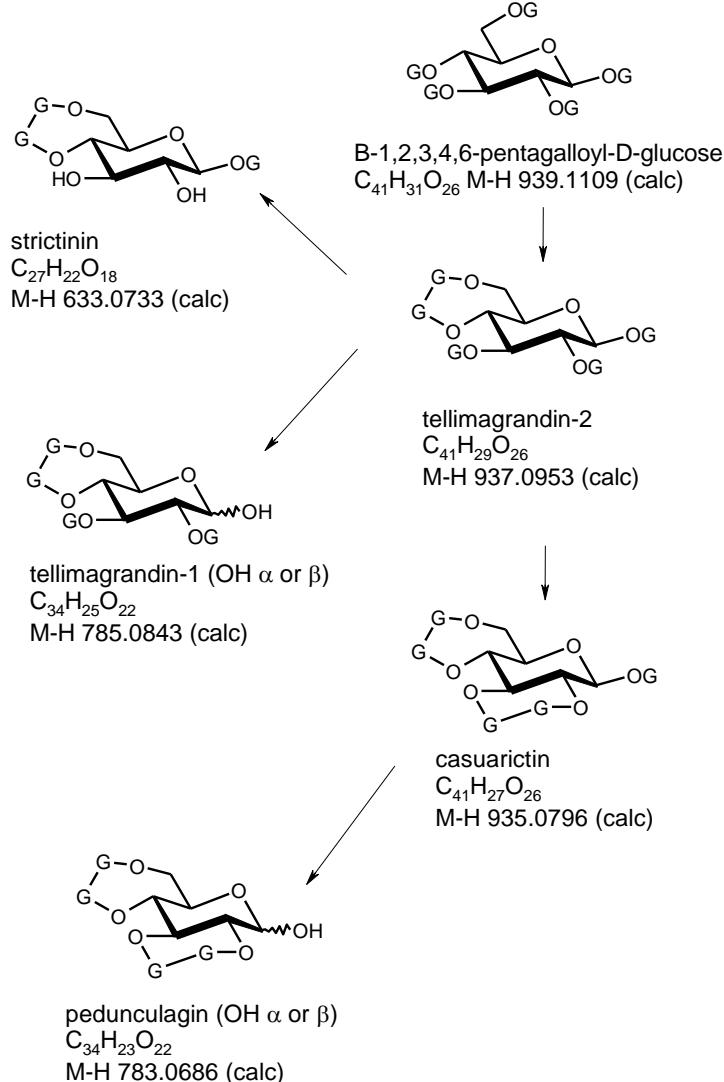


$^1\text{C}_4$  conformation  
glucopyranose

Alternative mode of transformation involves oxidative C-C coupling of 3-6 and 1-6; this leads to a far less thermodynamically stable conformation.

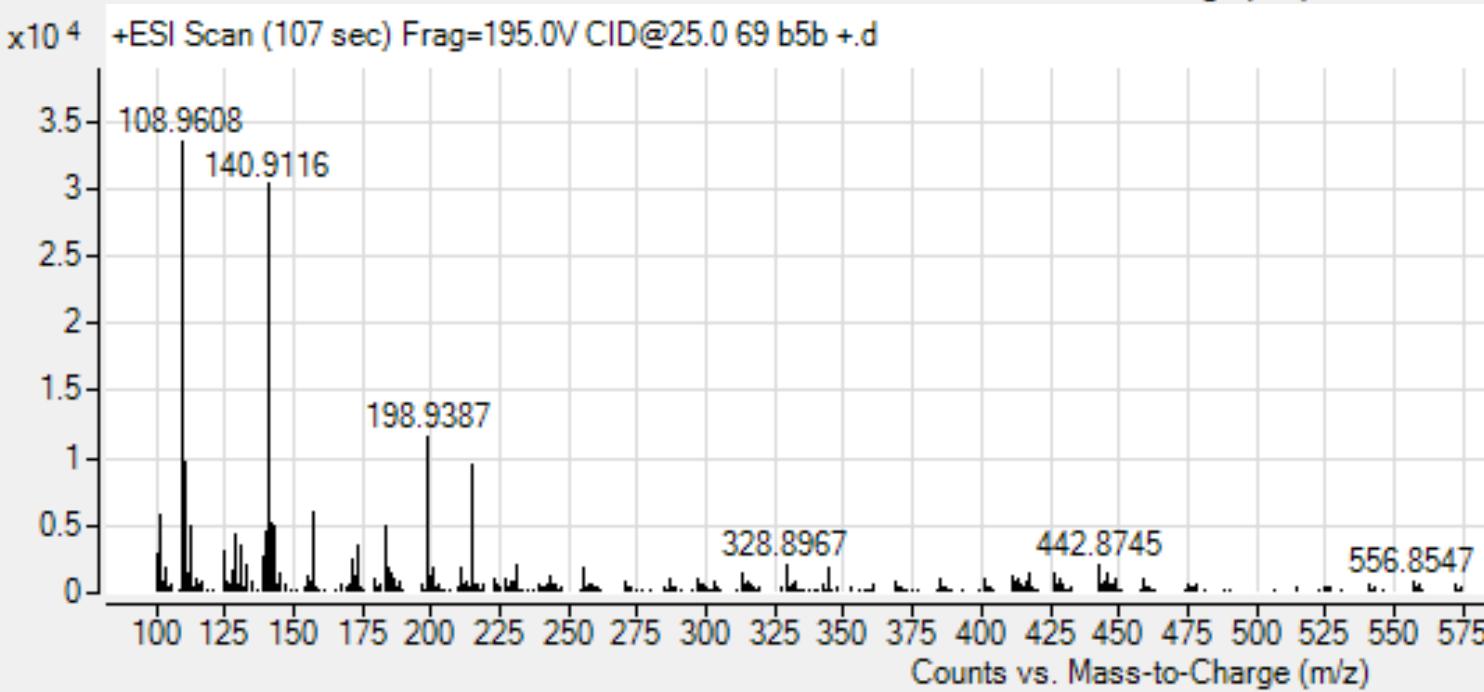
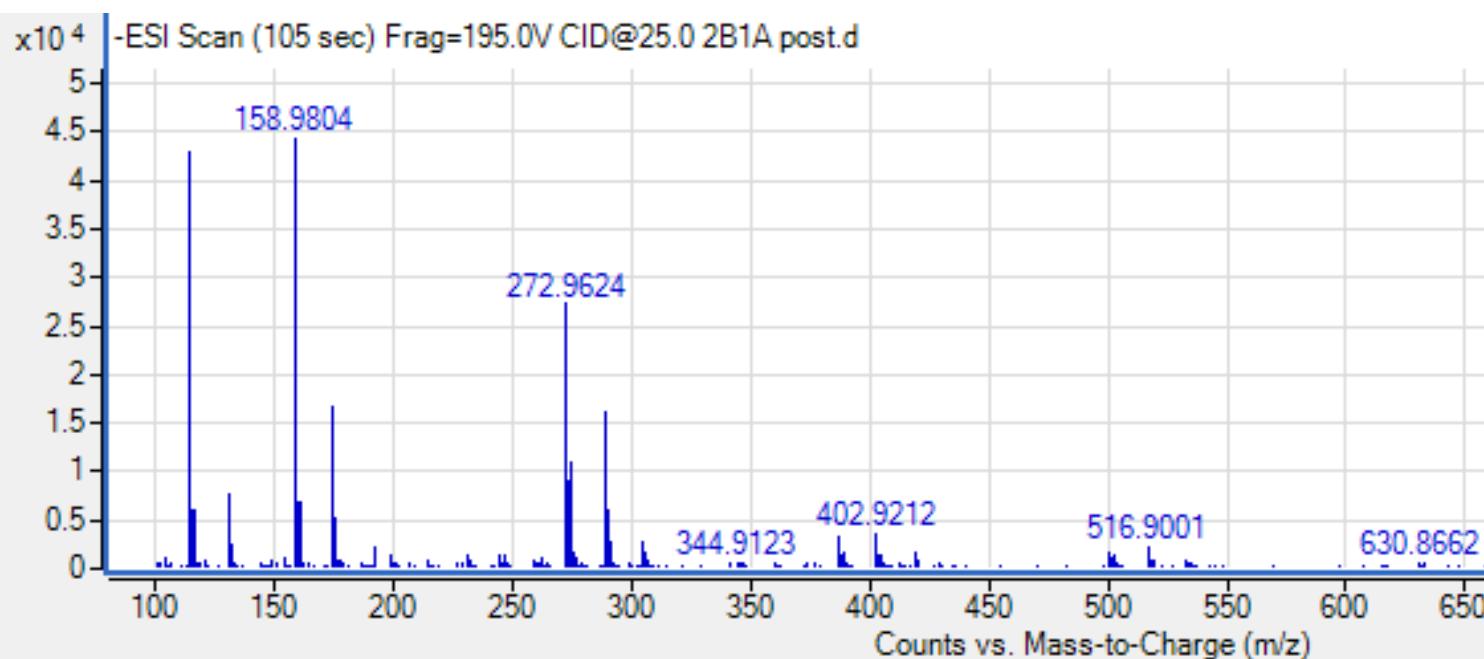
## Ellagitannin Biosynthesis from PGG from Haslam 1998

exact mass calculations from <http://homepages.warwick.ac.uk/staff/M.P.Barrow/massaccuracy.html>

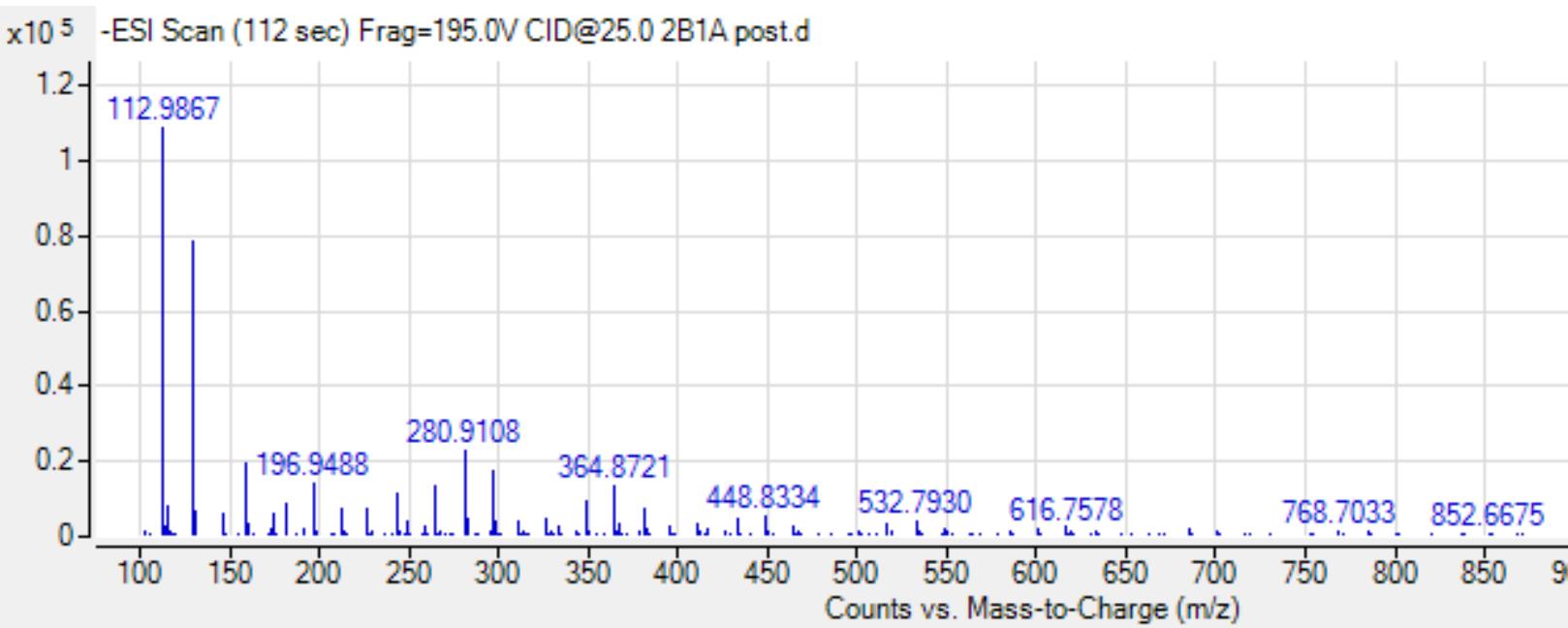


Each of these steps is catalyzed by a different enzyme. So this is not some generalized oxidation but is strictly controlled. These enzymes can have very different masses and are quite distinct.

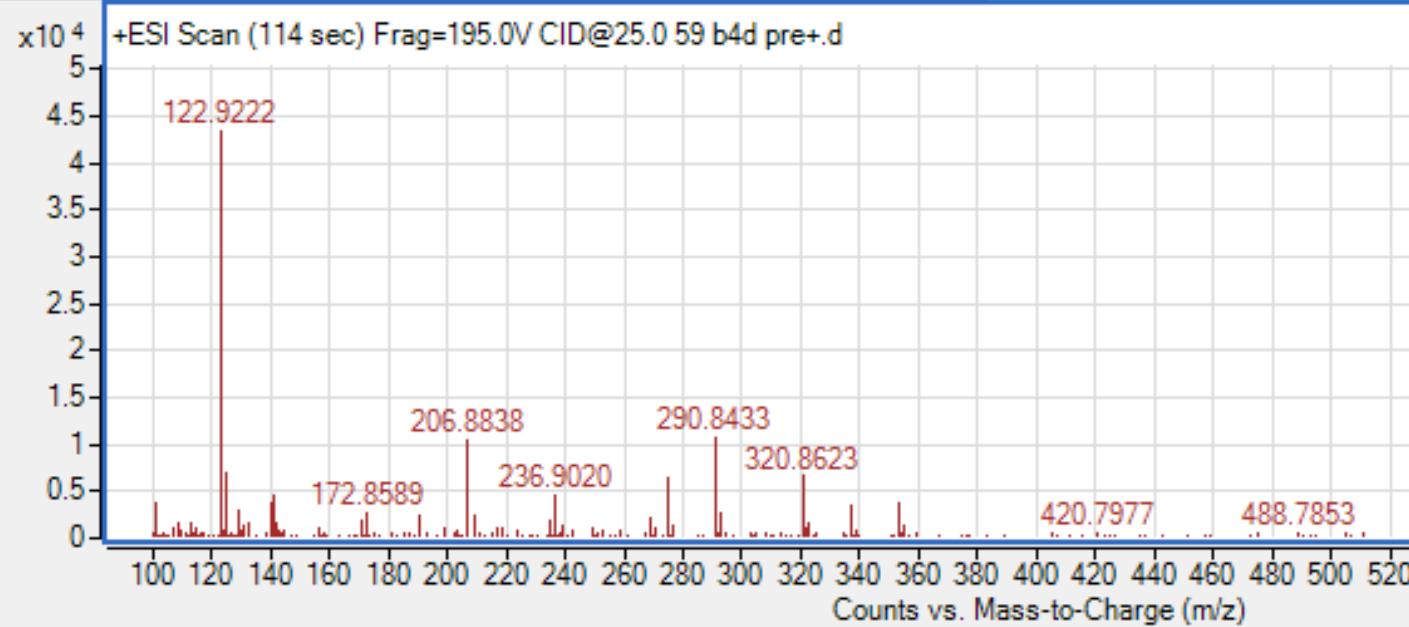
# Peak 1: 106 seconds BP 158.978 = unknown compound



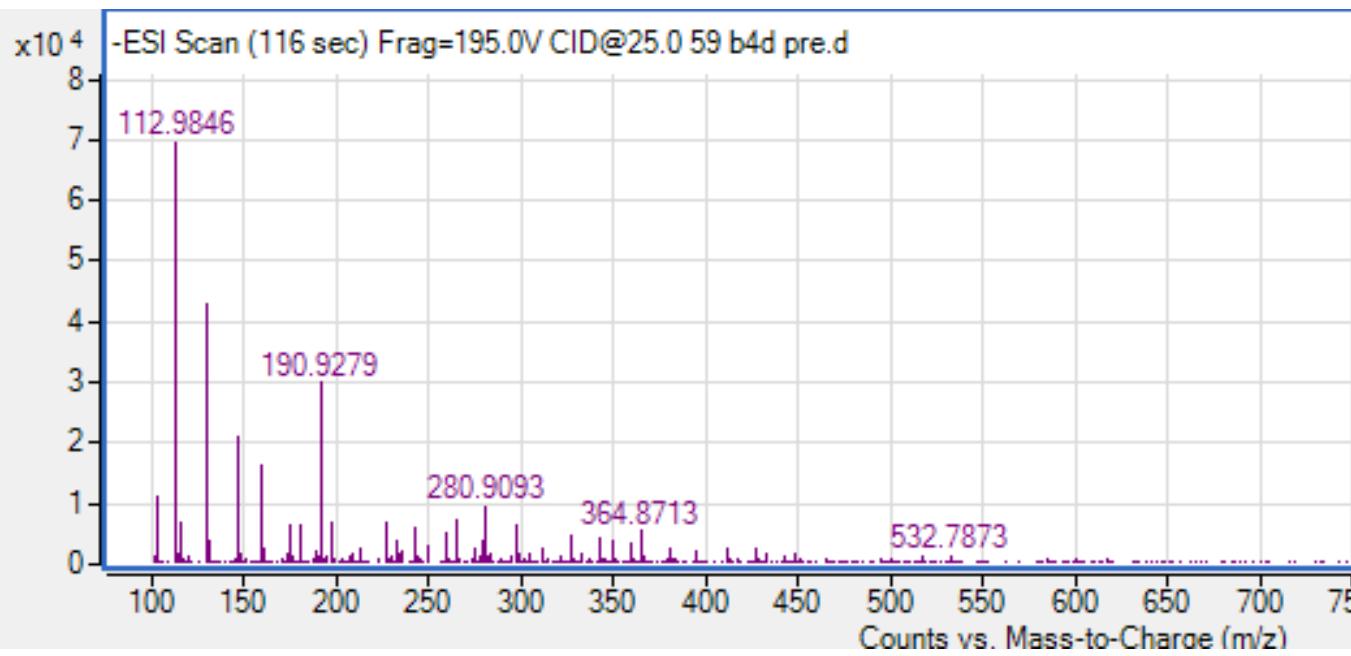
## Peak 2: 112 seconds BP 158.978 = unknown compound



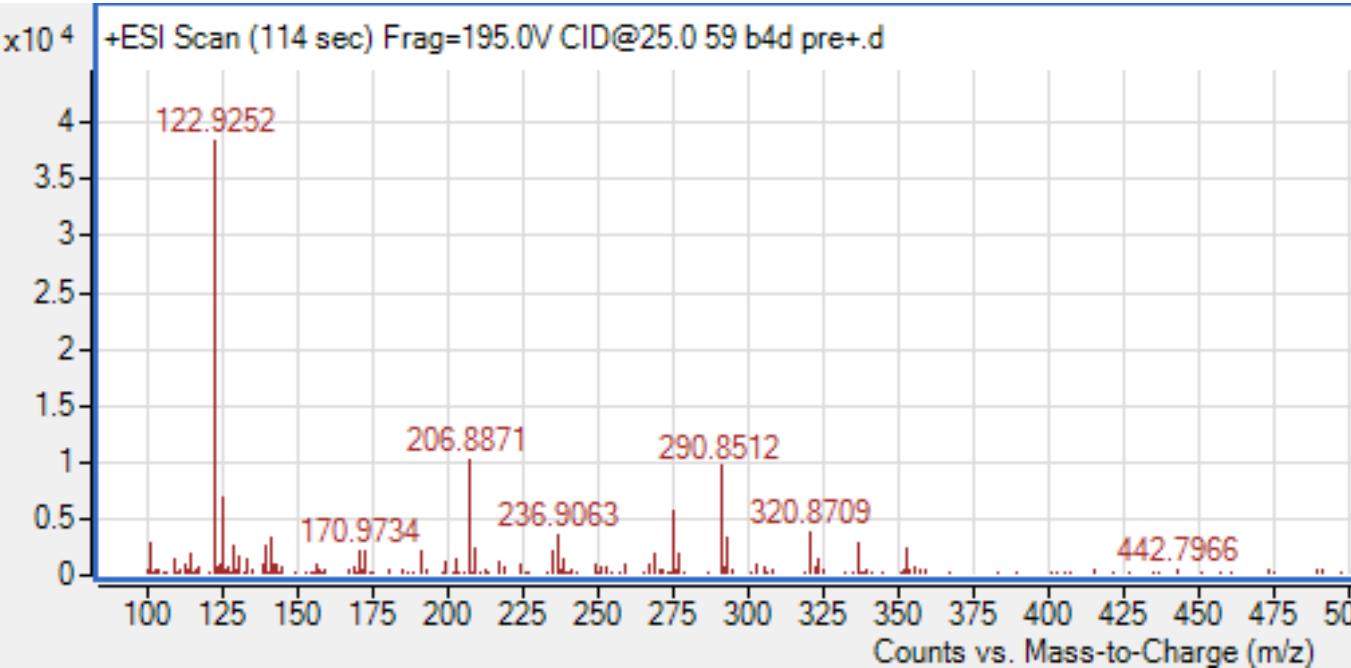
448.83  
364.87  
280.91  
196.949  
112.985  
43.437  
86.208  
14.440  
2  
112 sec  
158.978



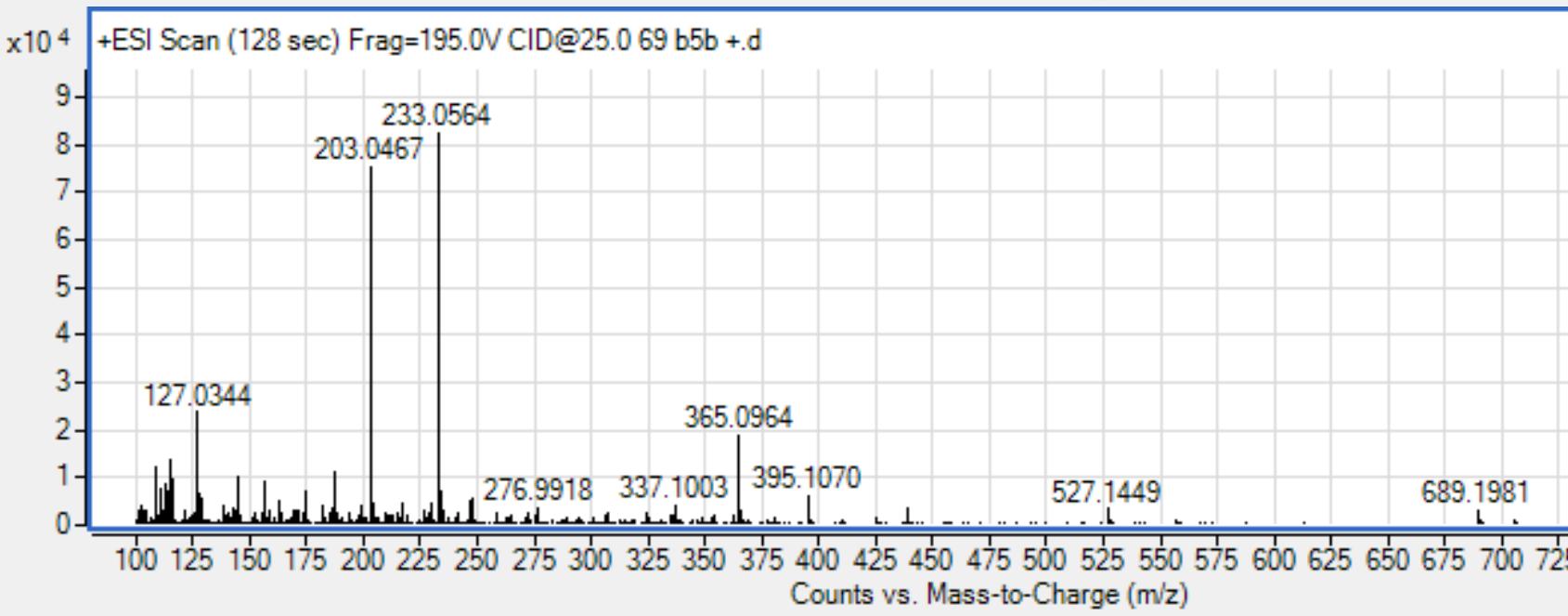
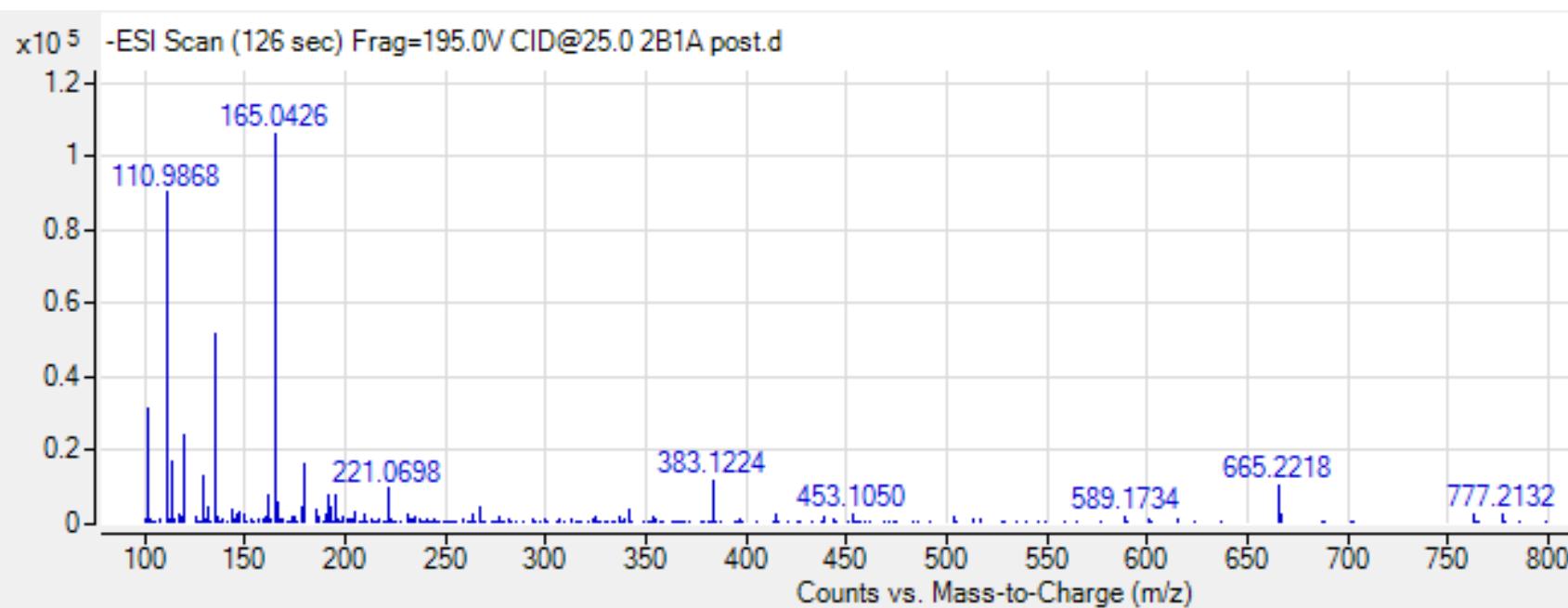
# Peak 3: 116 seconds BP 112.985 = chlorogenic acid derivatives



364.87  
280.91  
196.9279  
112.9846  
64,393  
132,142  
22,531  
3  
116 sec  
112.9848

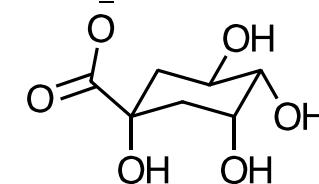
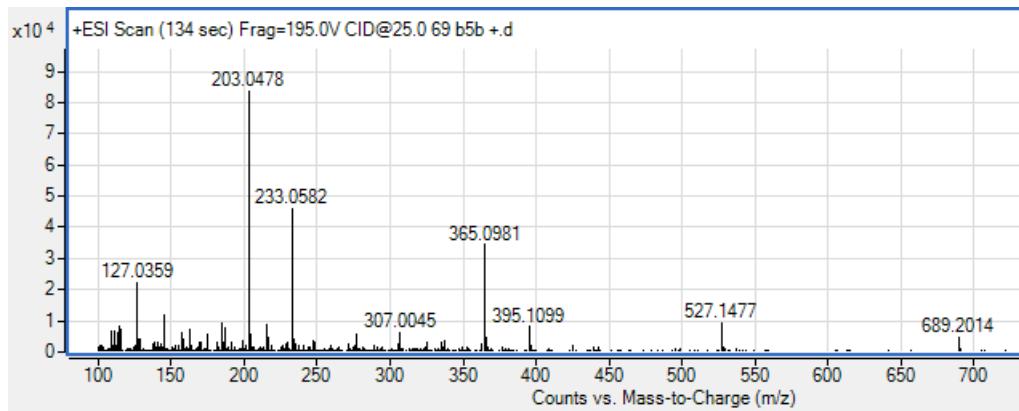
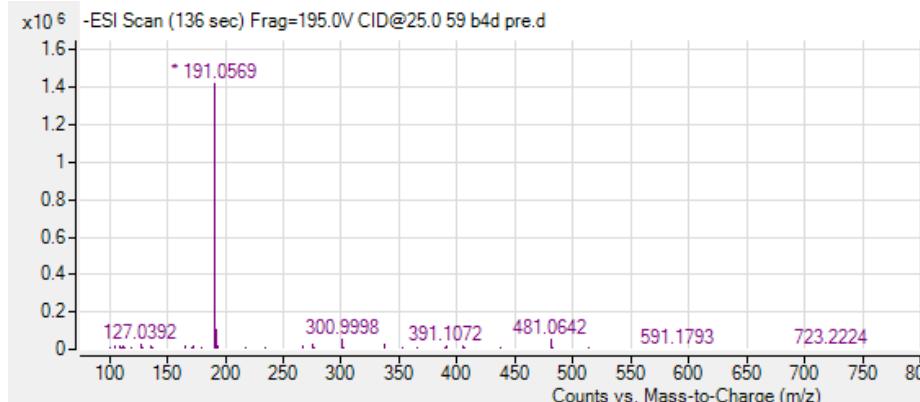


# Peak 4: 127 seconds BP 165.042 = unknown compound



665.2218  
453.105  
383.1224  
221.0698  
165.0426  
110.0426  
56,070  
129,458  
25,204  
4  
127 sec  
165.0417

# Peak 5: 136 seconds BP 191.0576 = Quinic acid



Monoisotopic Mass = 191.056 u

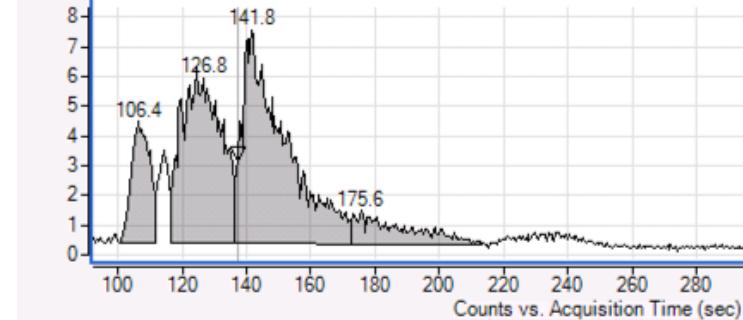
+4.19 ppm

723.2224  
591.1793  
481.0642  
300.9998  
191.0569  
771.777  
1,513,182  
345,318  
5  
136 sec  
191.0576

$\times 10^5$  -ESI BPC Scan Frag=195.0V CID@25.0 #29 B2d post.d



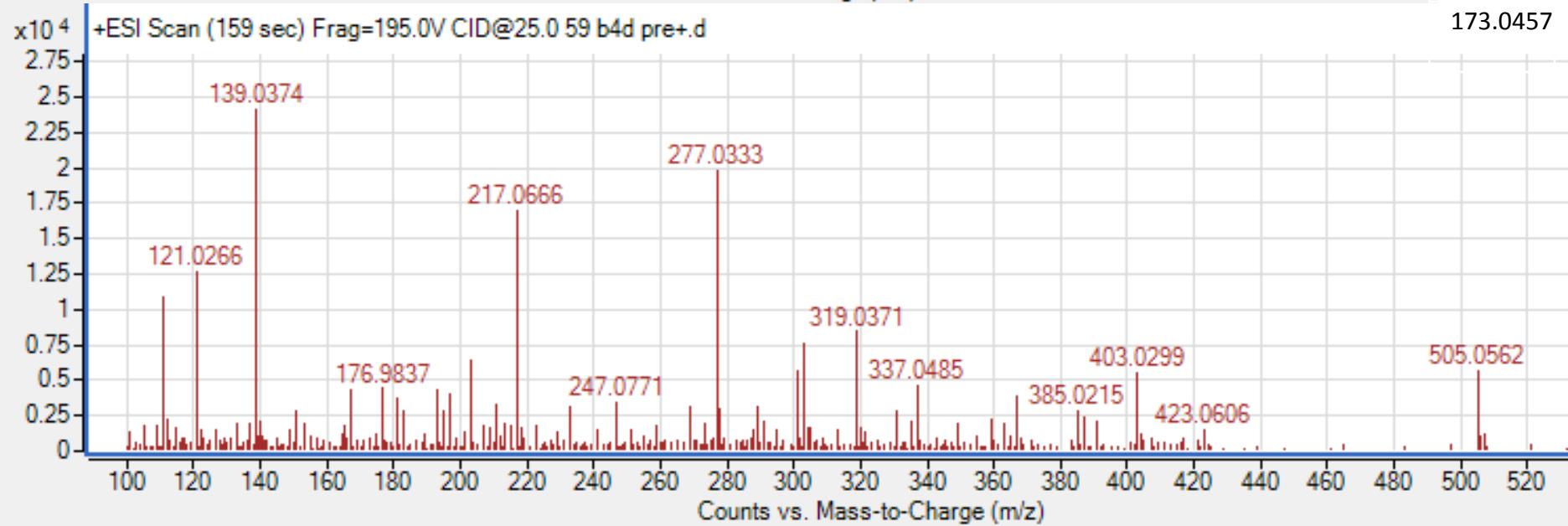
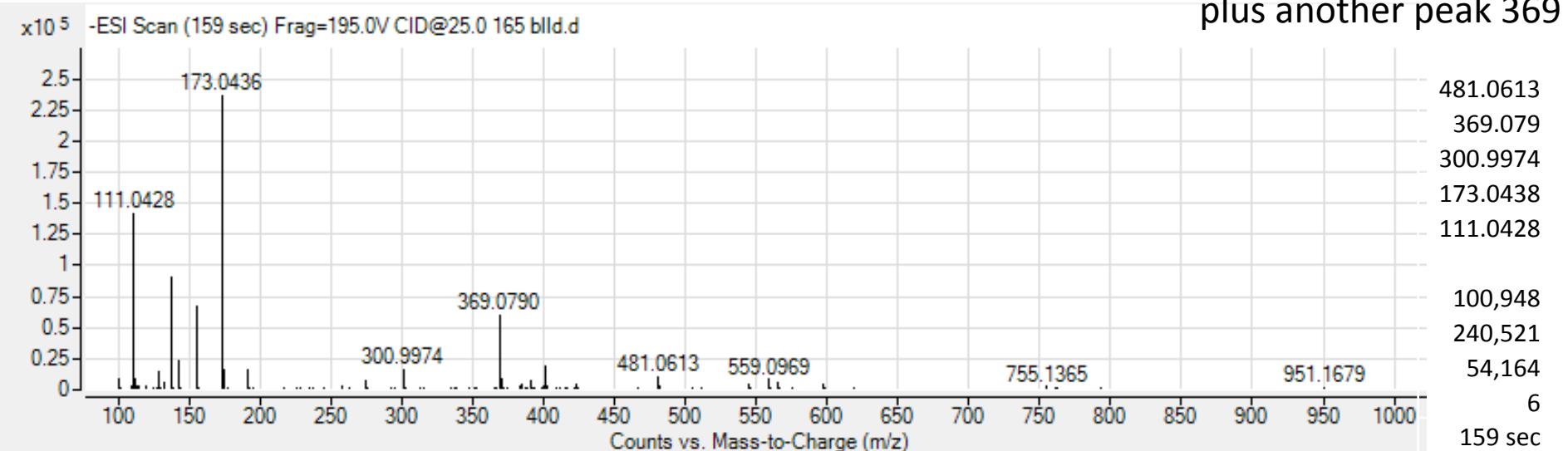
$\times 10^4$  +ESI BPC Scan Frag=195.0V CID@25.0 #29 B2d post+.d



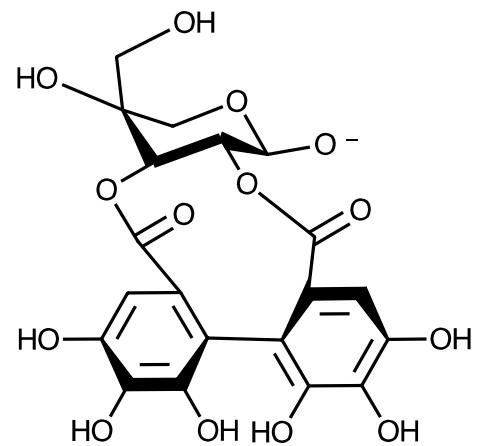
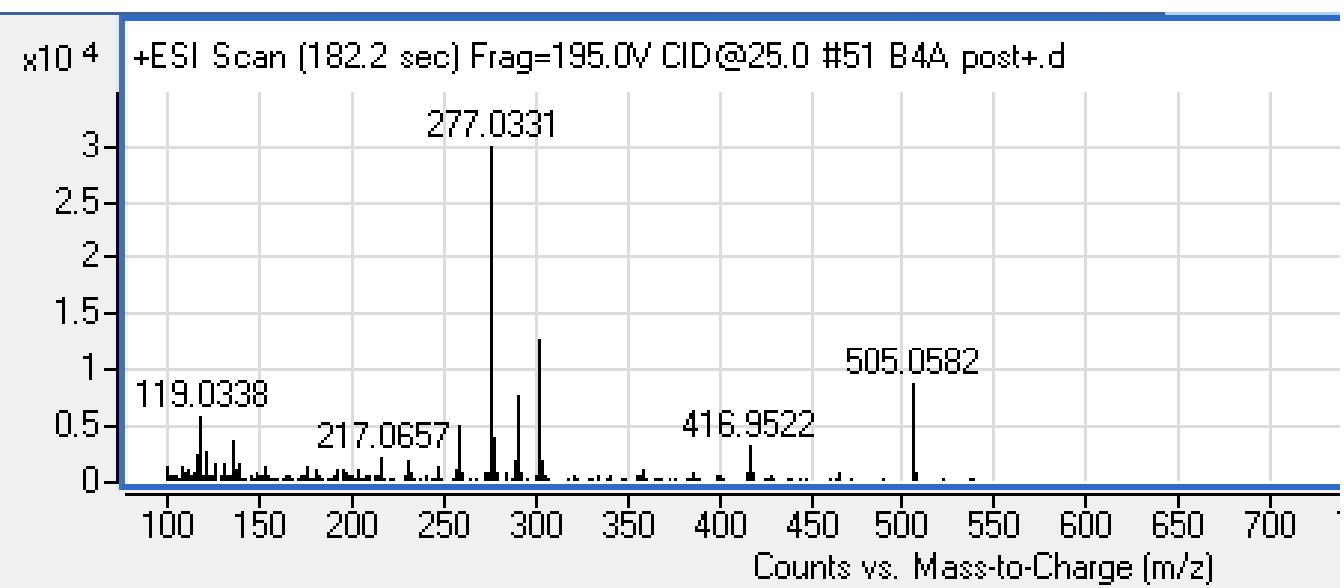
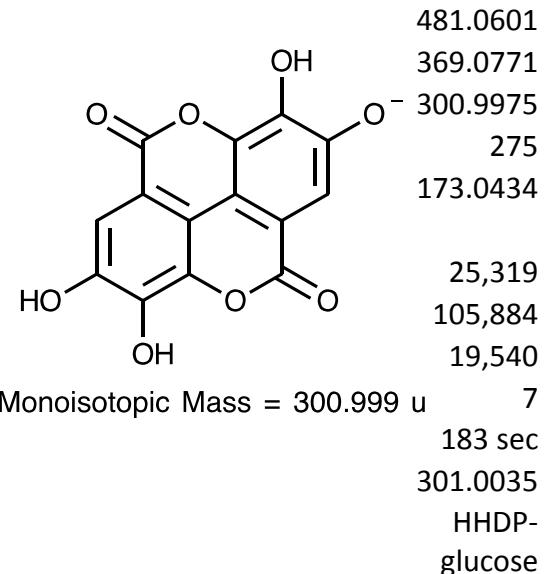
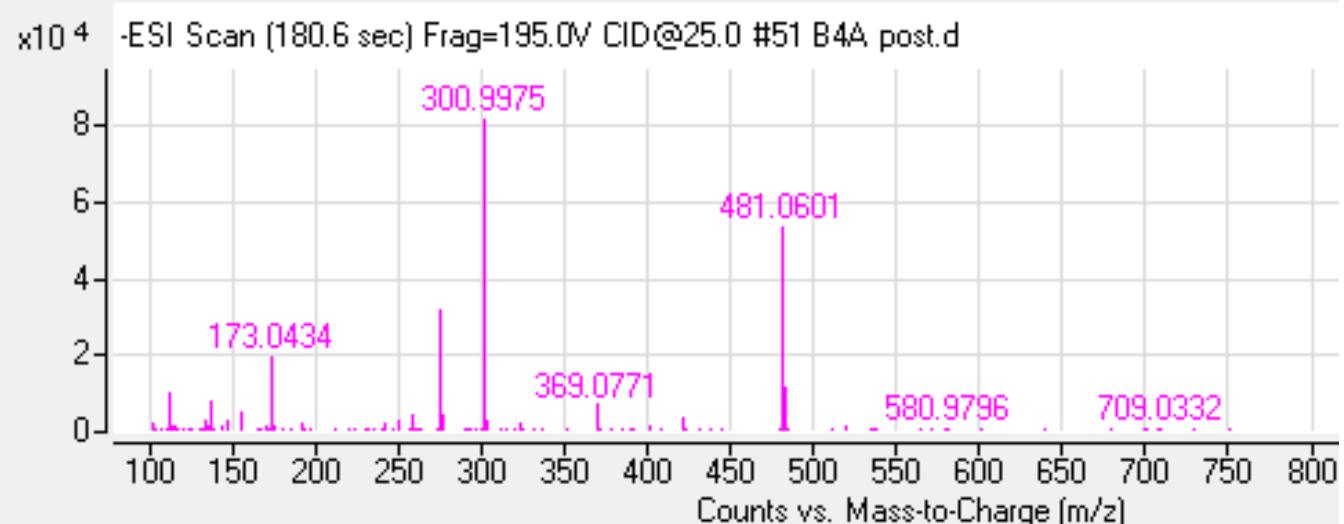
Possibly quinic acid that does not ionize in + mode.

# Peak 6: 159 seconds BP 173.046 = HHDP-glucose

HHDP-glucose?  
plus another peak 369

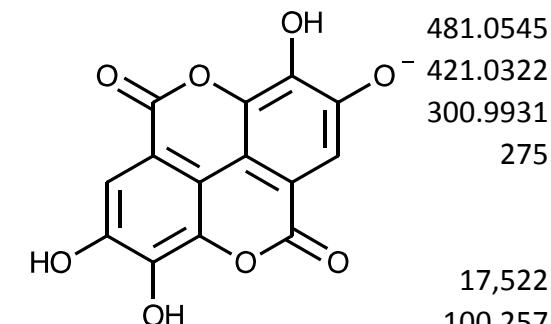
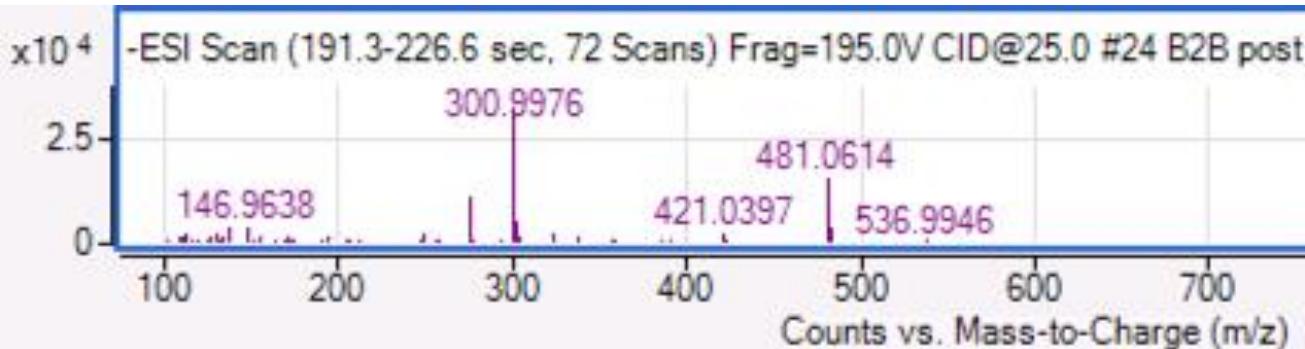


# Peak 7: 183 seconds BP 301.004 = HHDP-glucose



HHDP-glucose  
Monoisotopic mass = 481.0623  
ppm -4.57  
other forms possible

# Peak 8: 202 seconds BP 300.997 = HHDP-glucose



Monoisotopic Mass = 300.999 u 17,068

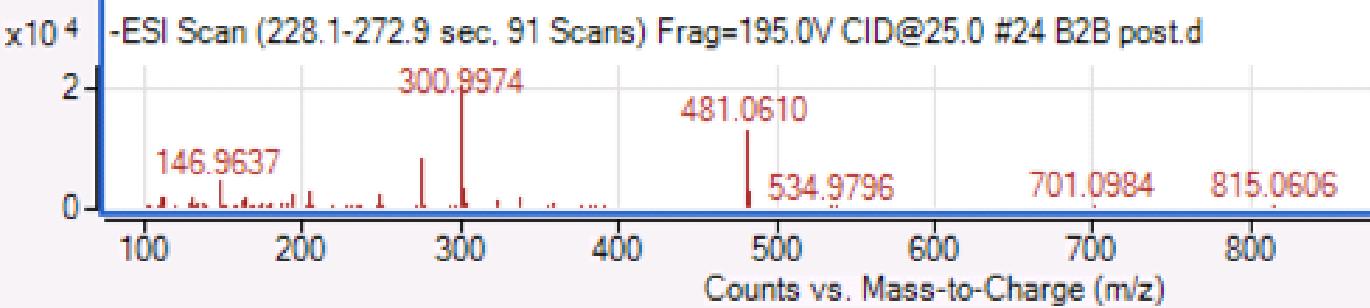
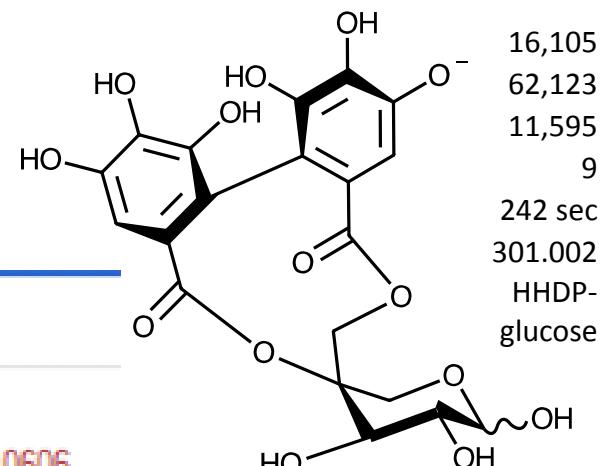
8  
202 sec

300.9967  
HHDP-

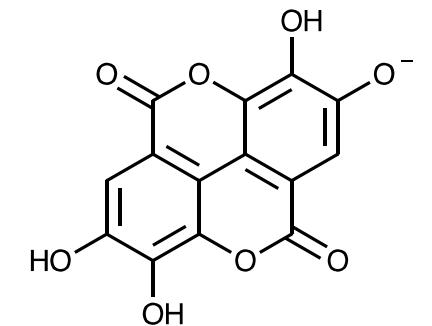
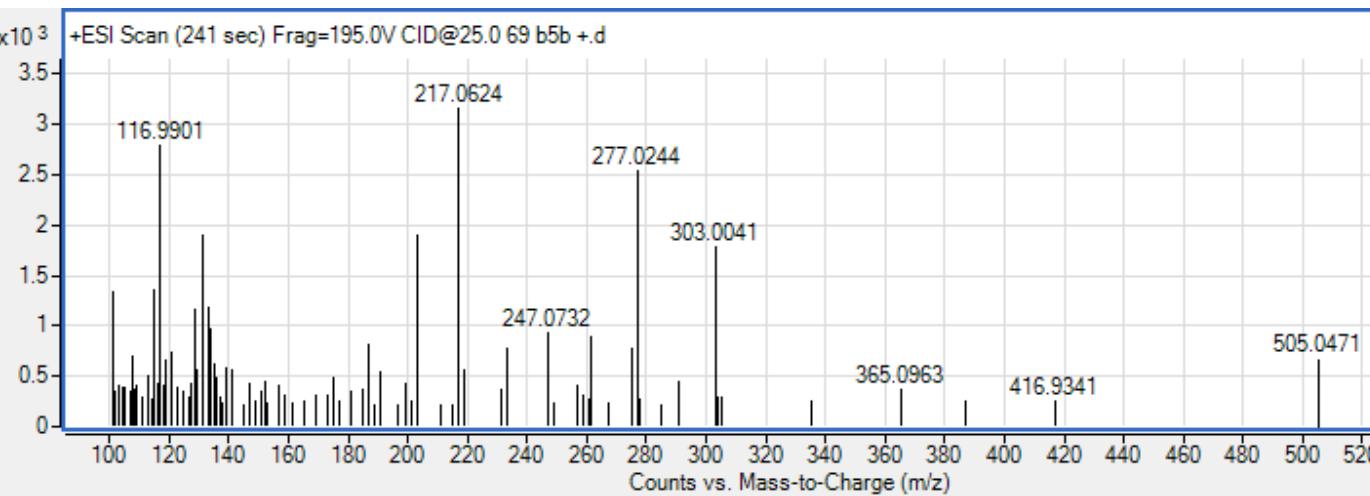
glucose

# Peak 9: 242 seconds BP 301.002 = HHDP-glucose

481.061  
390.967  
300.997  
275.018

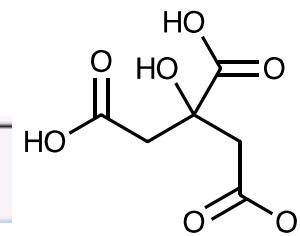
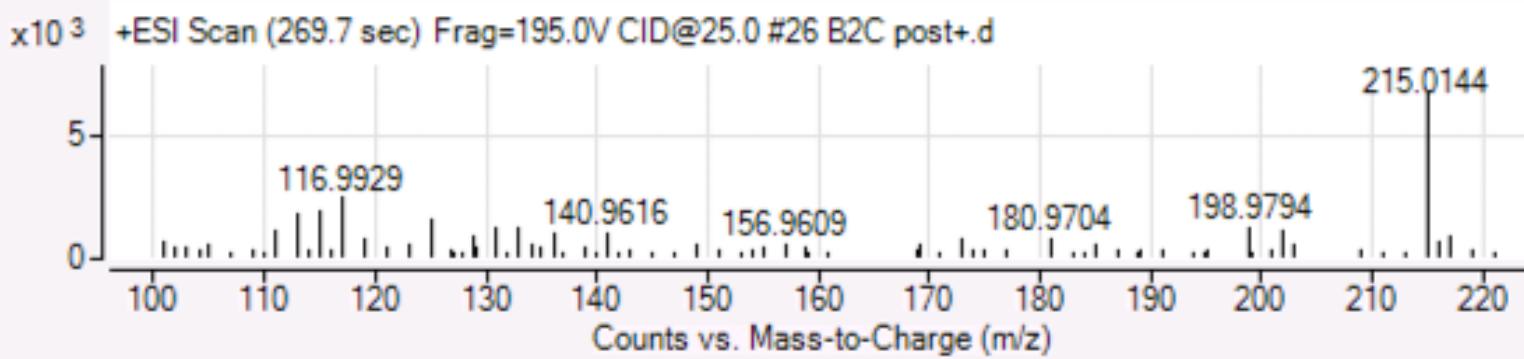
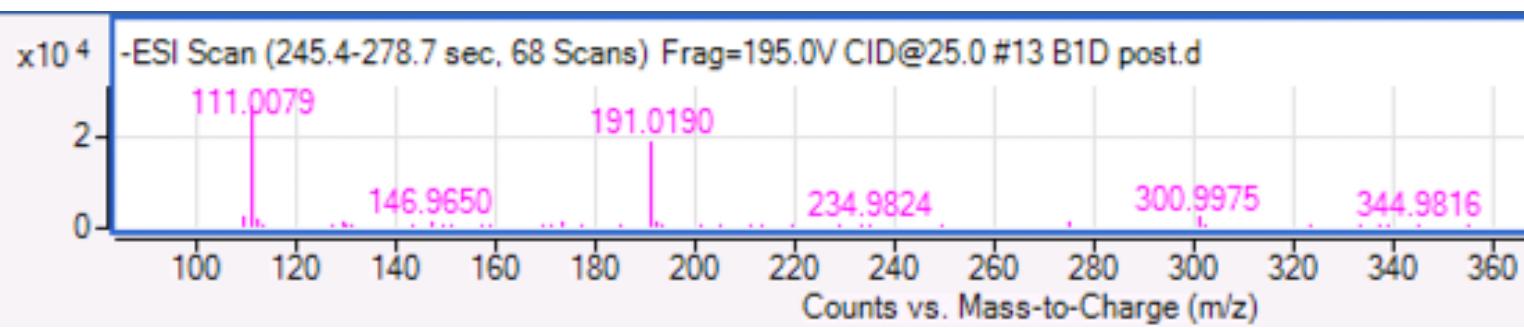


HHDP-glucose  
Monoisotopic mass = 481.0623  
ppm -2.70  
Similar to this



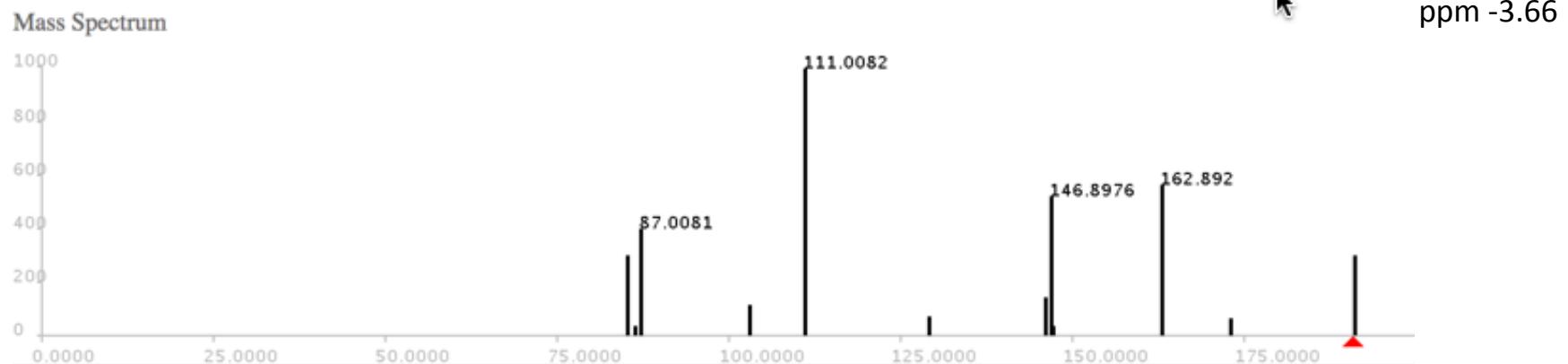
Monoisotopic Mass = 300.999 u

# Peak 10: 270 seconds BP 111.009 = Citric acid

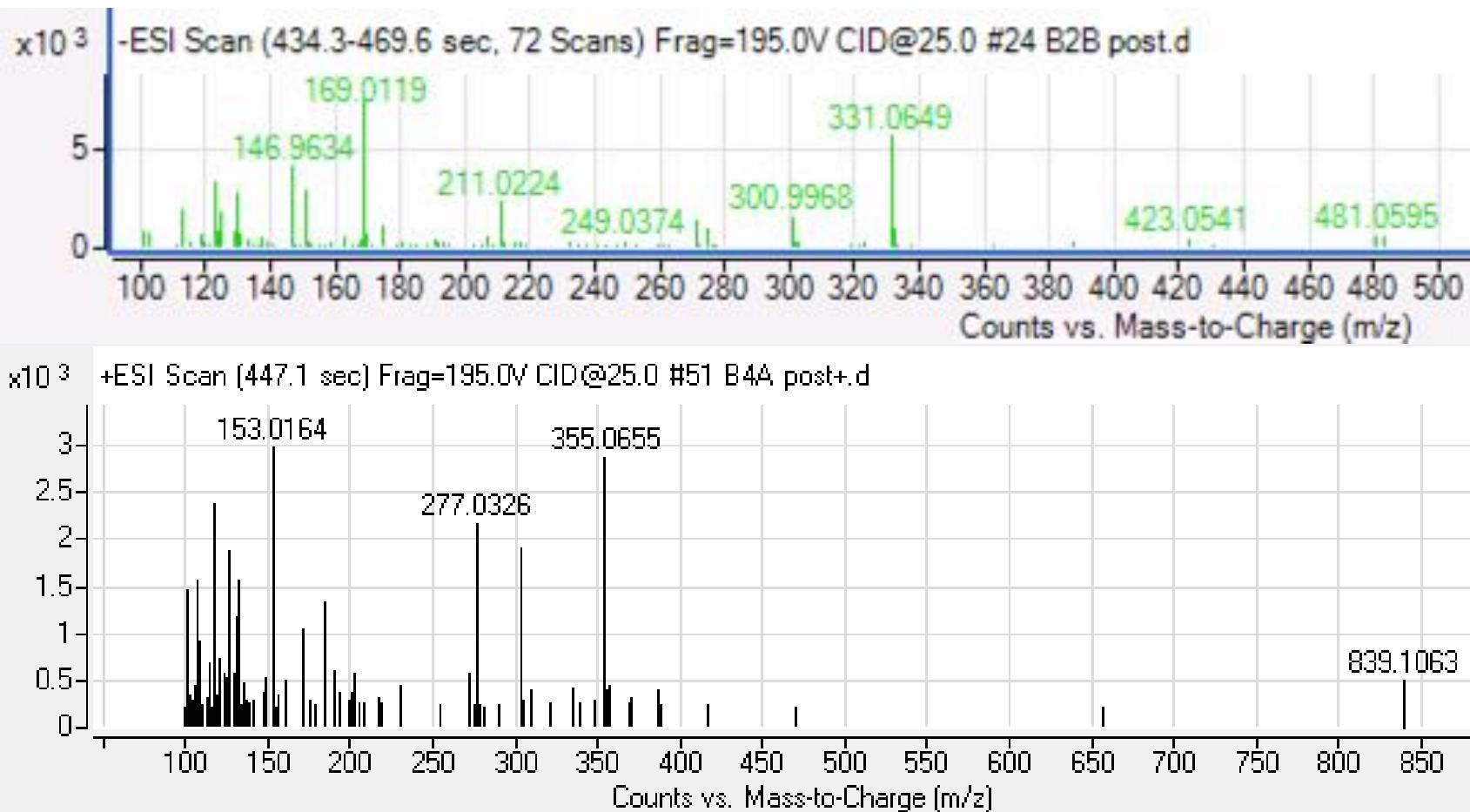


Citric acid; LC-ESI-QTOF; MS2; CE:Ramp 5-60 V; [M-H]-

Monoisotopic Mass = 191.020 u

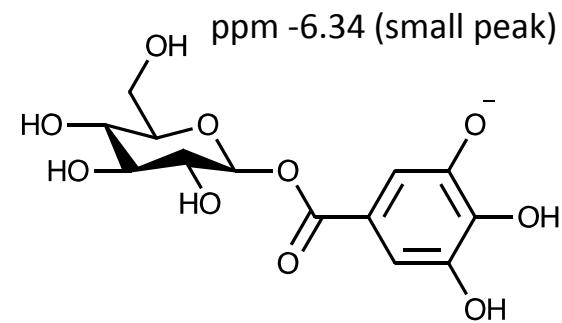


# Peak 11: 450 seconds BP 169.013 = galloyl glucose

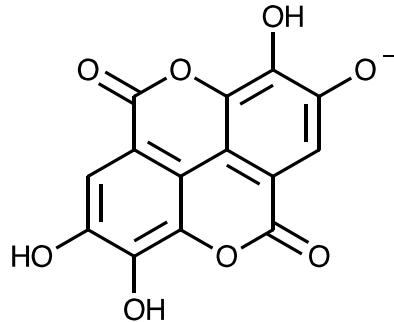
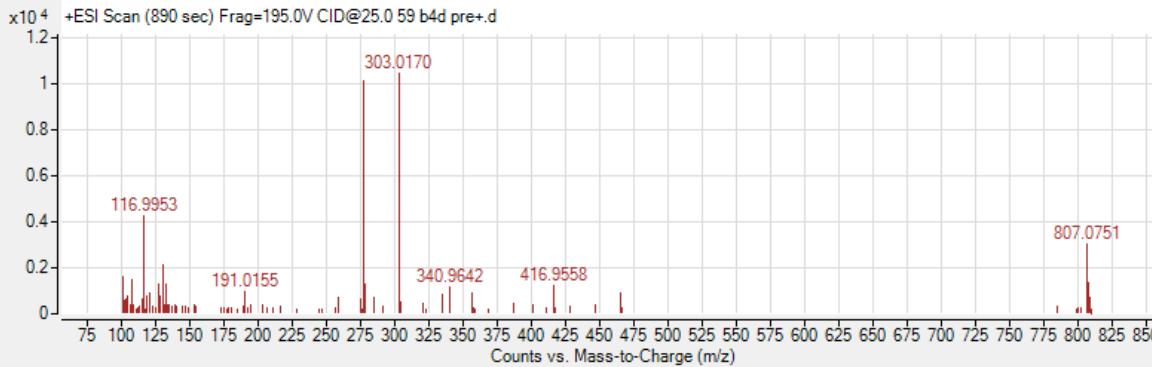
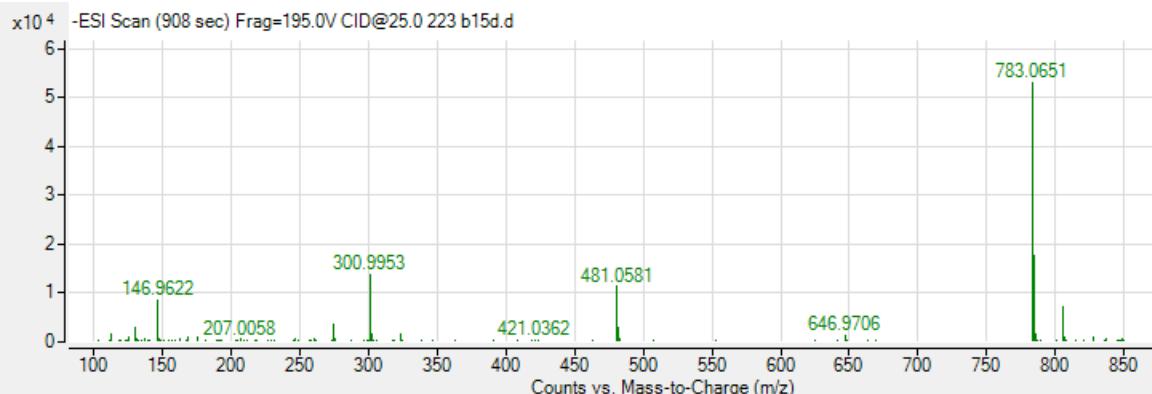


815/839 is something else  
633/657  
481

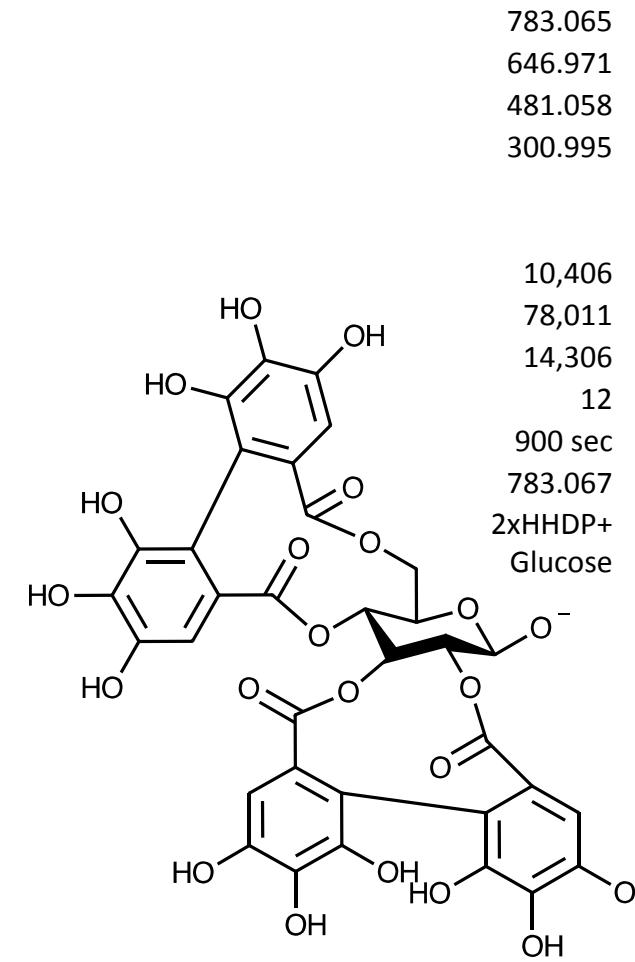
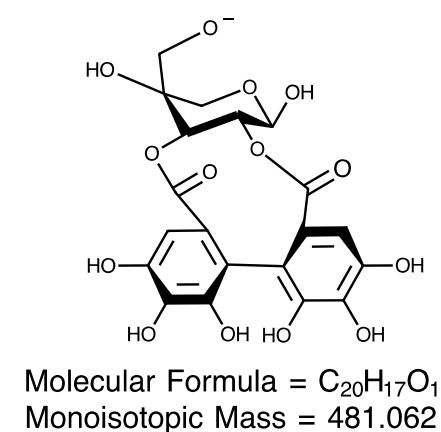
Molecular Formula =  $C_{13}H_{15}O_{10}^-$   
Monoisotopic Mass = 331.067 u  
galloyl-glucose



# Peak 12: 900 seconds BP 783.067 = 2xHHDP glucose (Pedunculain $\beta$ )

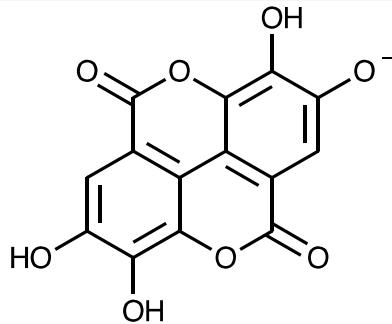
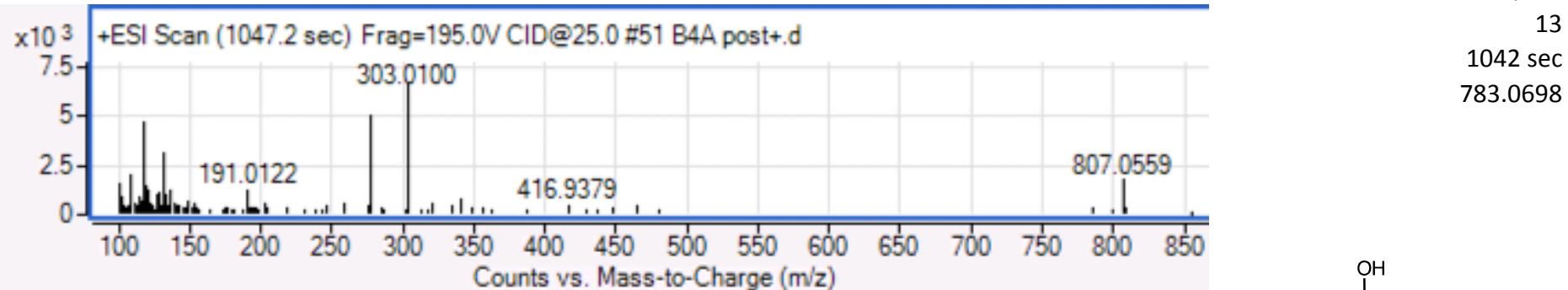
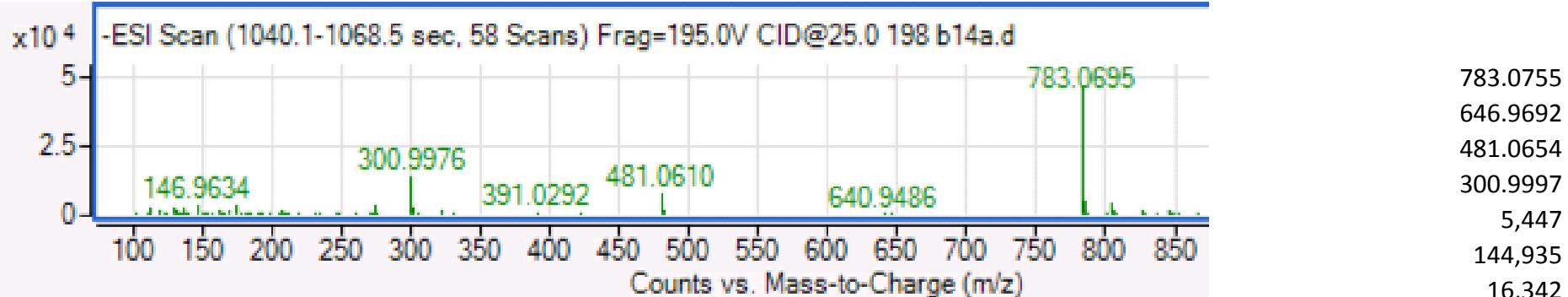


Molecular Formula =  $C_{14}H_{15}O_8^-$   
 Monoisotopic Mass = 300.999 u  
 ellagic acid



Molecular Formula =  $C_{34}H_{23}O_{22}^-$   
 Monoisotopic Mass = 783.069 u  
**Pedunculagin  $\beta$**   
 (no galloyl at 169)  
 ppm -4.47 (small peak)

# Peak 13: 1042 seconds BP 783.07 = 2xHHDP-glucose (Pedunculagin $\alpha$ )

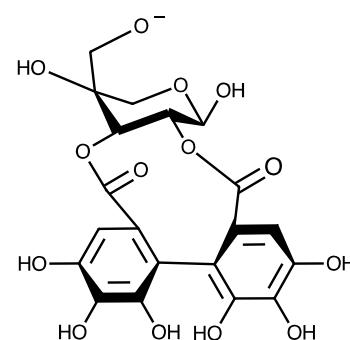


Monoisotopic Mass = 300.999 u

Molecular Formula =  $C_{14}H_5O_8^-$

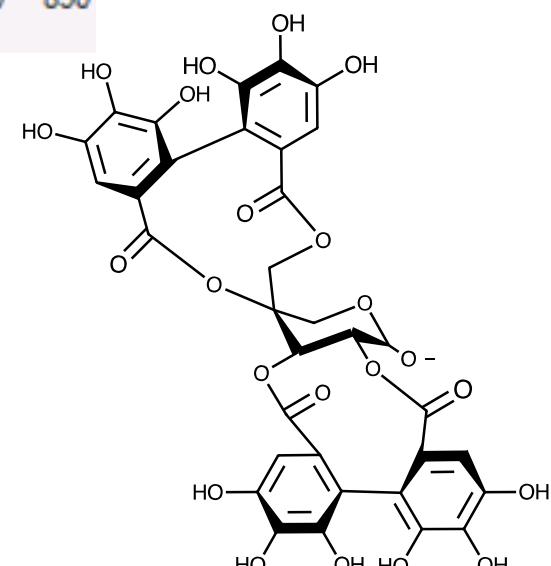
Monoisotopic Mass = 300.999 u

ellagic acid



Molecular Formula =  $C_{20}H_{17}O_{14}^-$

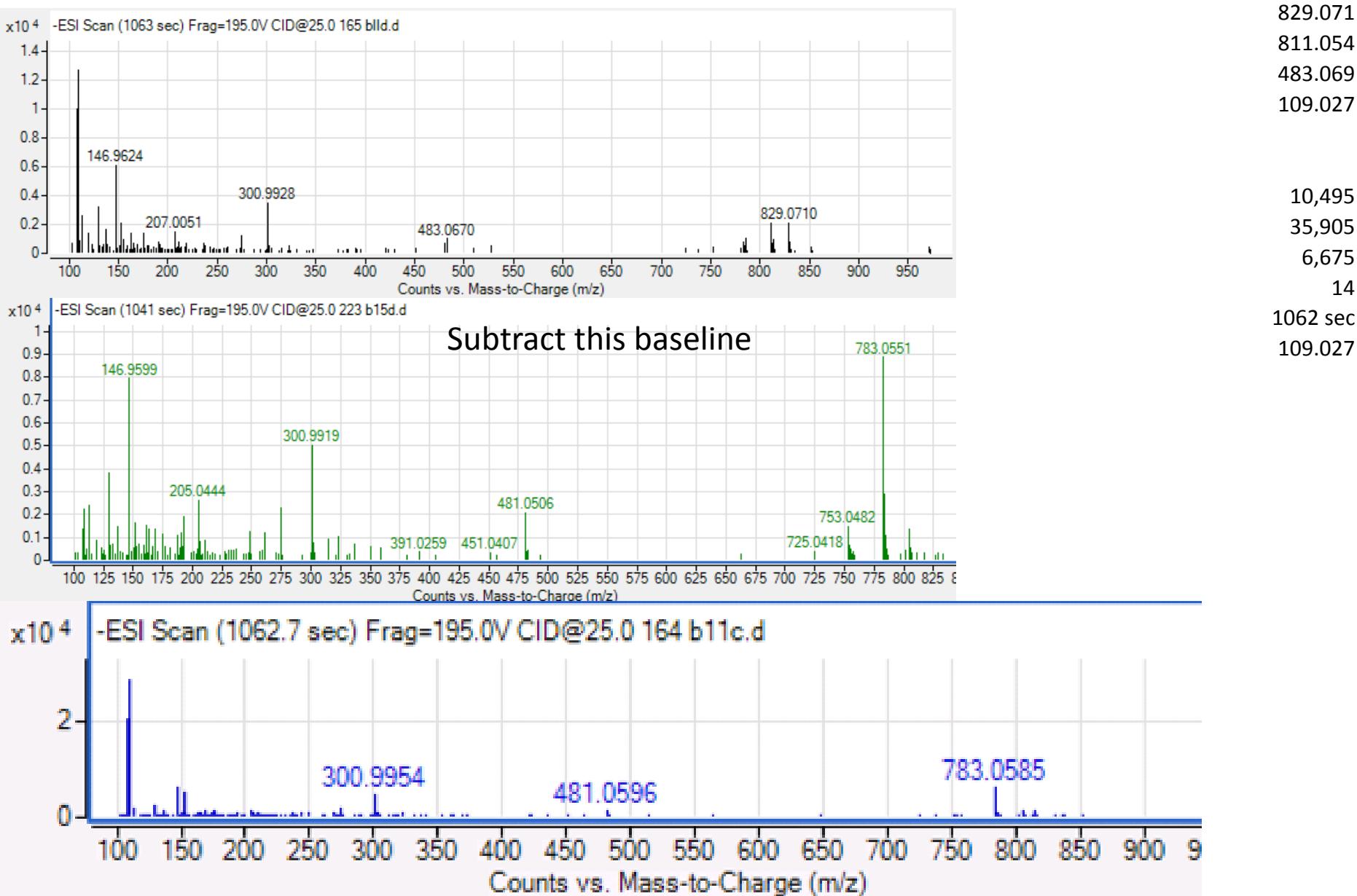
Monoisotopic Mass = 481.062 u



Similar to this (Pedunculagin  $\alpha$ ; other conformations possible      ppm +1.15

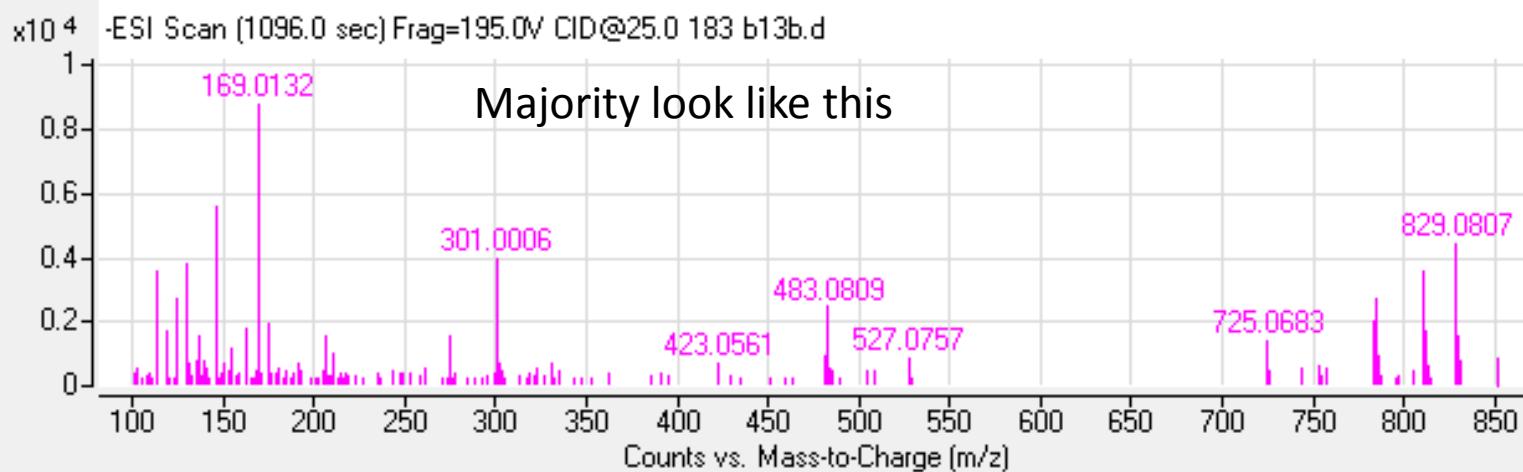
783.0755  
646.9692  
481.0654  
300.9997  
5,447  
144,935  
16,342  
13  
1042 sec  
783.0698

# Peak 14: 1062 seconds BP 109.027 = unknown ellagitannin

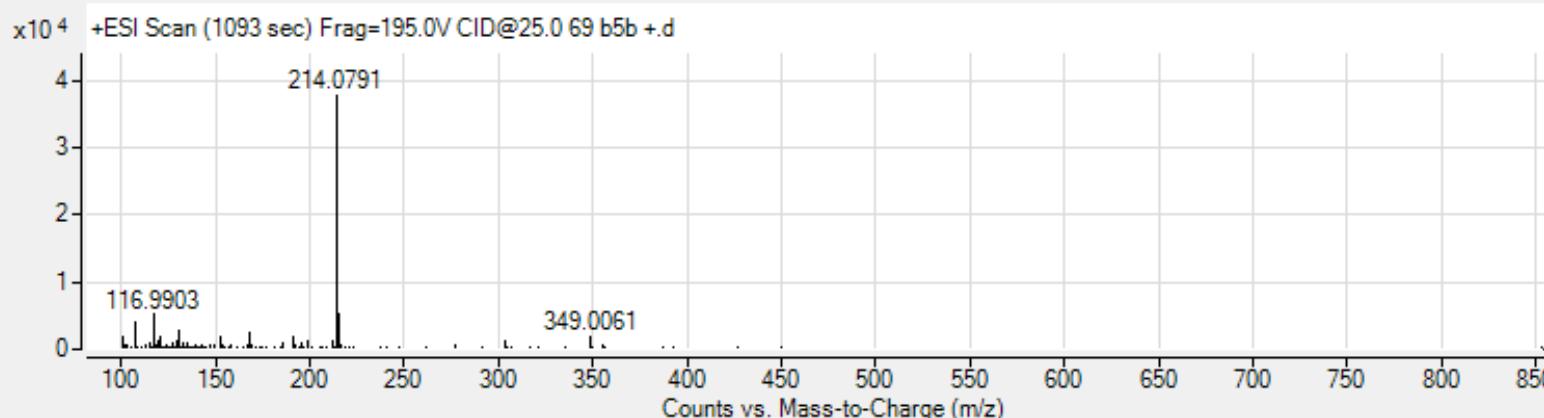


Small peak with 783/481 common along baseline; Other runs show 811/829 - 483

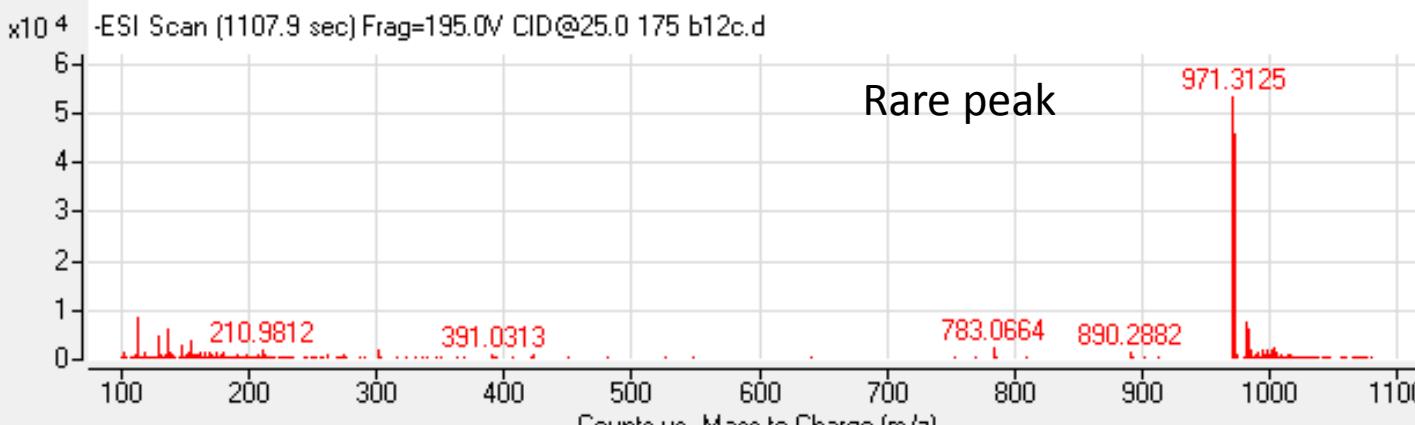
# Peak 15: 1096 seconds BP 971.316 = unknown ellagitannin



971.319

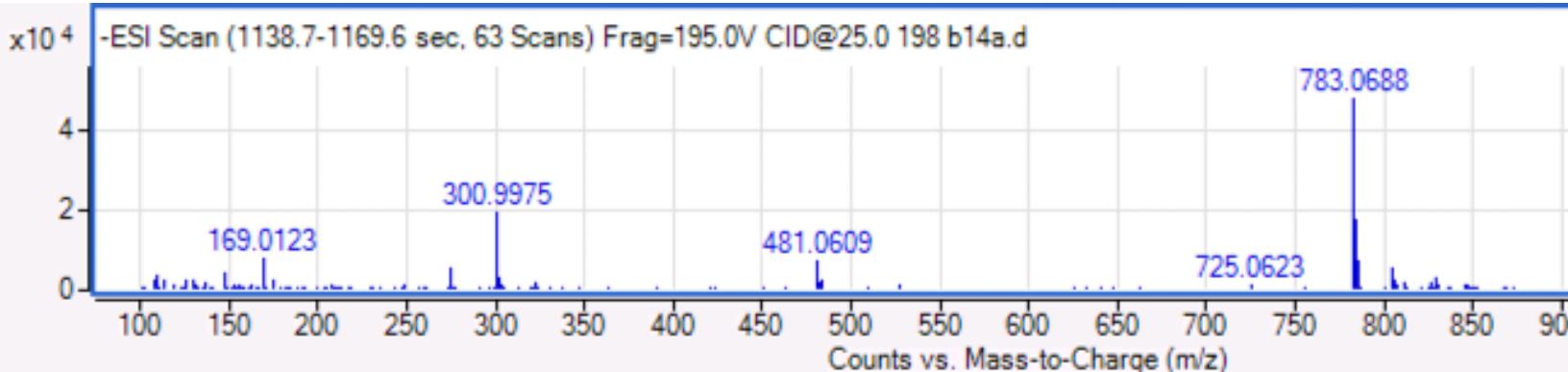


2,802  
67,610  
7,697  
15  
1096 sec  
971.316

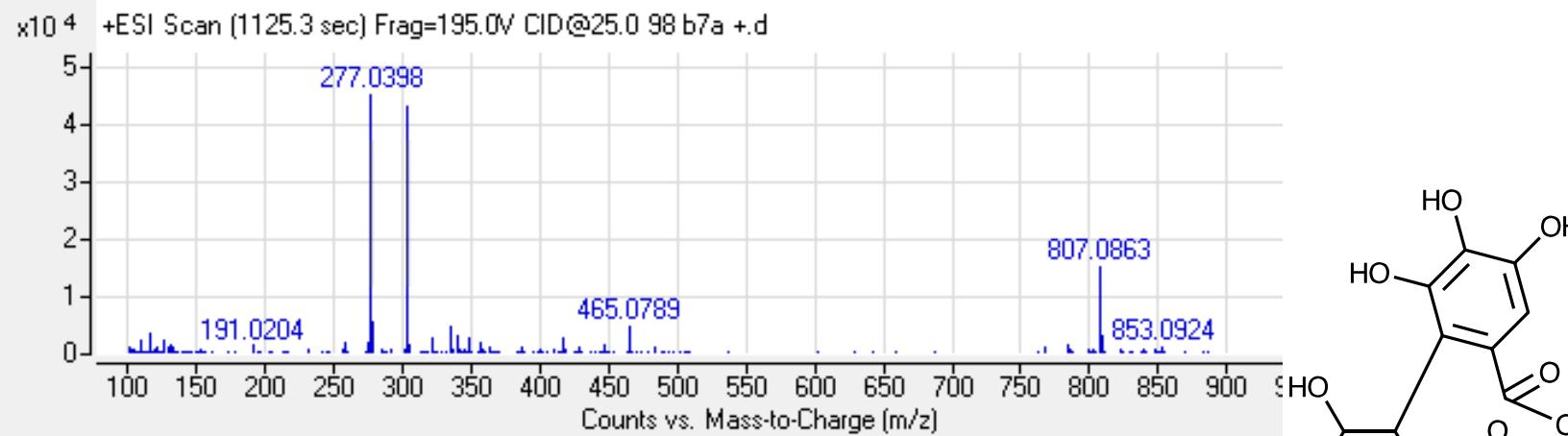


Note large galloyl 169

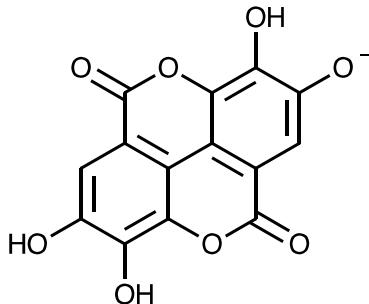
# Peak 16: 1125 seconds BP 783.057 = 2xHHDP-glucose



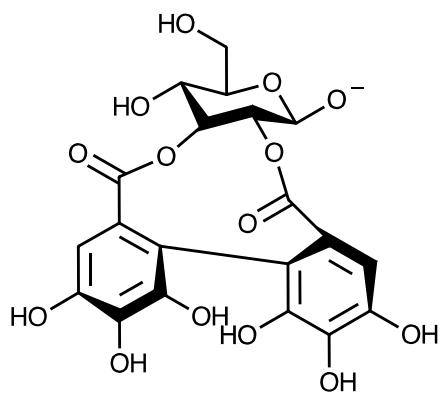
783.0859  
649.9791  
481.0714  
301.0033



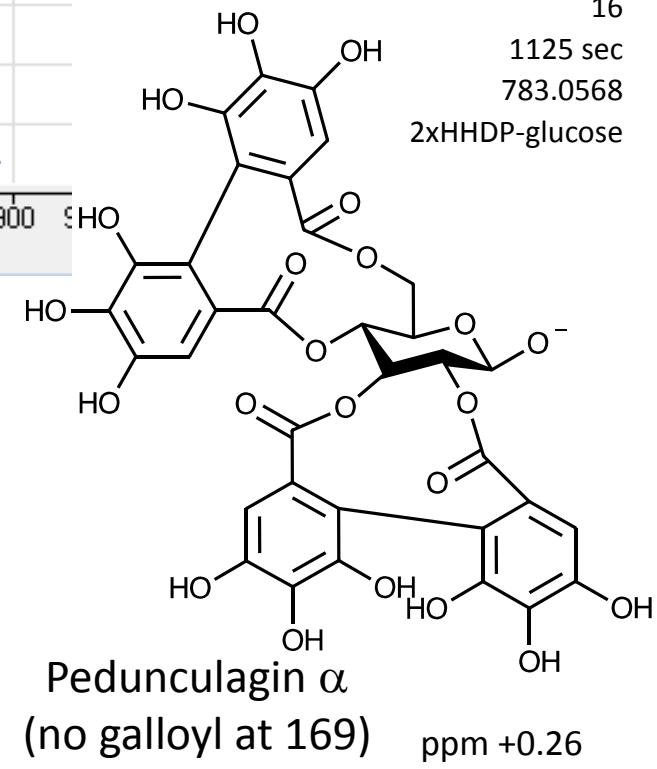
38,014  
272,341  
51,386  
16  
1125 sec  
783.0568  
2xHHDP-glucose



Monoisotopic Mass = 300.999 u

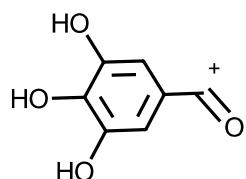
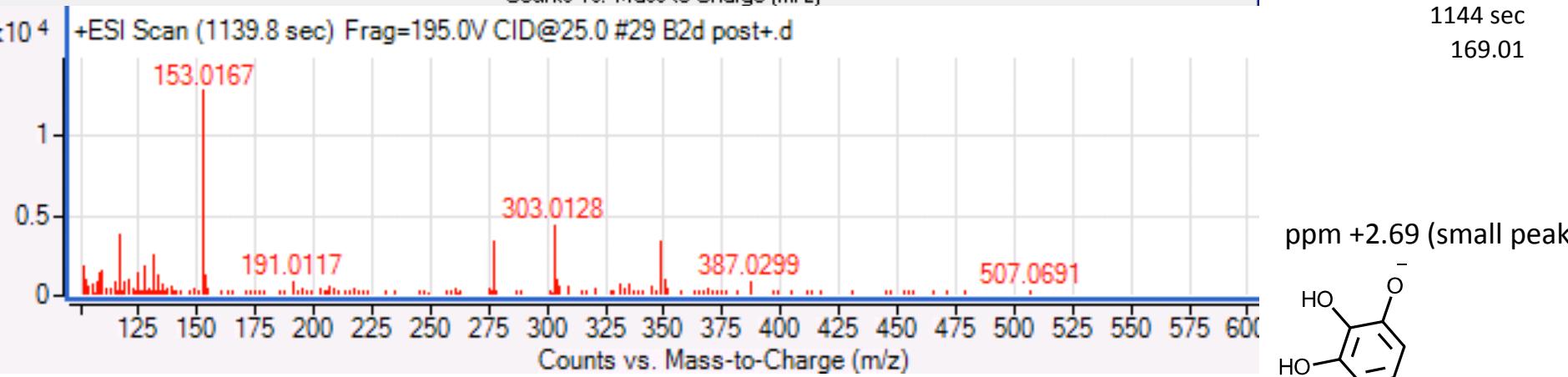
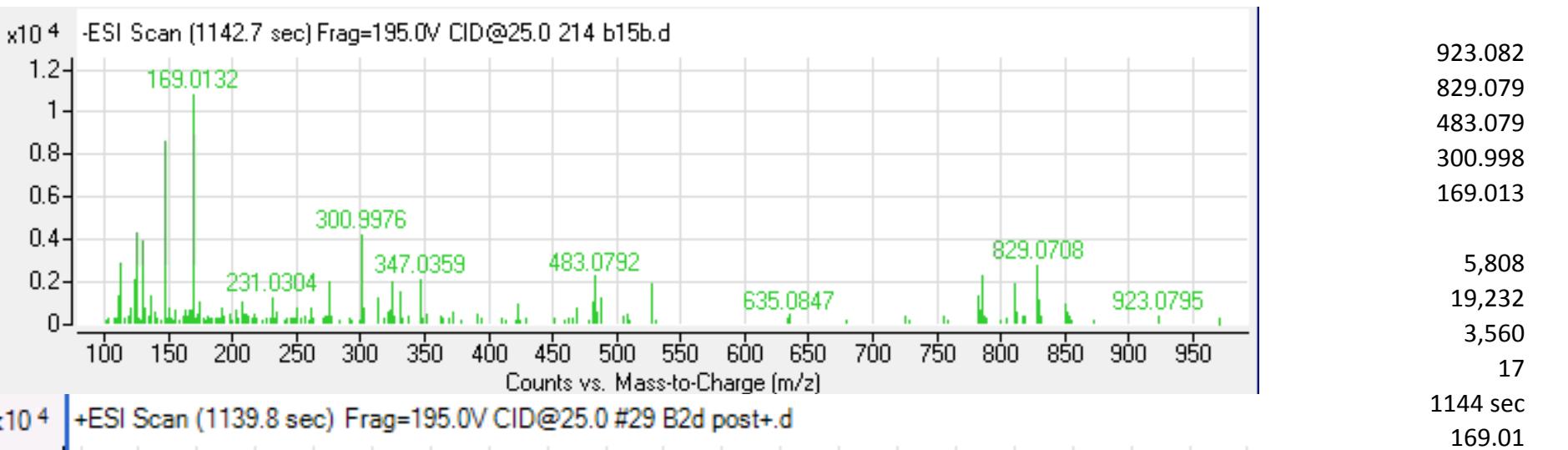


Monoisotopic Mass = 481.062 u

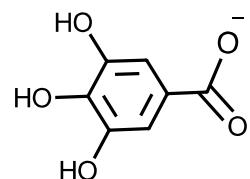


ppm +0.26

# Peak 17: 1144 seconds BP 169.01 = Digalloyl glucose

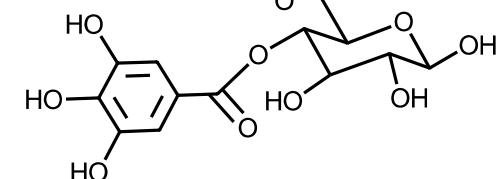
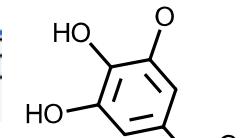


Monoisotopic Mass = 153.018 u



Monoisotopic Mass = 169.014 u

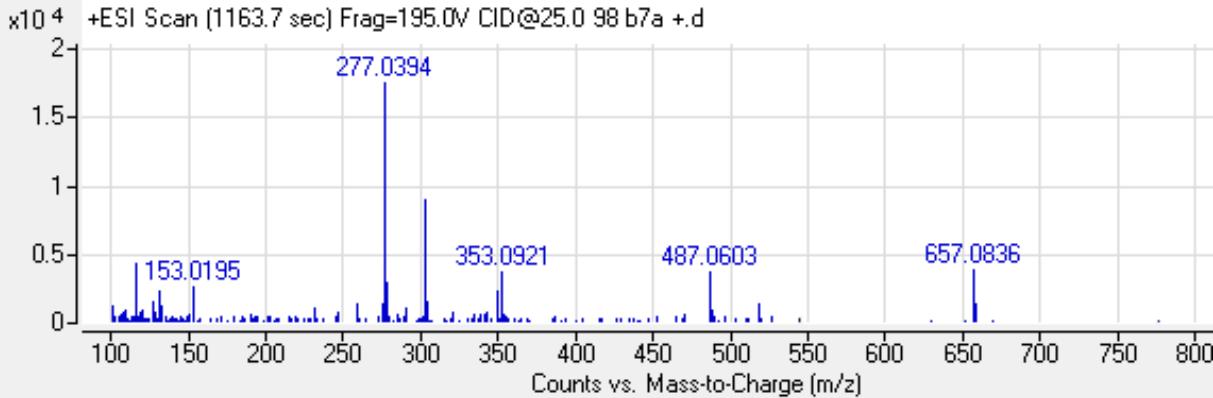
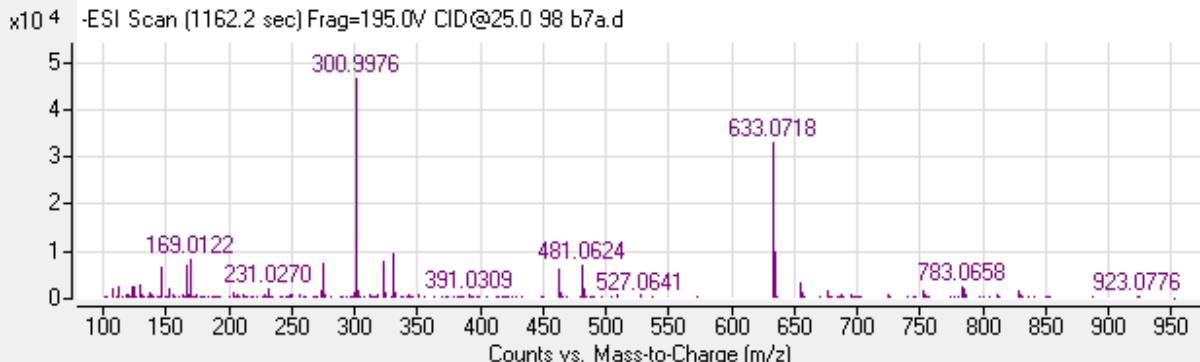
ppm +2.69 (small peak)



Monoisotopic Mass = 483.078 u

Digalloyl glucose weak support, small peak (more than one) but consistent with 483 -> 507 + strong galloyl fragment

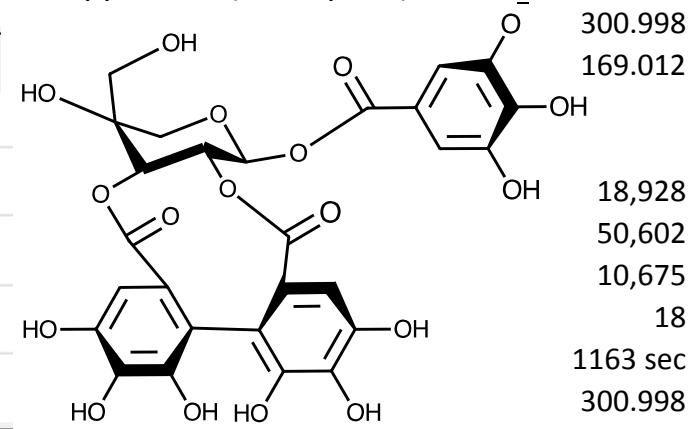
# Peak 18: 1163 seconds BP 300.998 = 1G+HHDP+glucose (Isostrictinin)



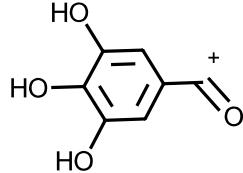
Monoisotopic Mass = 633.073 u  
Molecular Formula = C<sub>27</sub>H<sub>21</sub>O<sub>18</sub><sup>-</sup>

isostrictinin

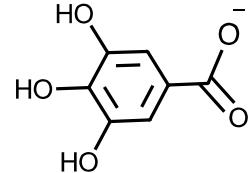
ppm -1.9 (small peak)



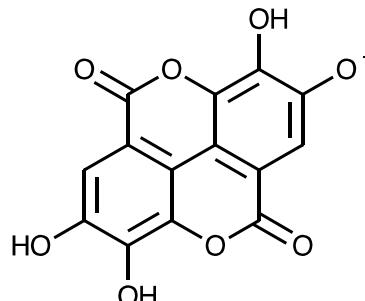
Isostrictinin here with strictinin eluting 2 minutes later (peak 23)



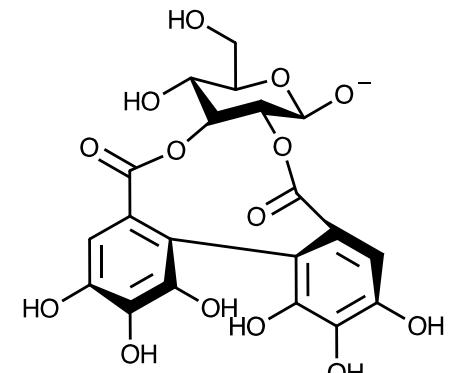
Monoisotopic Mass = 153.018 u



Monoisotopic Mass = 169.014 u

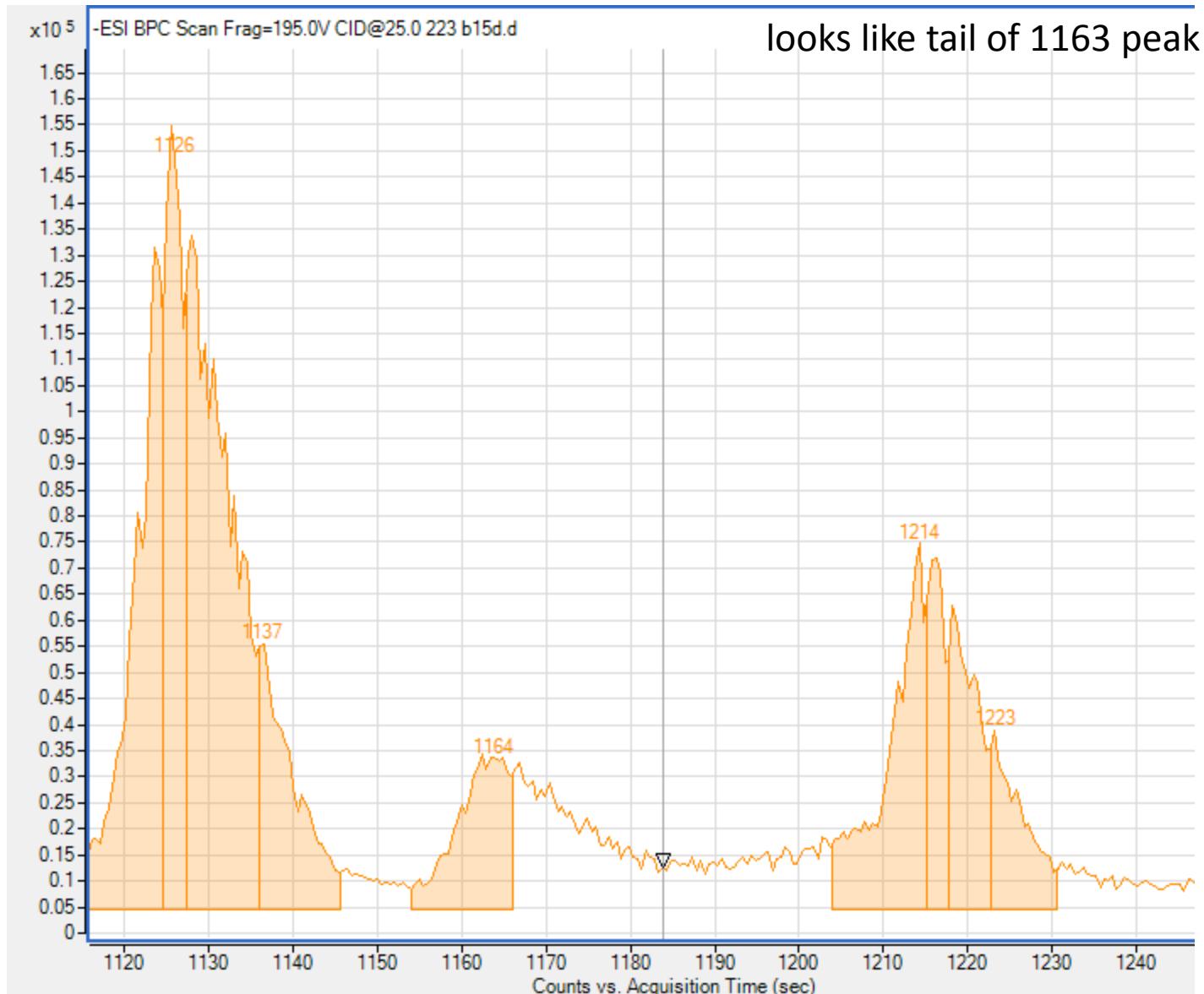


Monoisotopic Mass = 300.999 u

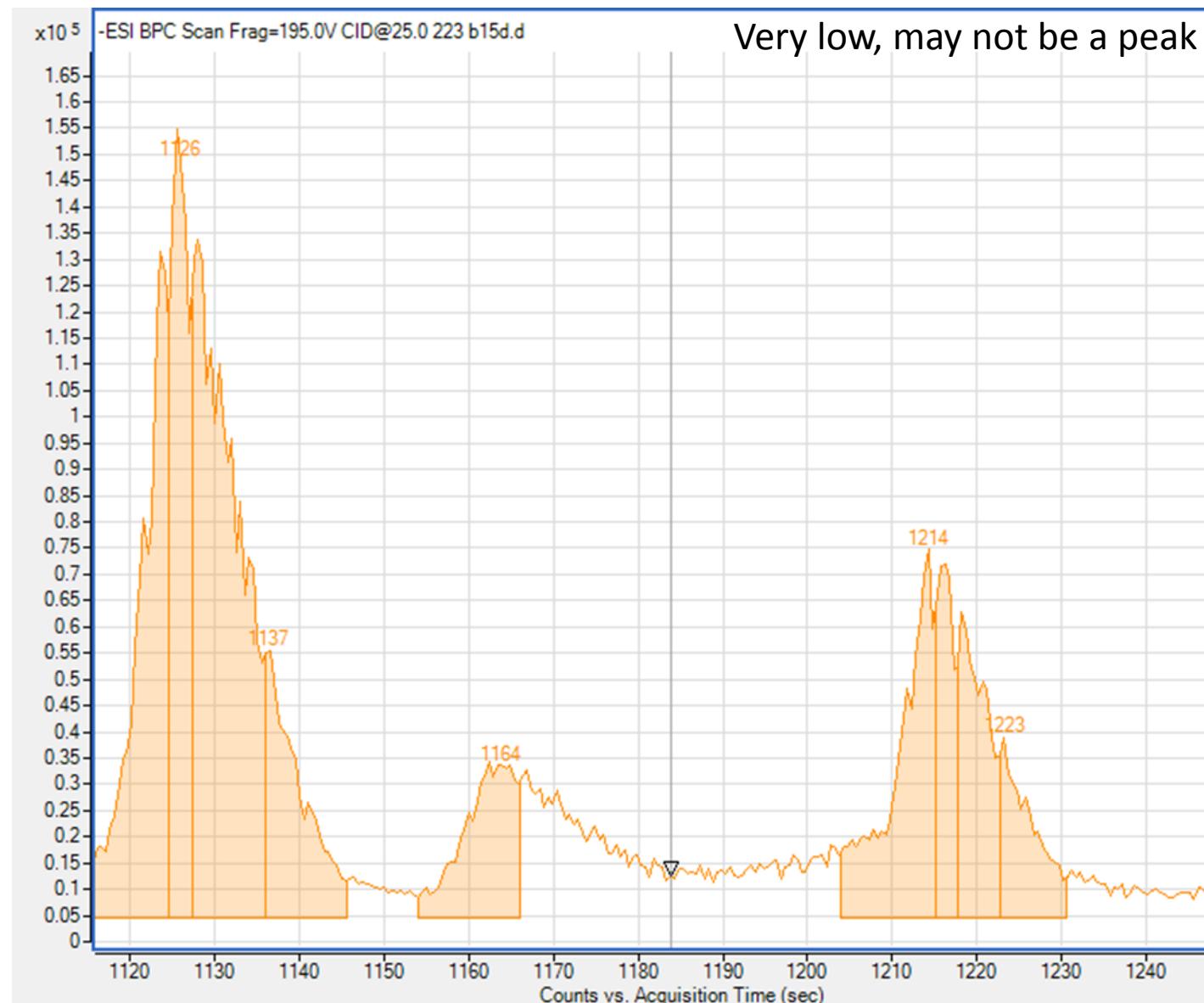


Monoisotopic Mass = 481.062 u

# Peak 19: 1173 seconds BP 300.997 = tail of Isostrictinin

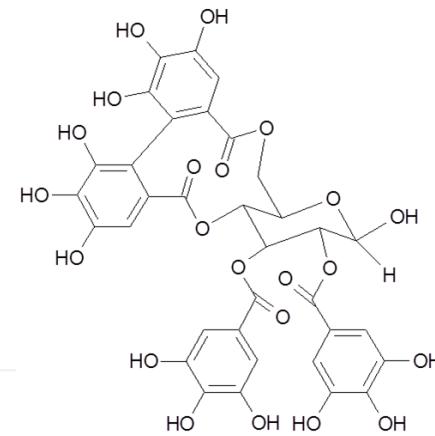
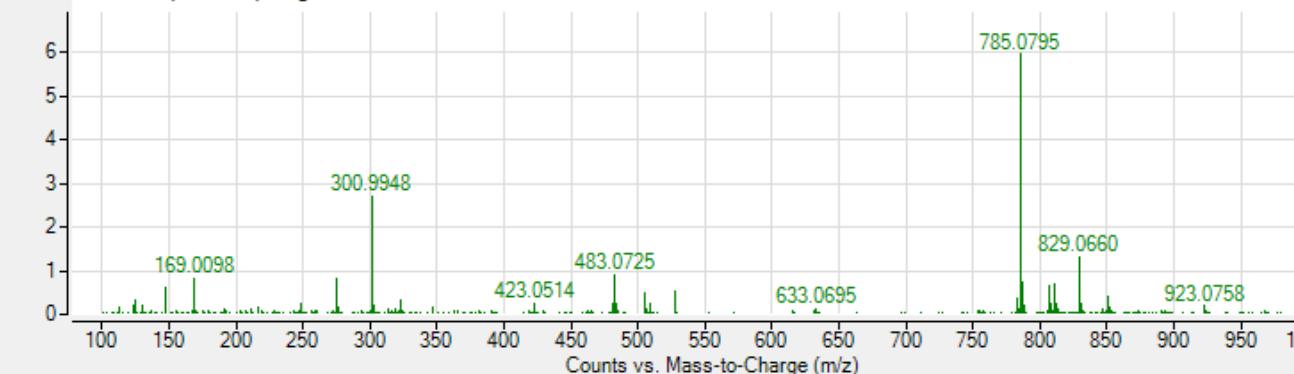


# Peak 20: 1200 seconds BP 300.993 = unknown ellagitannin



# Peak 21: 1213 seconds BP 300.998 = 2G+HHDP+glucose

x10<sup>4</sup> -ESI Scan (1215 sec) Frag=195.0V CID@25.0 223 b15d.d



9,808

31,825

5,822

21

1213 sec

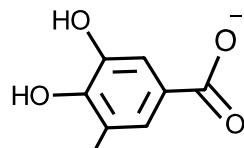
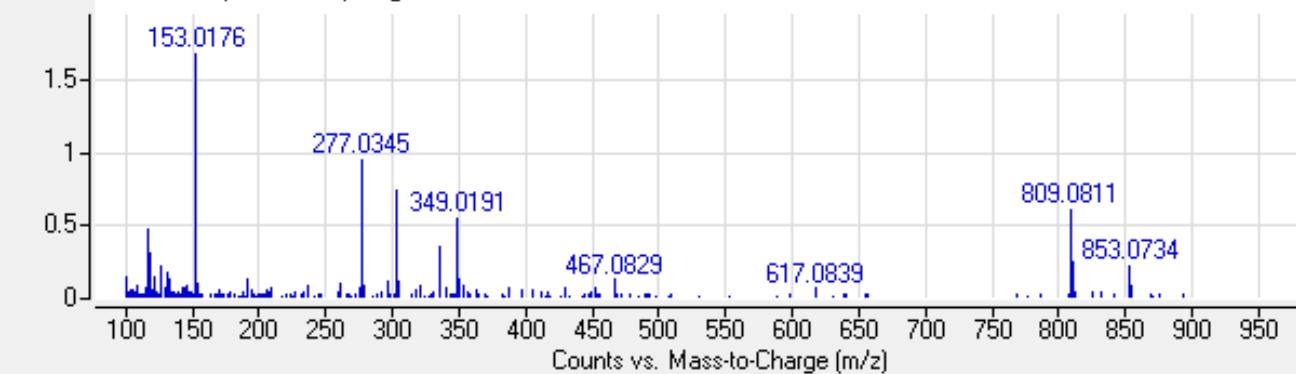
300.998

785 again

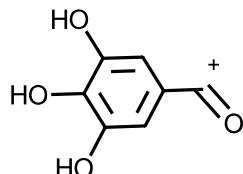
Similar to this

ppm -1.9 (small peak)

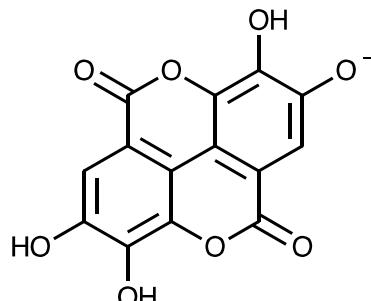
x10<sup>4</sup> +ESI Scan (1216.9 sec) Frag=195.0V CID@25.0 98 b7a +.d



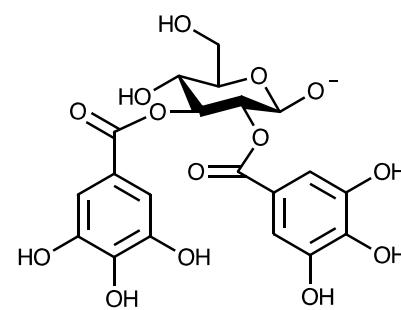
Monoisotopic Mass = 169.014 u



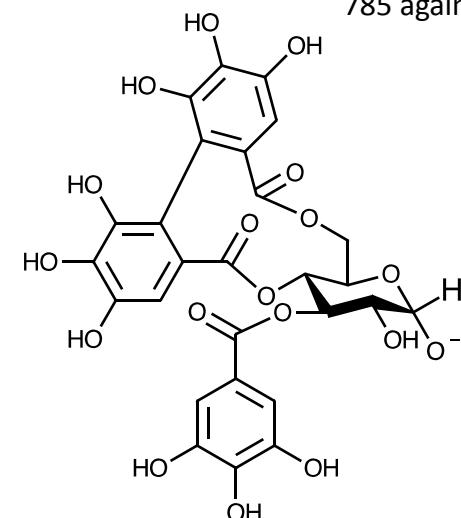
Monoisotopic Mass = 153.018 u



Monoisotopic Mass = 300.999 u

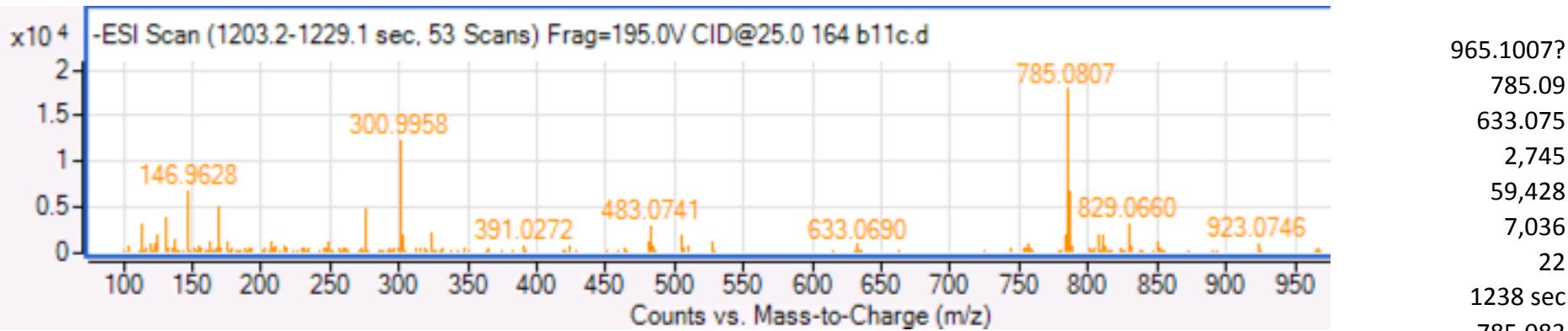


Monoisotopic Mass = 483.078 u

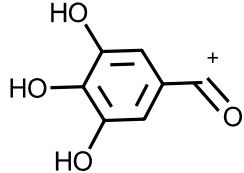


Monoisotopic Mass = 633.073 u

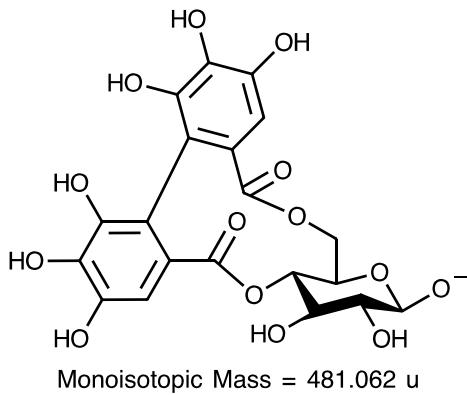
Peak 22: 1238 seconds BP 785.083 ( 965?) = 2G+HHDP+glucose (Tellimagrandin- $\beta$ )



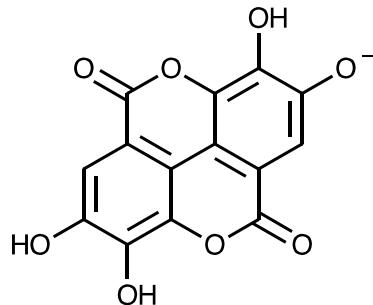
Find + mode and compare EIC 965 to 785



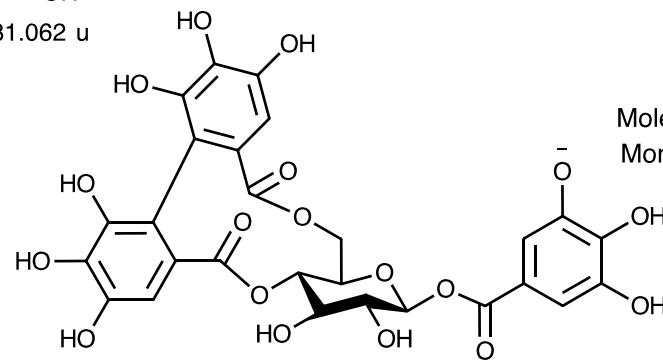
Monoisotopic Mass = 153.018 u



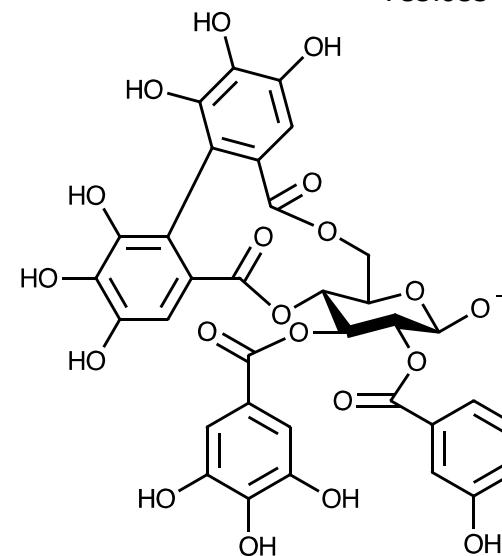
Monoisotopic Mass = 481.062 u



Monoisotopic Mass = 300.999 u



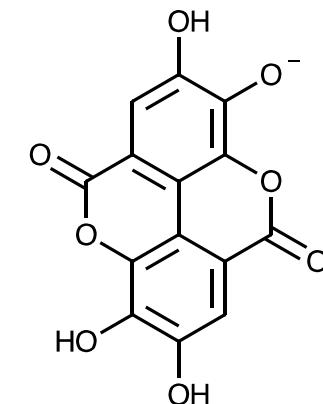
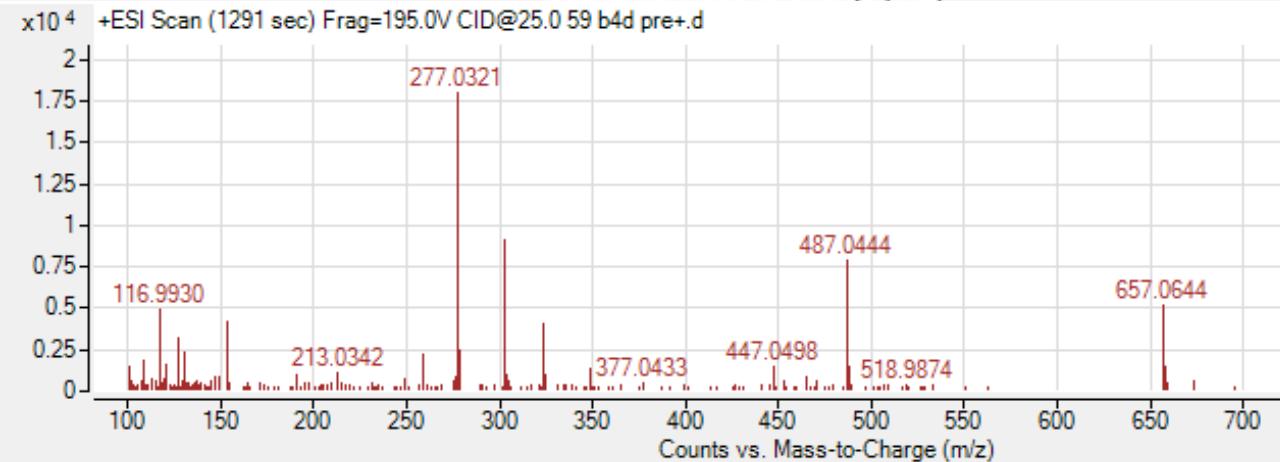
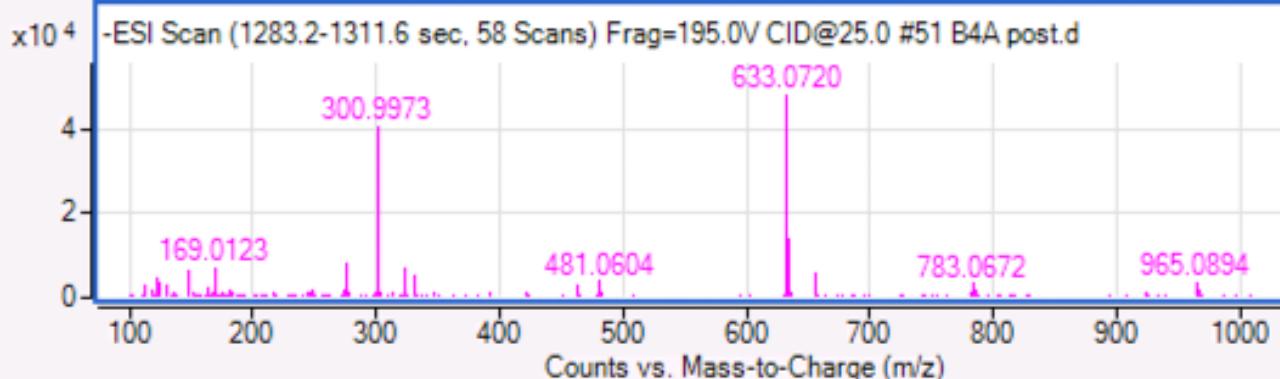
Monoisotopic Mass = 633.073 u  
Molecular Formula = C<sub>27</sub>H<sub>21</sub>O<sub>18</sub><sup>-</sup>



Molecular Formula = C<sub>34</sub>H<sub>25</sub>O<sub>22</sub><sup>-</sup>  
Monoisotopic Mass = 785.084 u

ppm -4.2 (small peak)

# Peak 23: 1294 seconds BP 633.072 = 1G+HHDP+glucose (Strictinin)



Monoisotopic Mass = 300.999 u

Ellagic acid

633.0681

481.0585

300.995

20,382

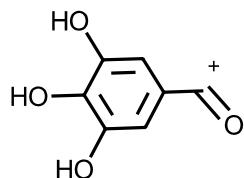
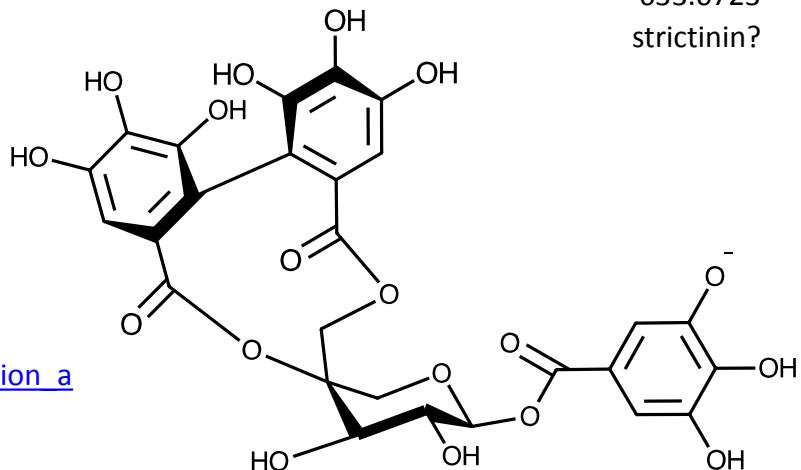
125,382

22,735

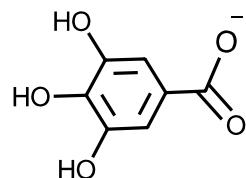
23

strictinin  $C_{27}H_{21}O_{18}^-$

ppm -2.05



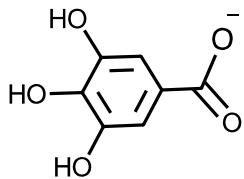
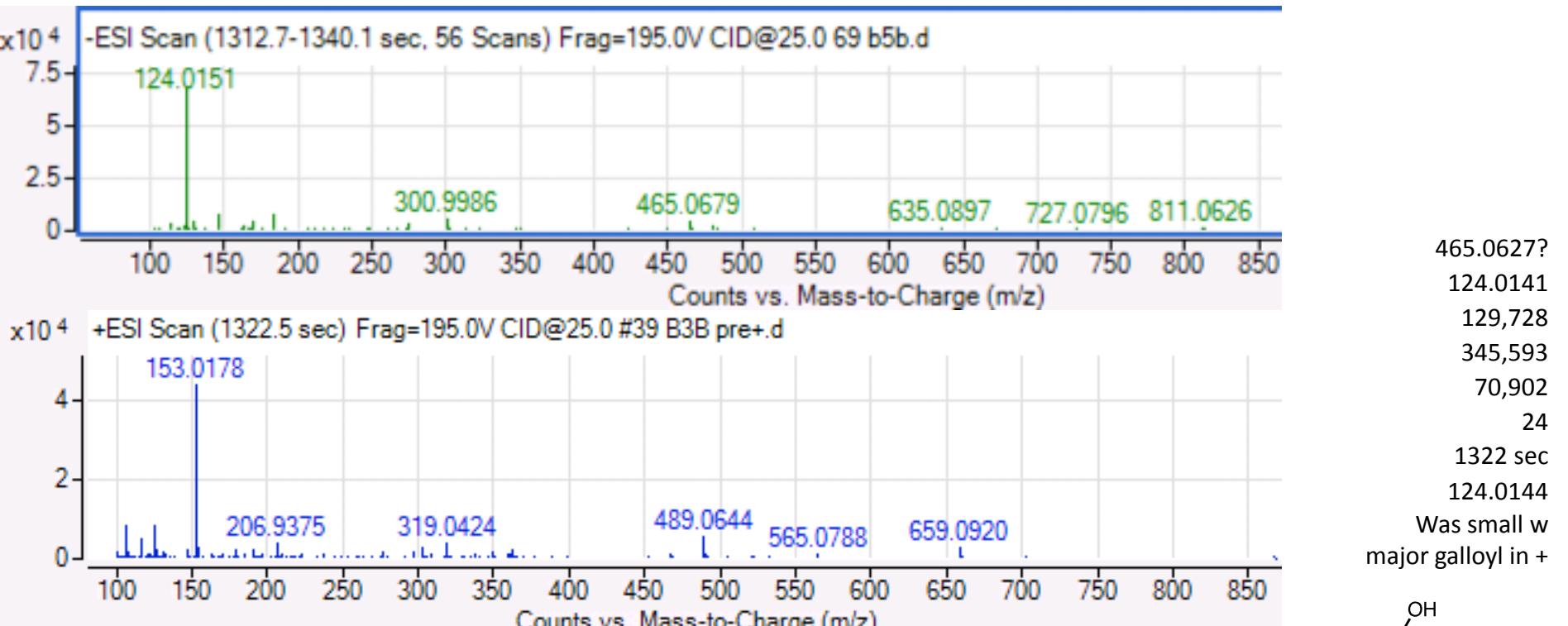
Monoisotopic Mass = 153.018 u



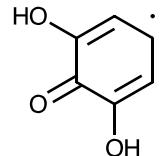
Monoisotopic Mass = 169.014 u

[https://www.researchgate.net/publication/260910872\\_Efficient\\_preparative\\_isolation\\_and\\_identification\\_of\\_walnut\\_bioactive\\_components\\_using\\_high-speed\\_counter-current\\_chromatography\\_and\\_LC-ESI-IT-TOF-MS](https://www.researchgate.net/publication/260910872_Efficient_preparative_isolation_and_identification_of_walnut_bioactive_components_using_high-speed_counter-current_chromatography_and_LC-ESI-IT-TOF-MS)

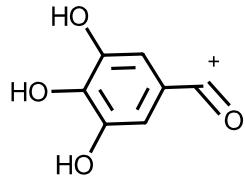
# Peak 24: 1322 seconds BP 124.014 (B-1,2,4, trigalloyl-D-glucose)



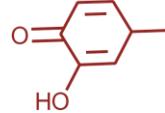
Monoisotopic Mass = 169.014 u



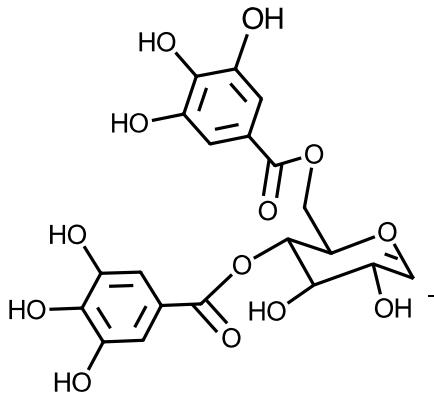
Monoisotopic Mass = 124.017 u



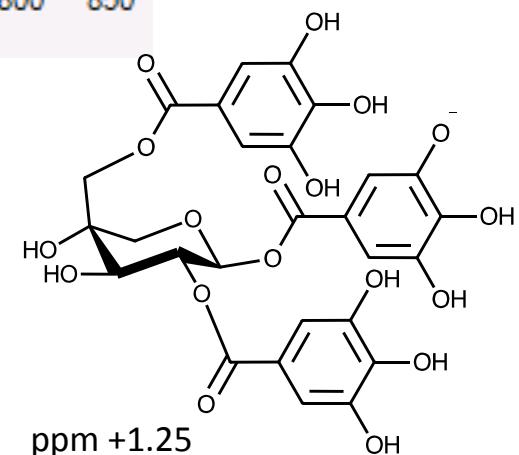
Monoisotopic Mass = 153.018 u



Monoisotopic Mass = 124.052 u

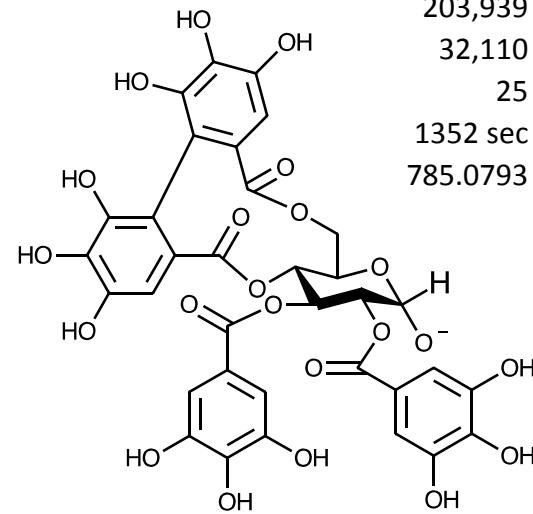
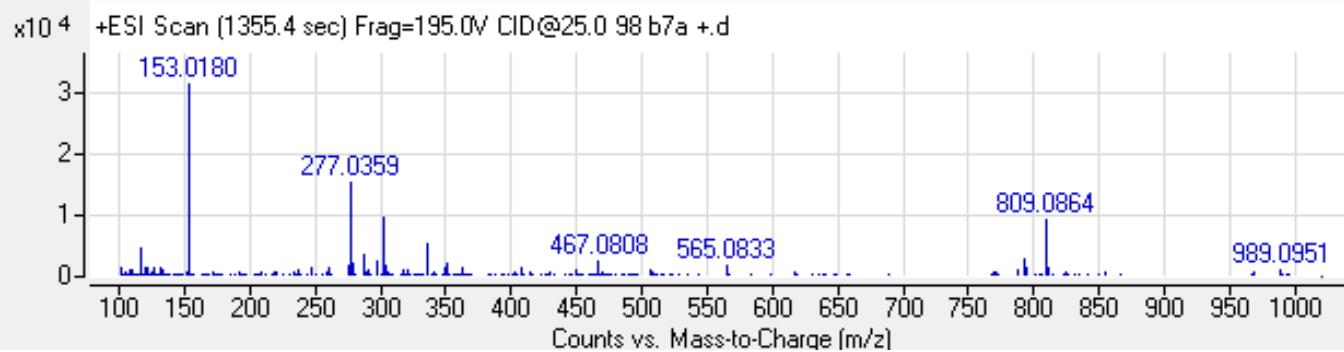
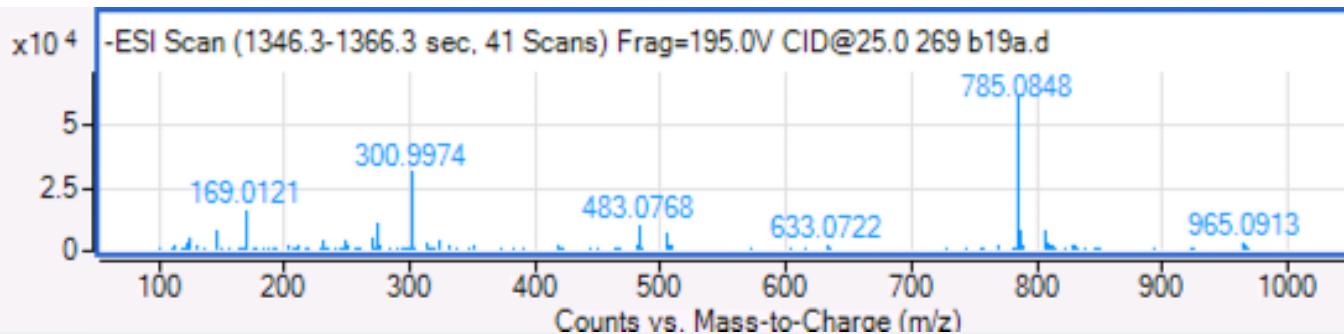


Monoisotopic Mass = 465.067 u

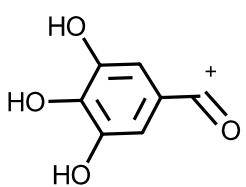


ppm +1.25  
B-1,2,6 trigalloyl-D-glucose  
 $C_{27}H_{23}O_{18}$   
635.0889

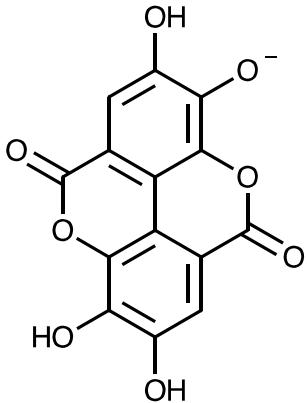
# Peak 25: 1352 seconds BP 785.079 HHDP+2G-glucose (Tellimagrandin- $\alpha$ )



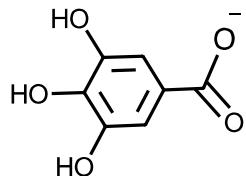
Molecular Formula =  $C_{34}H_{25}O_{22}^-$   
Monoisotopic Mass = 785.084 u  
tellimagrandin-1 OH alpha



Monoisotopic Mass = 153.018 u

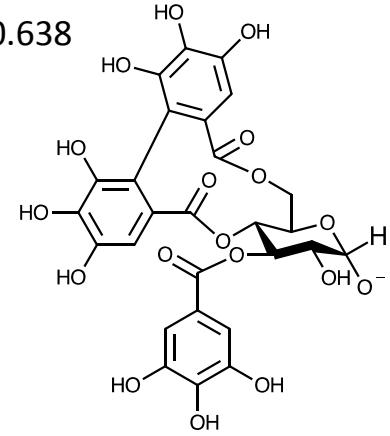
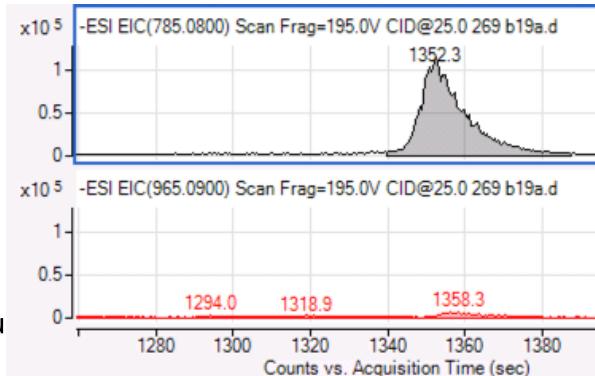


Monoisotopic Mass = 300.999 u



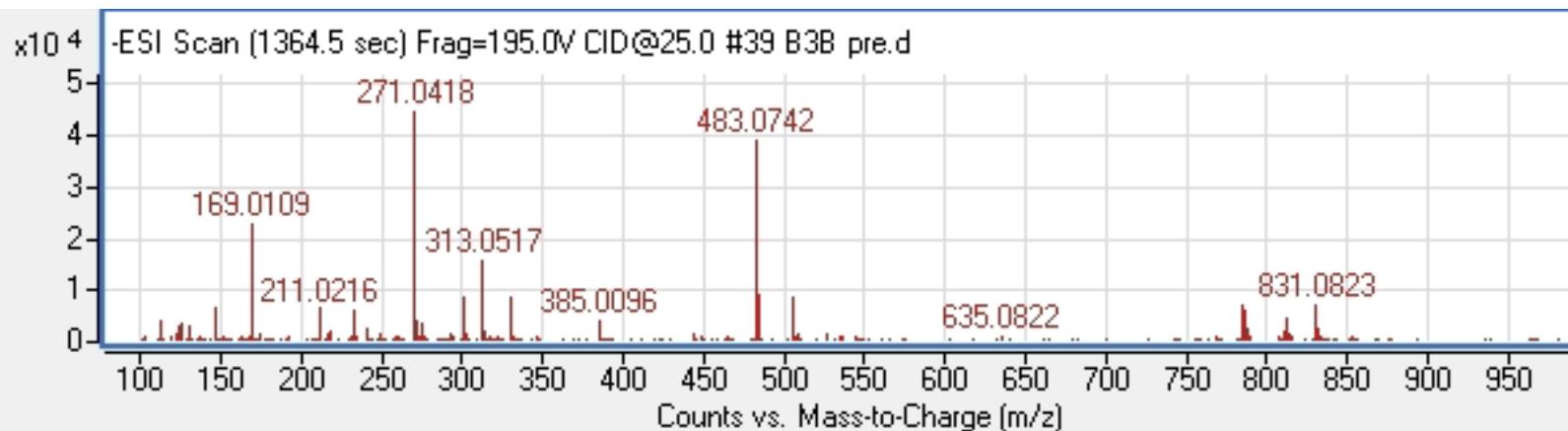
Monoisotopic Mass = 169.014 u

Ellagic acid

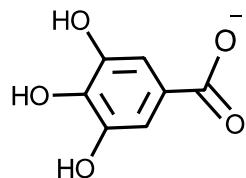
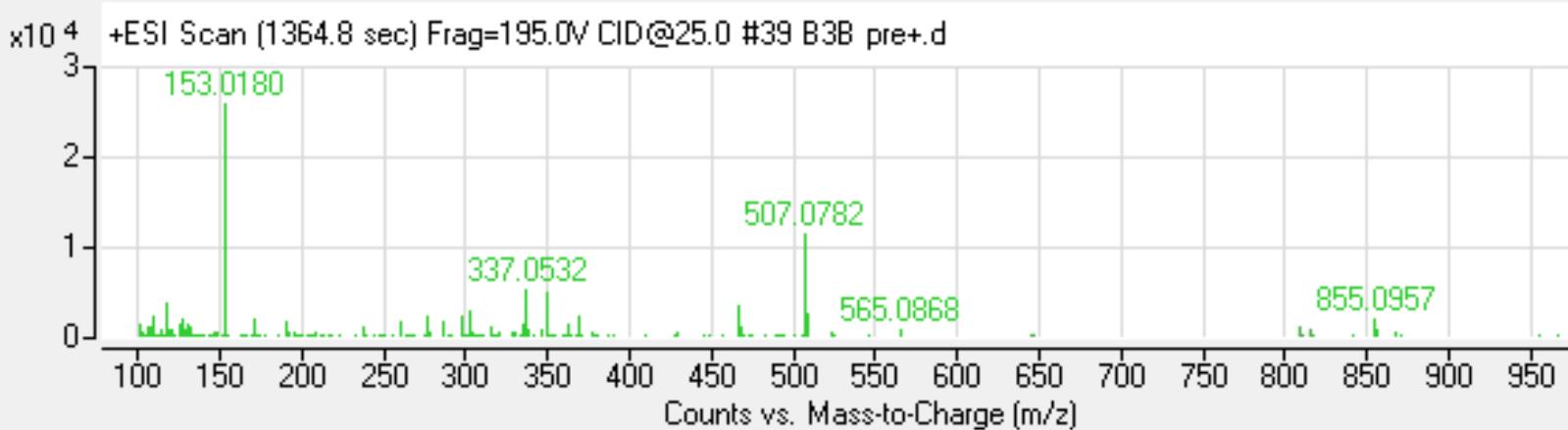


Monoisotopic Mass = 633.073 u

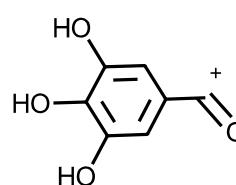
# Peak 26: 1365 seconds BP 271.044 = unknown compound



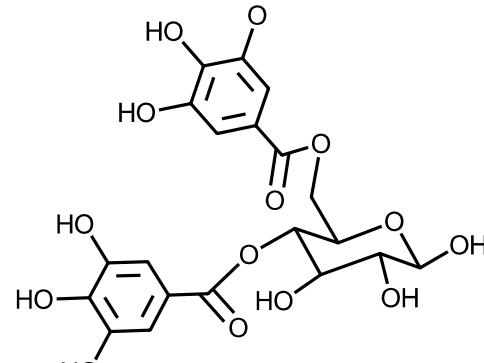
831.0823  
483.0742  
271.042  
169.011  
13,228  
62,468  
12,020  
26  
1365 sec  
271.044



Monoisotopic Mass = 169.014 u

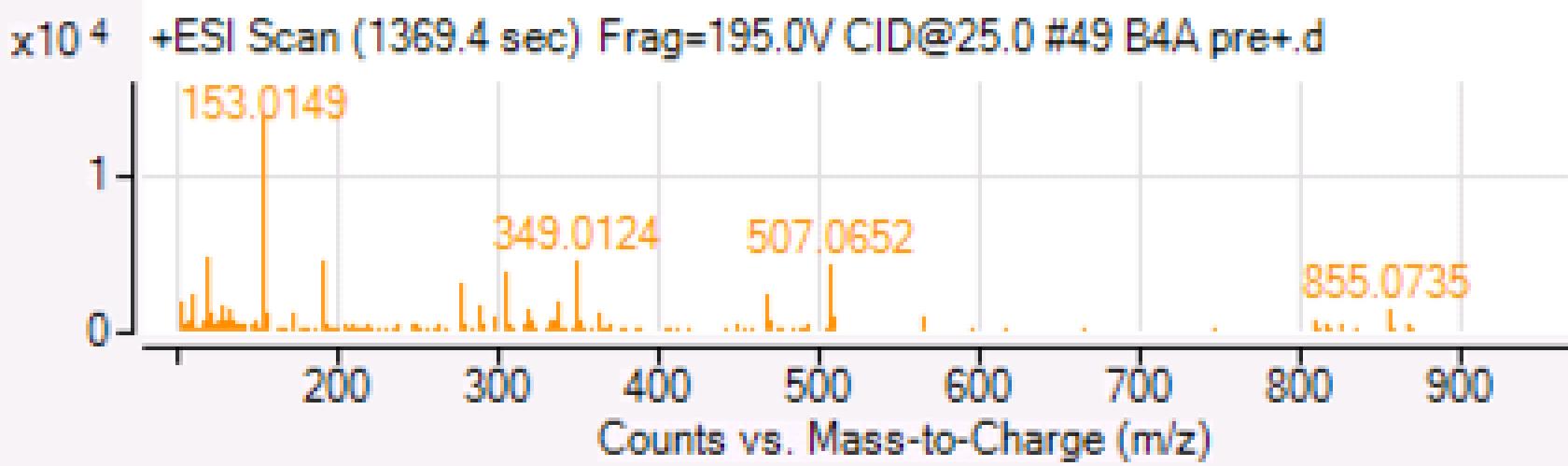
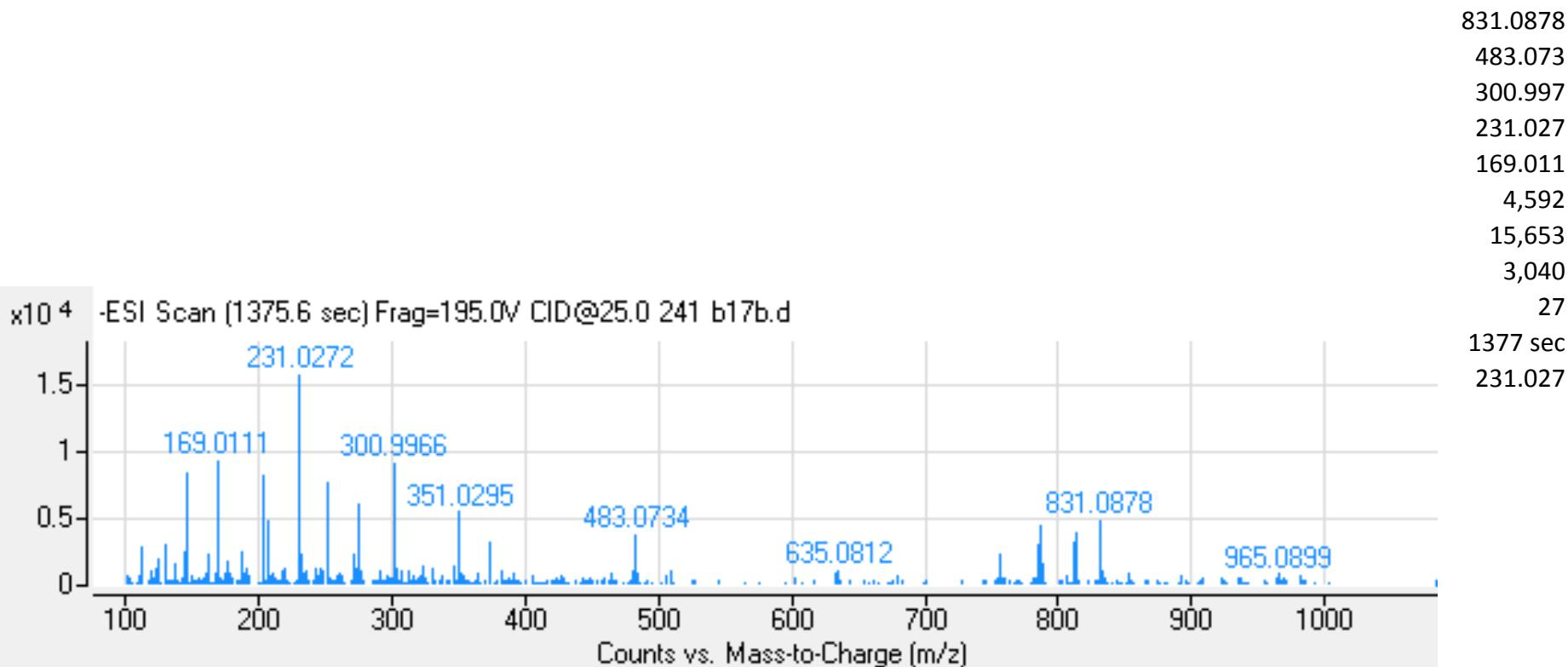


Monoisotopic Mass = 153.018 u

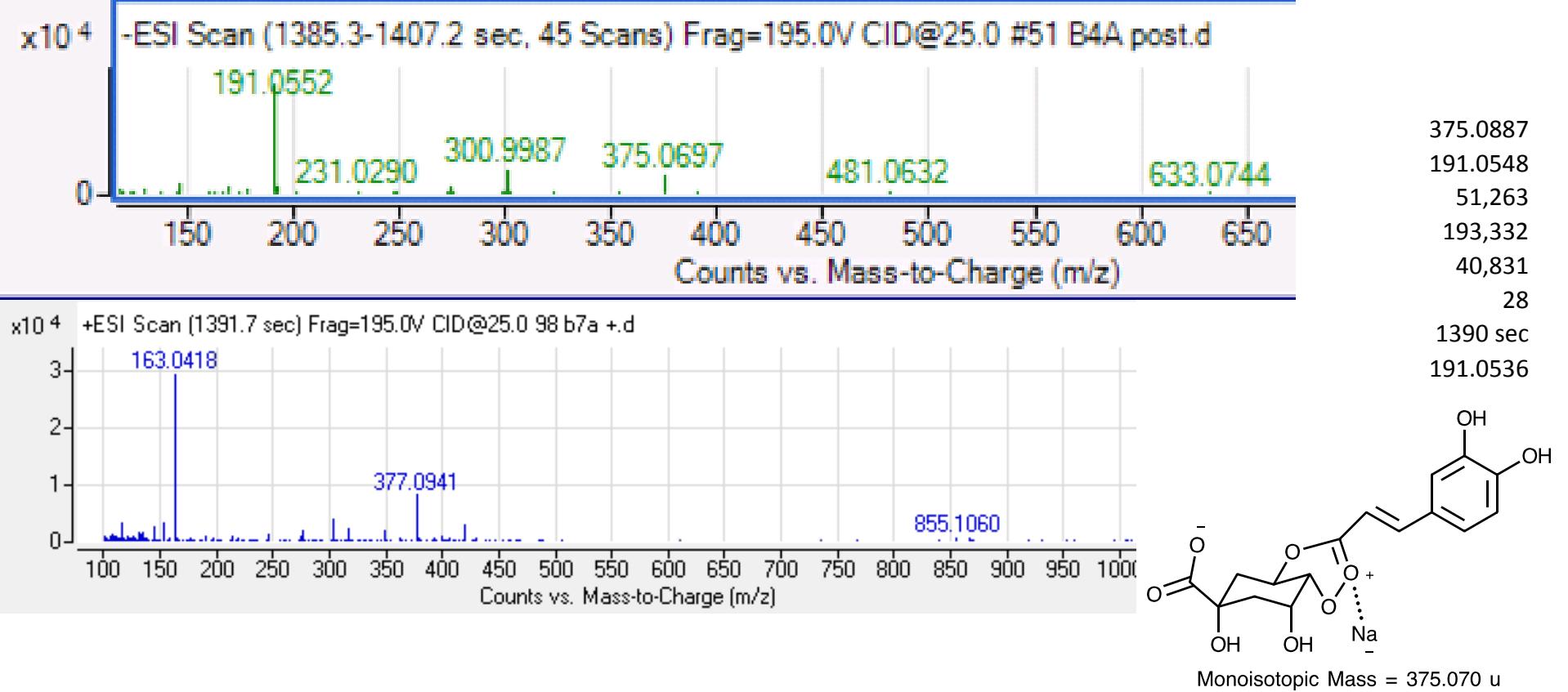


Monoisotopic Mass = 483.078 u

# Peak 27: 1377 seconds BP 231.027 = unknown compound



# Peak 28: 1390 seconds BP 191.054 = 3-O-caffeoylequinic acid



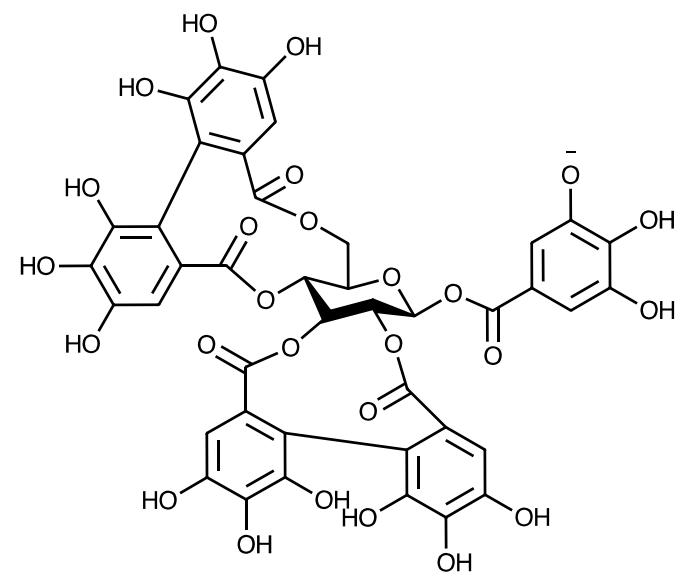
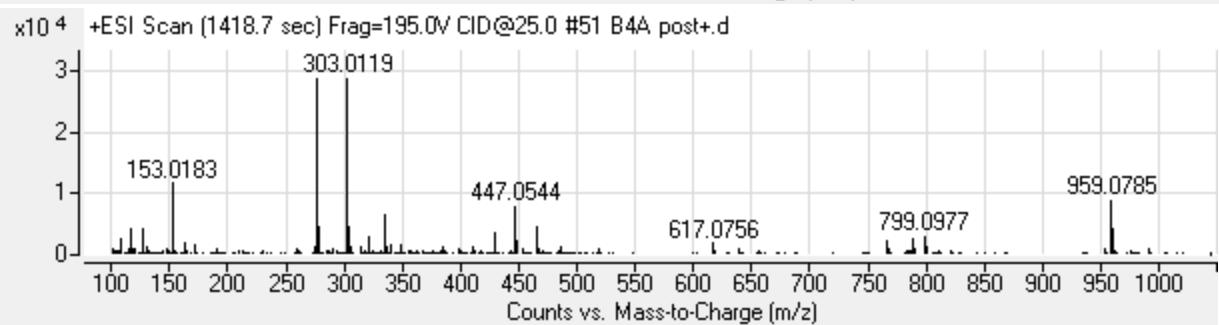
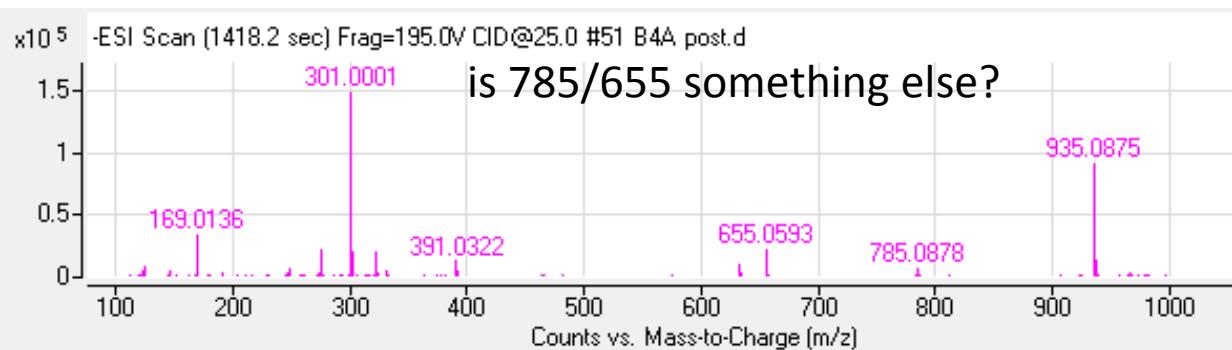
Chlorogenic acid; LC-ESI-QTOF; MS2; [M-H]<sup>-</sup>; CE: 10eV



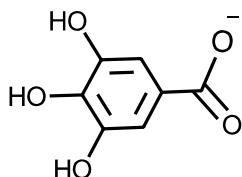
<http://dx.doi.org/10.1016/j.talanta.2016.03.101>  
3-CQA > 5-CQA > 4-CQA

Chlorogenic acid sodium salt

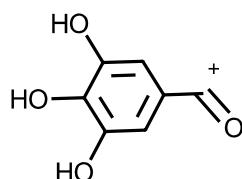
# Peak 29: 1418 seconds BP 300.996 = 1G+2HHDP+glucose (Casuarictin)



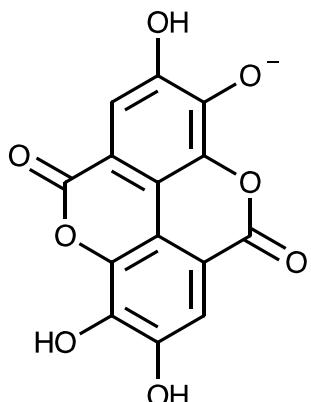
Monoisotopic Mass = 935.080 u  
Molecular Formula = C<sub>41</sub>H<sub>27</sub>O<sub>26</sub><sup>-</sup>  
casuarictin



Monoisotopic Mass = 169.014 u

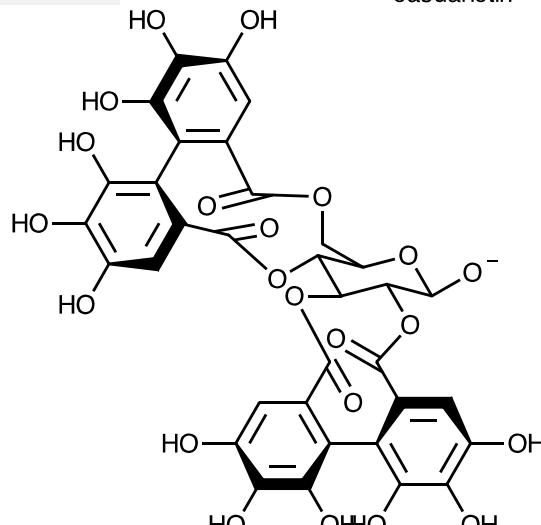


Monoisotopic Mass = 153.018 u



Monoisotopic Mass = 300.999 u

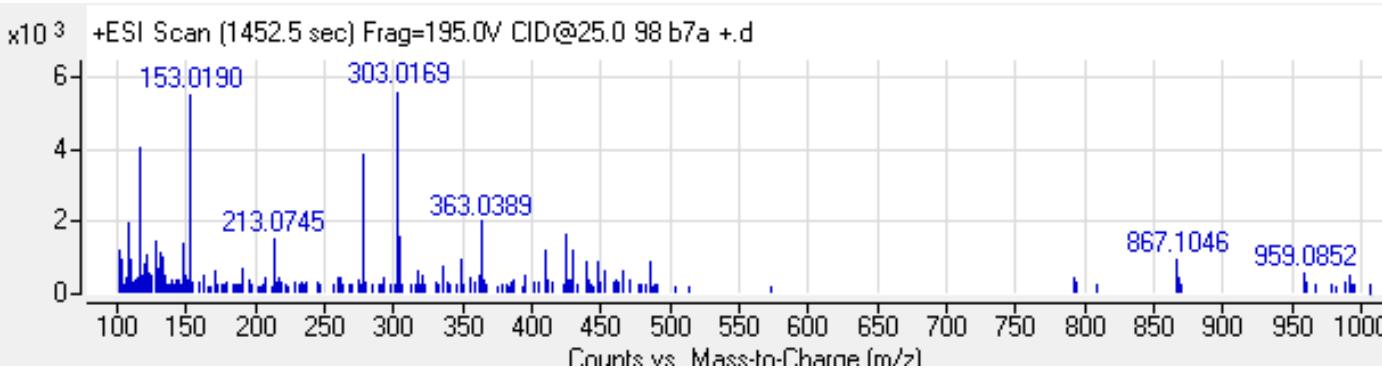
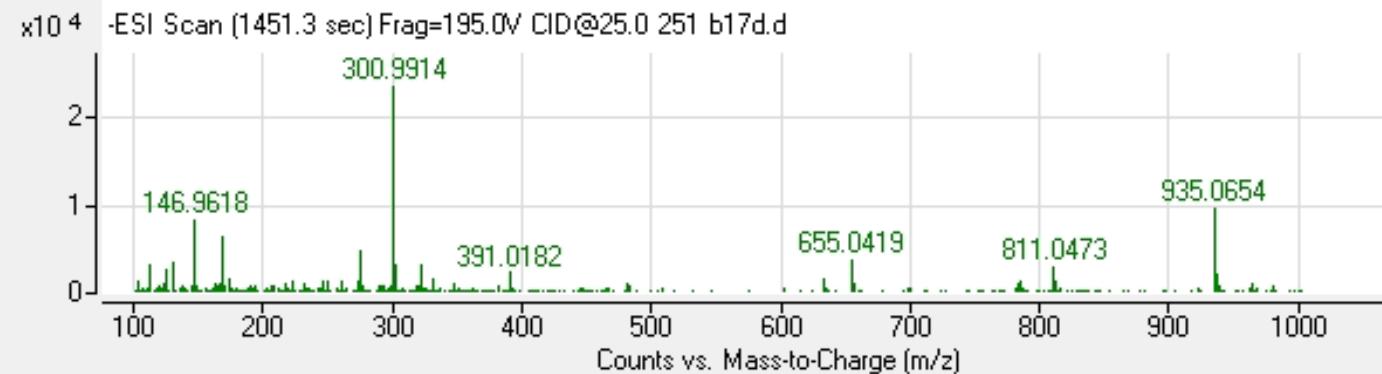
Ellagic acid



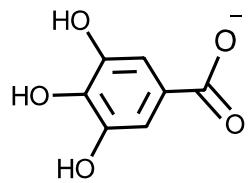
Monoisotopic Mass = 783.069 u

935.0875  
785.0878  
655.0593  
301.0001  
169.0099  
41,235  
174,170  
33,470  
29  
1418 sec  
300.9958

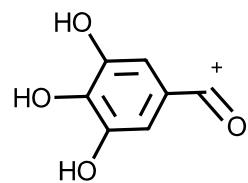
# Peak 30: 1452 seconds BP 300.995 = 1G+2HHDP+glucose (Potentillin)



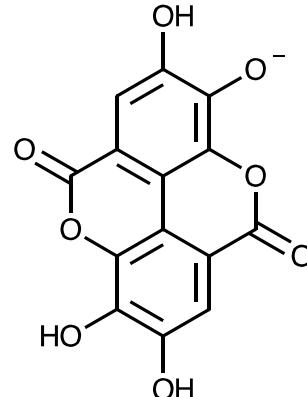
935.0654  
 811.0754  
 655.0575  
 301.003  
 169.0157  
 12,336  
 38,035  
 7,547  
 30  
 1452 sec  
 300.9952  
 2xHHDP+1  
 G-glucose



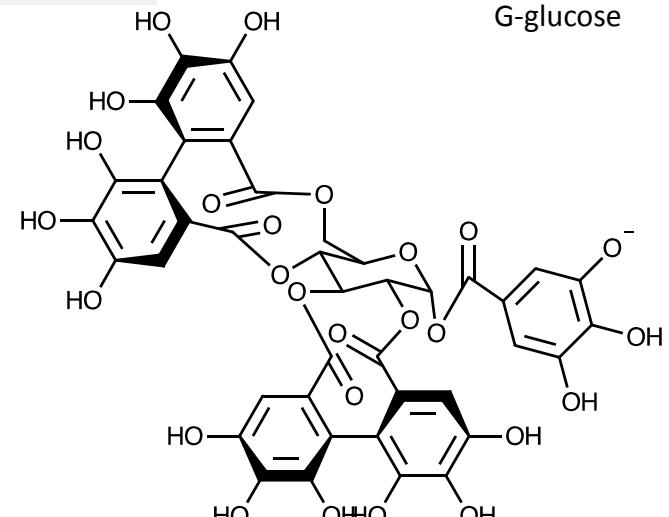
Monoisotopic Mass = 169.014 u



Monoisotopic Mass = 153.018 u

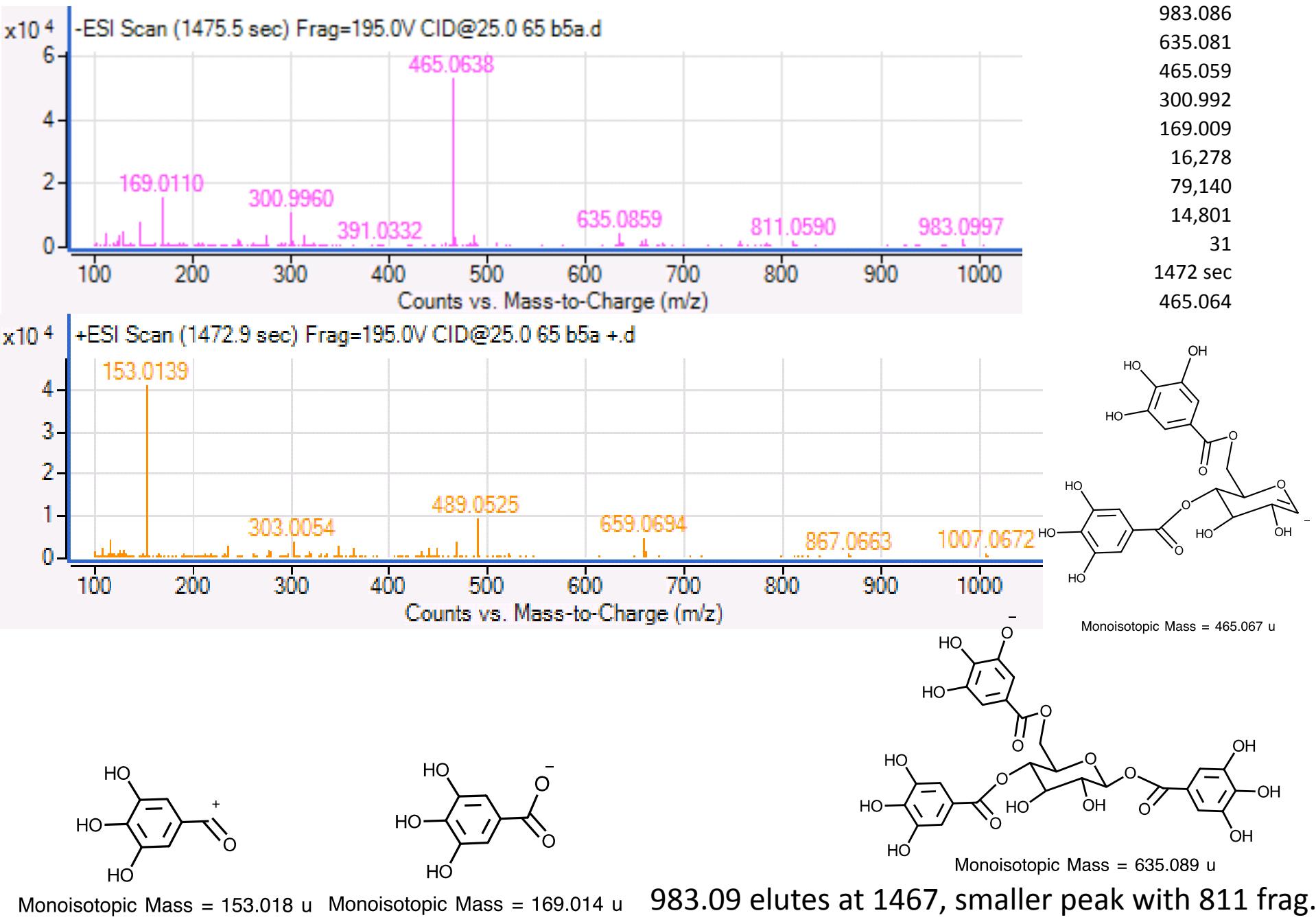


Monoisotopic Mass = 300.999 u  
 Ellagic acid

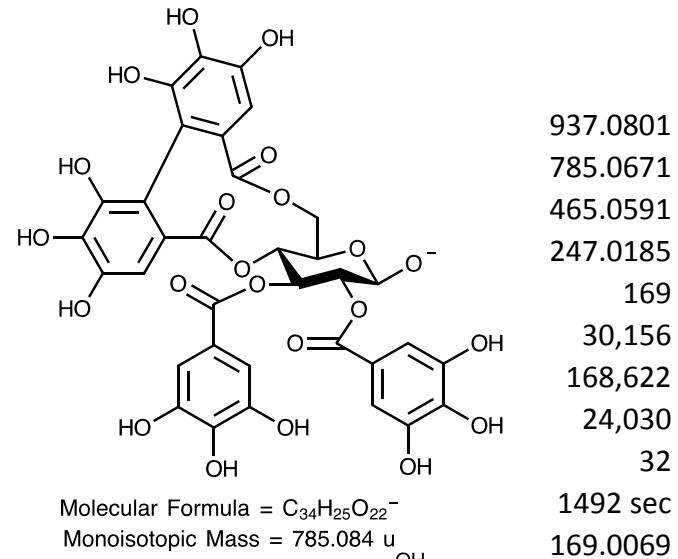
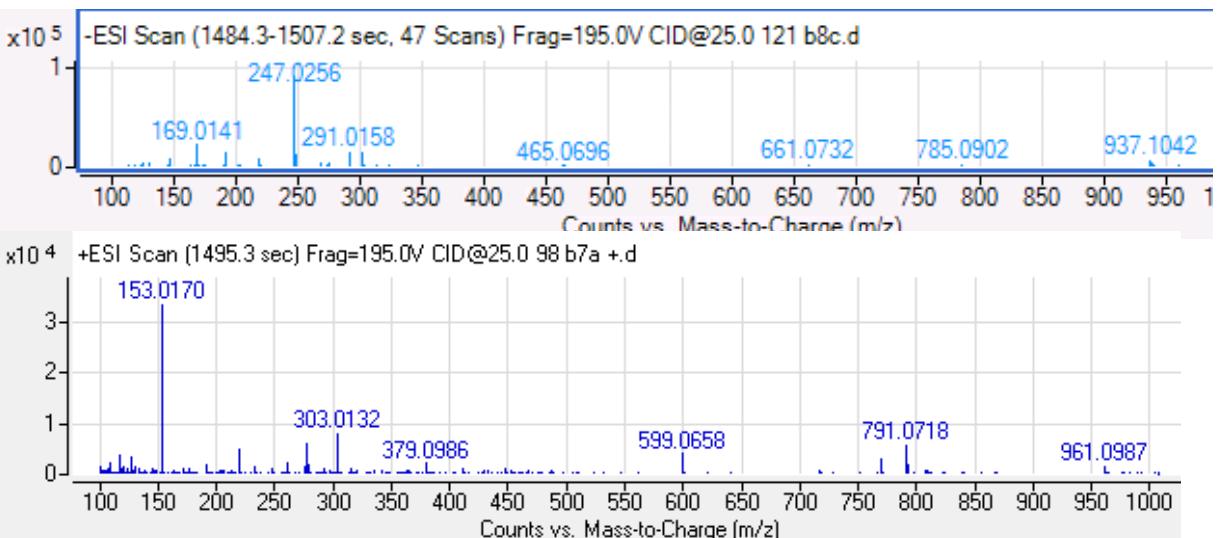


Monoisotopic Mass = 935.080 u

# Peak 31: 1472 seconds BP 465.064 = unknown ellagitannin

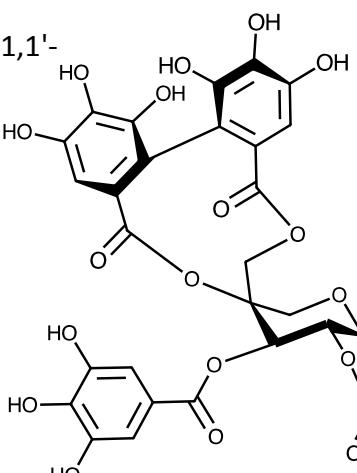
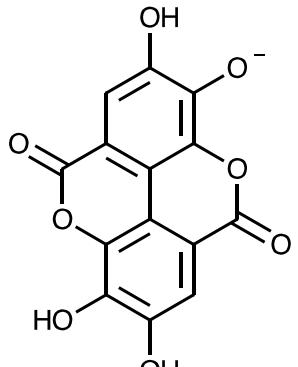
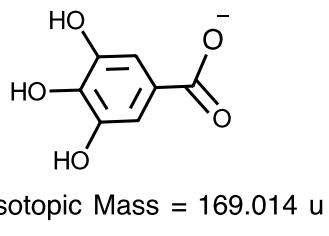


# Peak 32: 1492 seconds BP 169.007 = 1HHDP+3G-glucose (Tellimagrandin II)



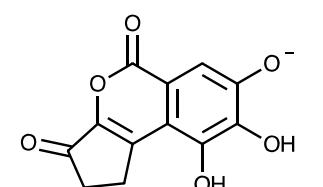
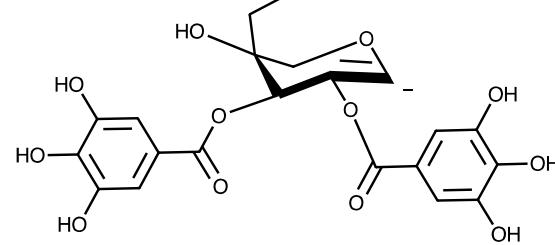
<http://pubchem.ncbi.nlm.nih.gov/compound/151590#section=Top>

Beta-D-Glucopyranose, cyclic 4,6-((1S)-4,4',5,5',6,6'-hexahydroxy(1,1'-biphenyl)-2,2'-dicarboxylate) 1,2,3-tris(3,4,5-trihydroxybenzoate)



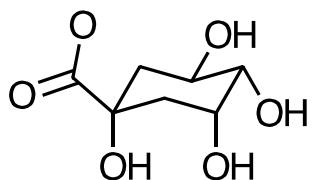
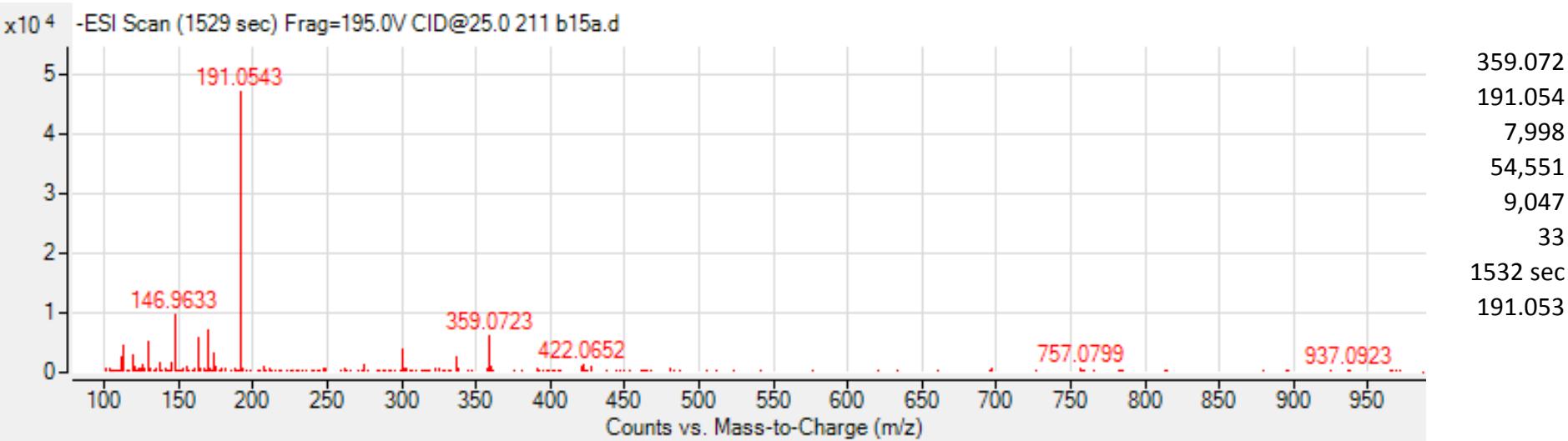
tellimagrandin II  $C_{41}H_{29}O_{26}^-$   
937.0952

Ellagic acid

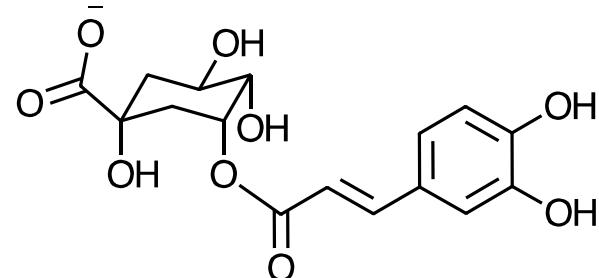


Monoisotopic Mass = 247.025 u  
obs. 247.0256 3.24ppm

# Peak 33: 1532 seconds BP 191.053 = 5-O-caffeoylequinic acid



Monoisotopic Mass = 191.056 u

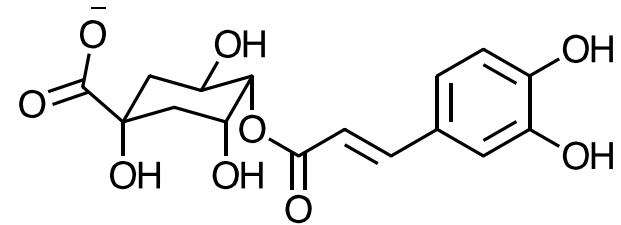
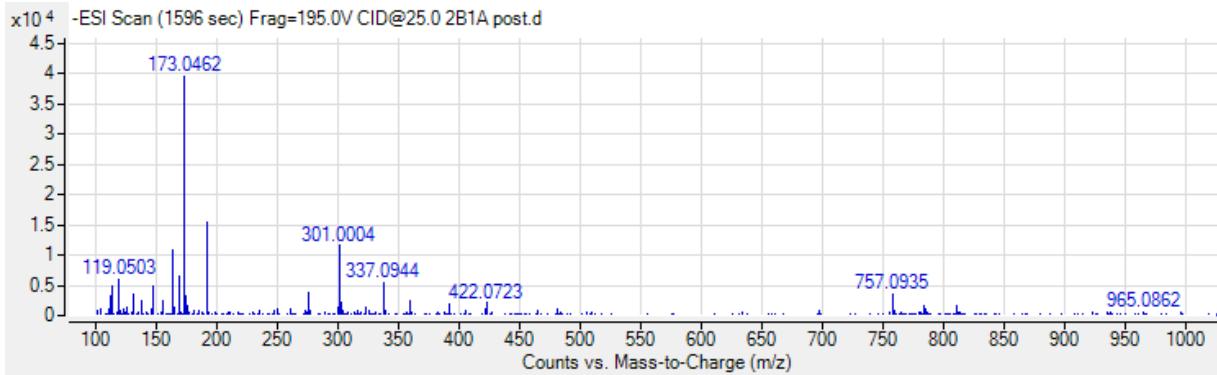


Monoisotopic Mass = 353.088 u

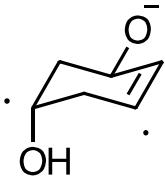
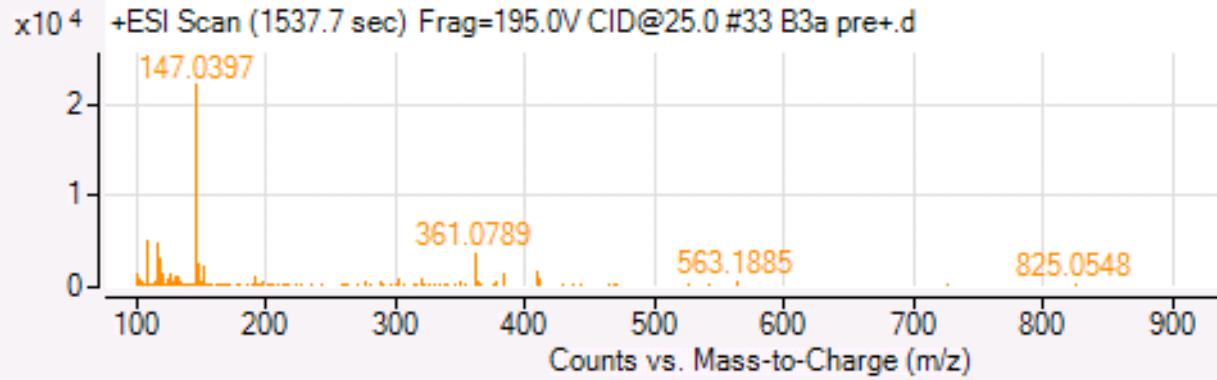
5-O-caffeoylequinic acid

359.072  
191.054  
7,998  
54,551  
9,047  
33  
1532 sec  
191.053

# Peak 34: 1539 seconds BP 173.042 = 4-O-caffeoylequinic acid

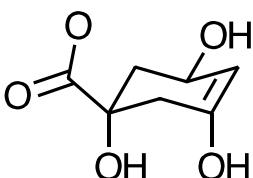


Monoisotopic Mass = 353.088 u  
4-O-caffeoylequinic acid



Monoisotopic Mass = 111.045 u Monoisotopic Mass = 173.046 u

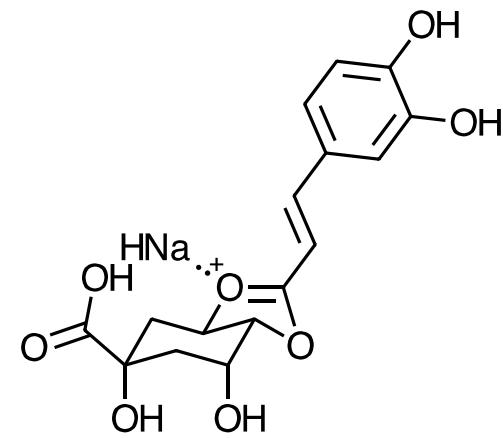
Q6 fragment of quinic



Q2 fragment of quinic

4-caffeoylequinic acid (similar to chlorogenic acid); + mode does not show peak

More importantly, it is easy to distinguish a 4-acyl CGA by its “dehydrated” MS<sup>2</sup> base peak Q<sub>2</sub> at *m/z* ~173.5 (**Figure 5**), supported by strong MS<sup>3</sup> ions at *m/z* ~93.3 (unassigned) and Q<sub>6</sub> at *m/z* ~111.2 (**Figure 6**). In contrast, all three 5-acyl CGA (II, V, and VIII) and 3-CQA (I) produce an MS<sup>2</sup> base peak at *m/z* ~191.5 (Q<sub>1</sub>), supported by strong MS<sup>3</sup> ions at *m/z* ~85.6 (Q<sub>5</sub>), ~127.0 (Q<sub>7</sub>), and ~172.0 (Q<sub>3</sub>). The distinctive MS<sup>2</sup> behavior of 4-CQA (III) has been reported previously ([23](#)).... *J. Agric. Food Chem.*, **2003**, 51 (10), pp 2900–2911.



Monoisotopic Mass = 361.089 u

-water from C-5  
by 1,2 acyl participation

<sup>337.094</sup>  
<sup>173.042</sup>

<sup>12,982</sup>

<sup>63,025</sup>

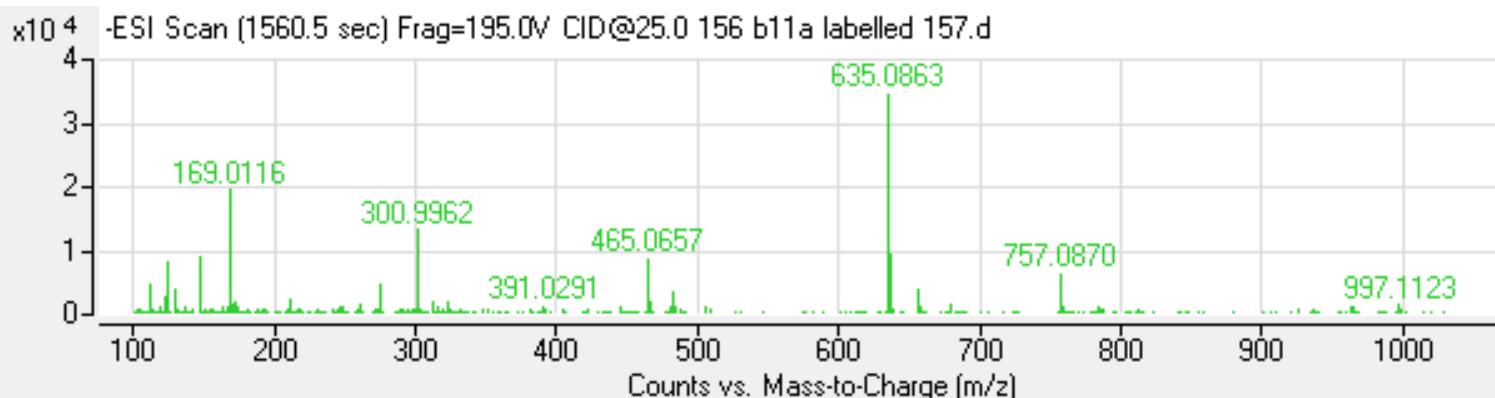
<sup>12,342</sup>

<sup>34</sup>

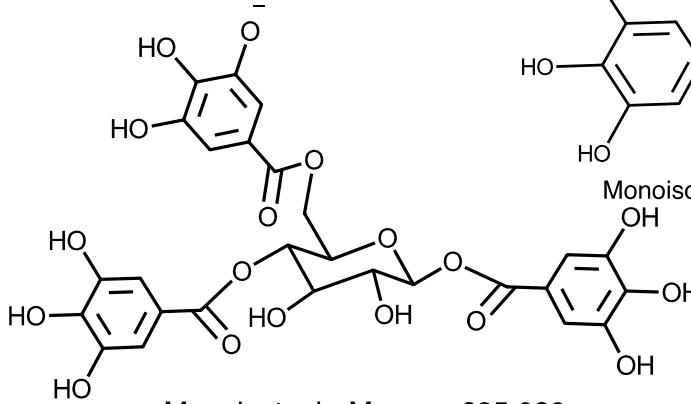
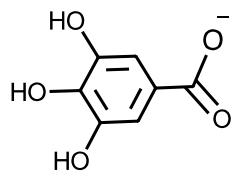
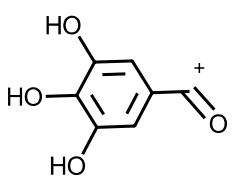
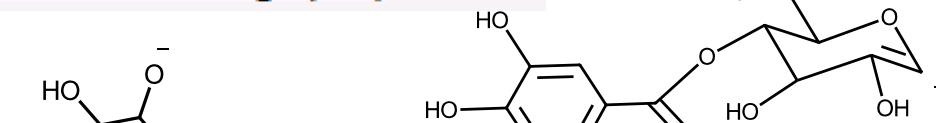
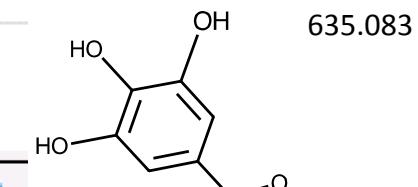
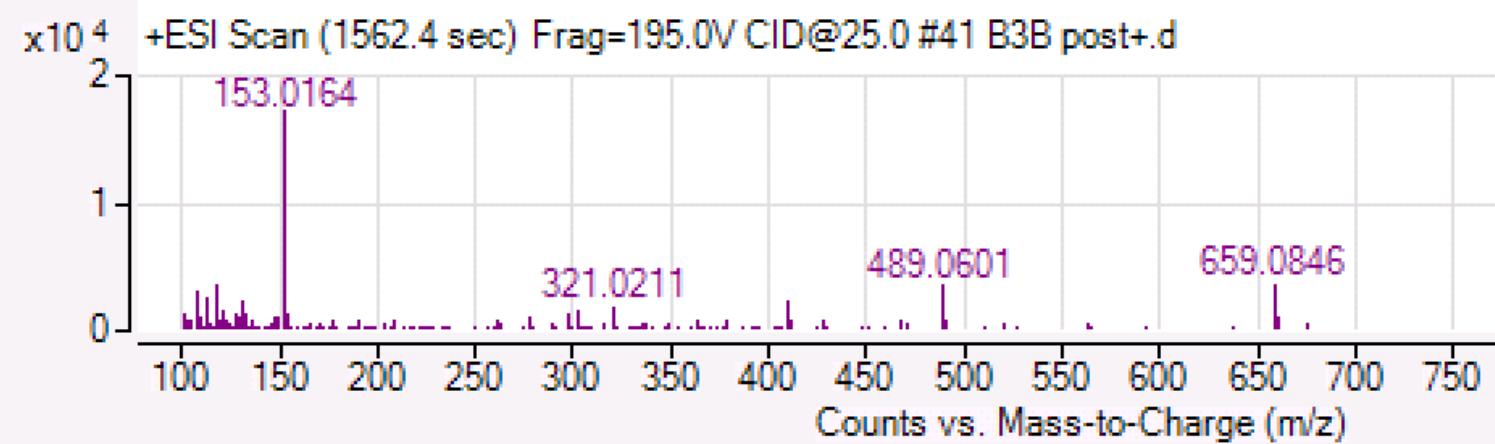
<sup>1539 sec</sup>

<sup>173.042</sup>

# Peak 35: 1565 seconds BP 635.083 = Tri-galloyl-glucose



997.112  
757.087  
635.083  
465.066  
300.996  
169.002  
8,125  
34,534  
6,787  
35  
1565 sec  
635.083

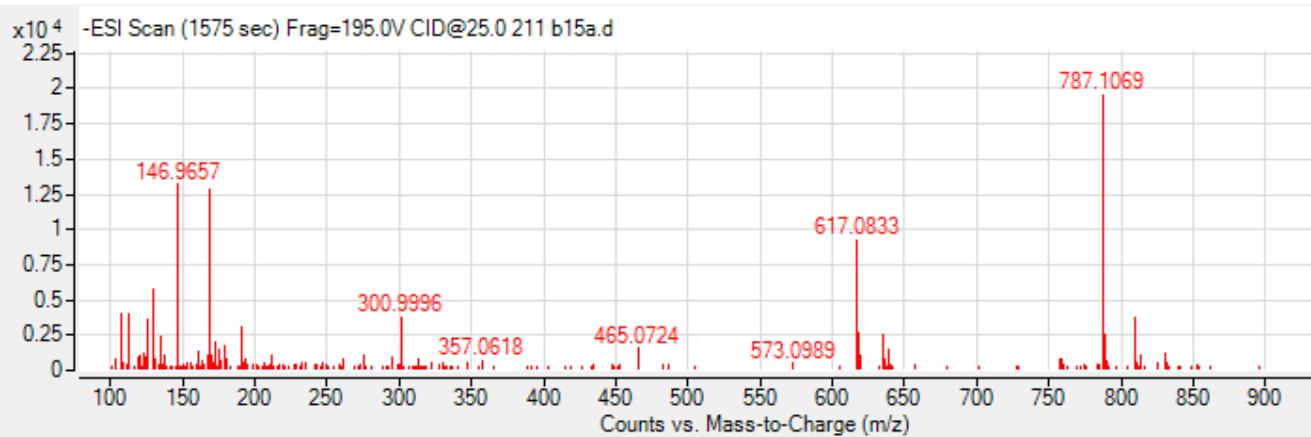


Monoisotopic Mass = 153.018 u Monoisotopic Mass = 169.014 u

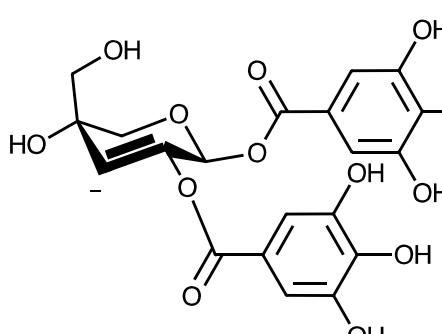
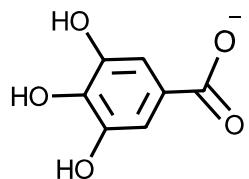
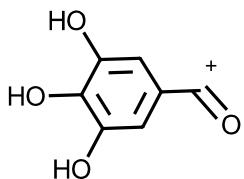
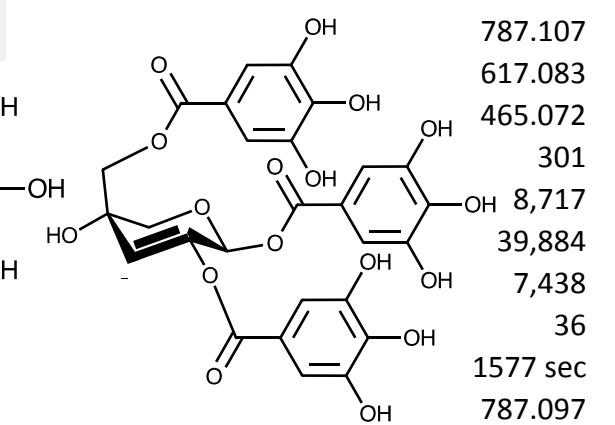
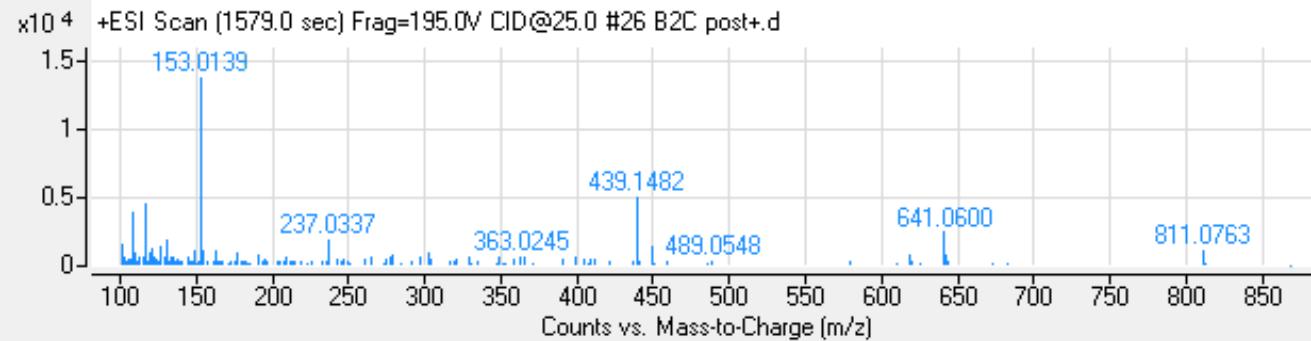
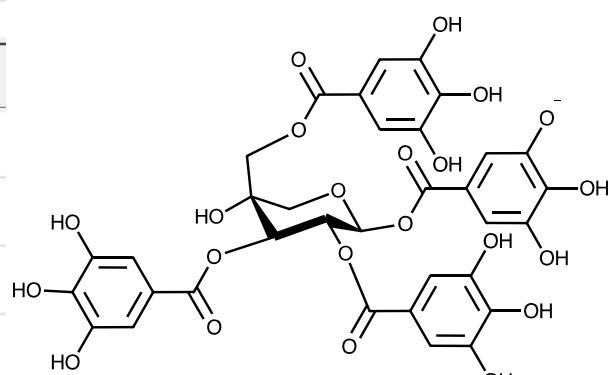
Monoisotopic Mass = 635.089 u

Monoisotopic Mass = 465.067 u

# Peak 36: 1577 seconds BP 787.097 = Tetra-galloyl-glucose



B-1,2,3,6 tetragalloyl-D-glucose  
 $C_{34}H_{27}O_{22}$   
 787.0999

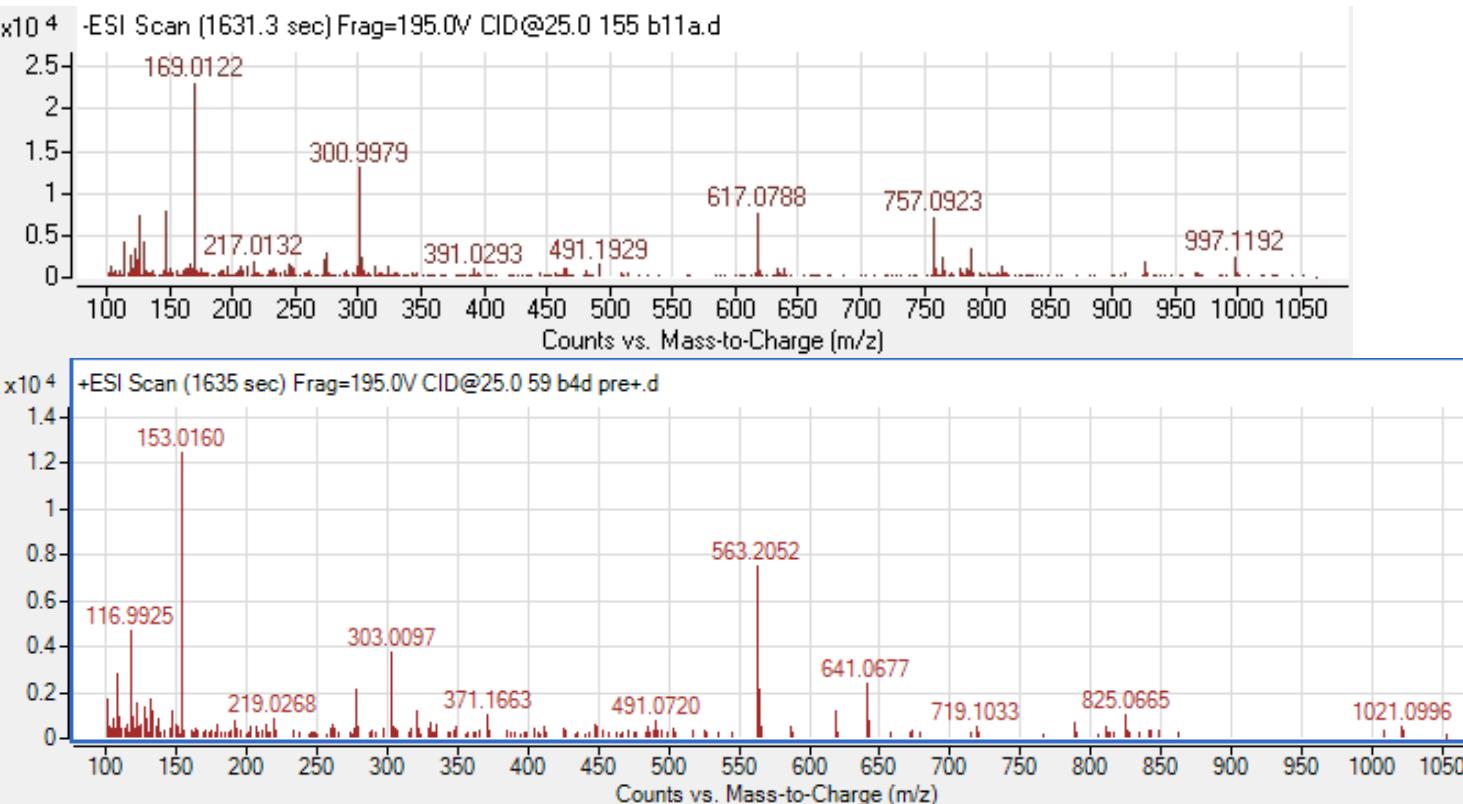


Monoisotopic Mass = 617.079 u

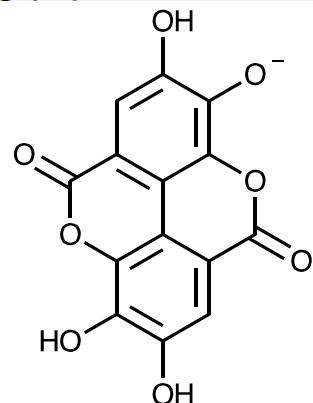
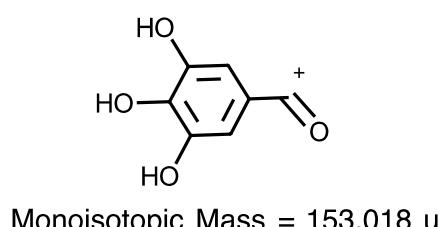
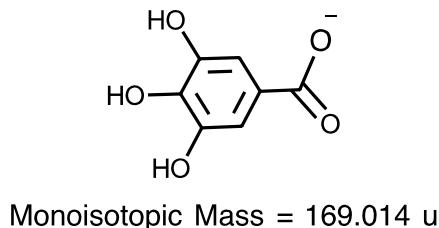
TGG

Monoisotopic Mass = 153.018 u   Monoisotopic Mass = 169.014 u   Monoisotopic Mass = 465.067 u

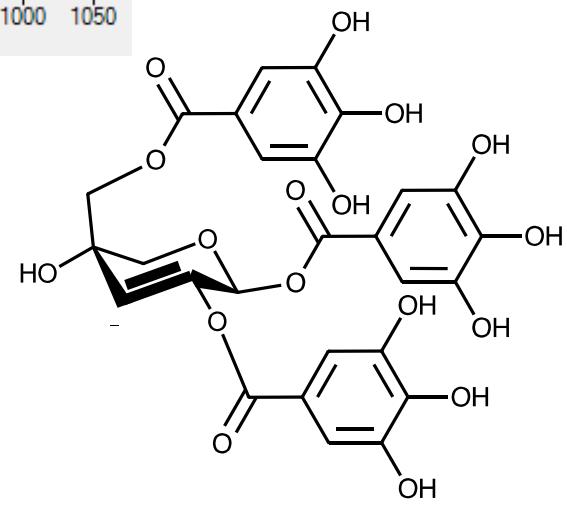
# Peak 38: 1631 seconds BP 169.011 = unknown ellagitannin



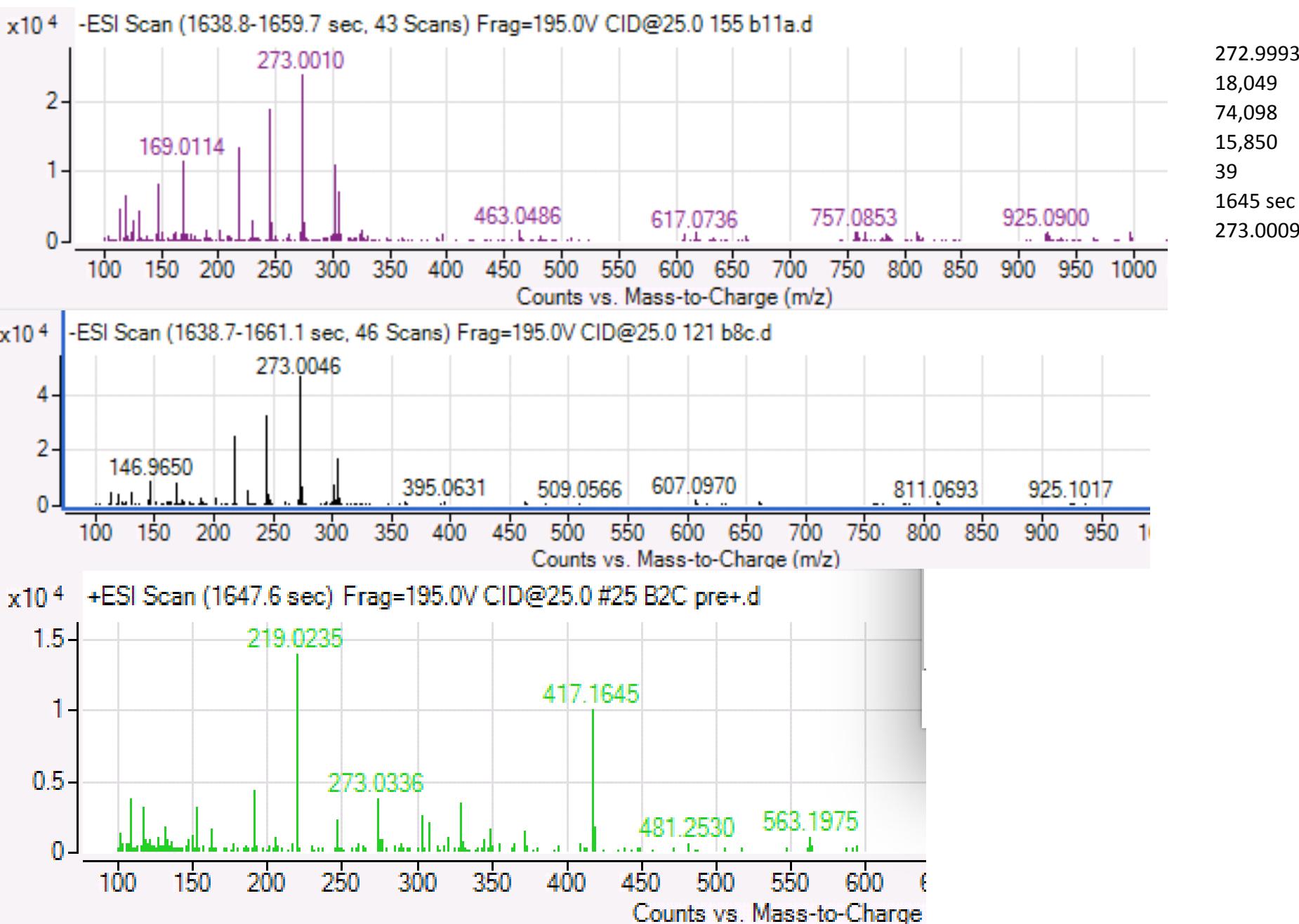
997.119  
757.092  
617.079  
300.998  
169.012  
9,016  
22,264  
3,942  
38  
1631 sec  
169.011



Ellagic acid



# Peak 39: 1645 seconds BP 273.001 = unknown compound

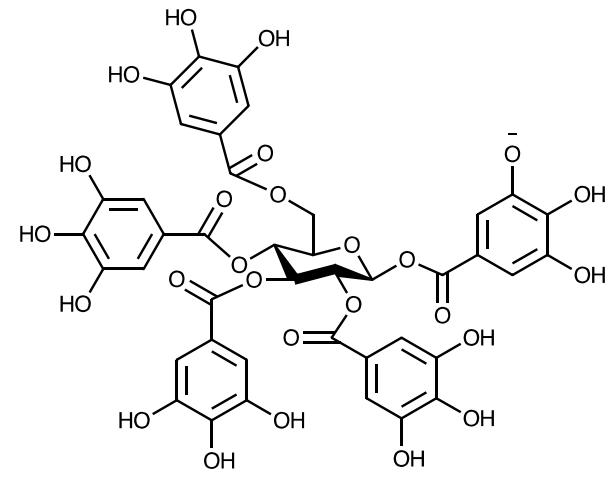
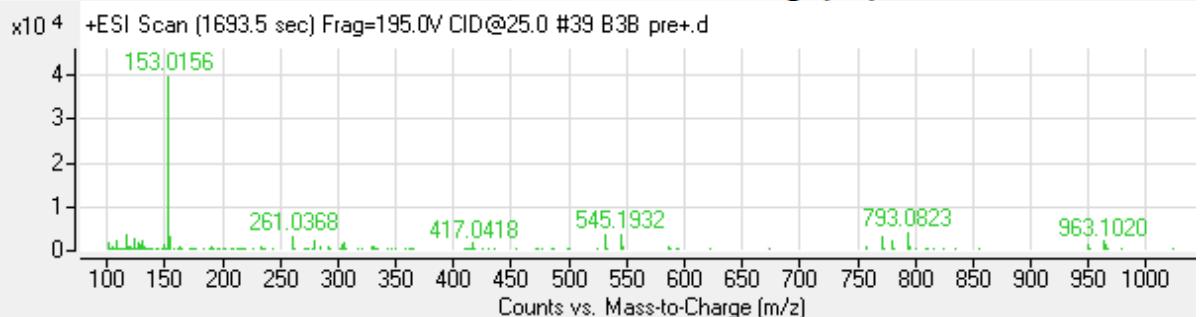
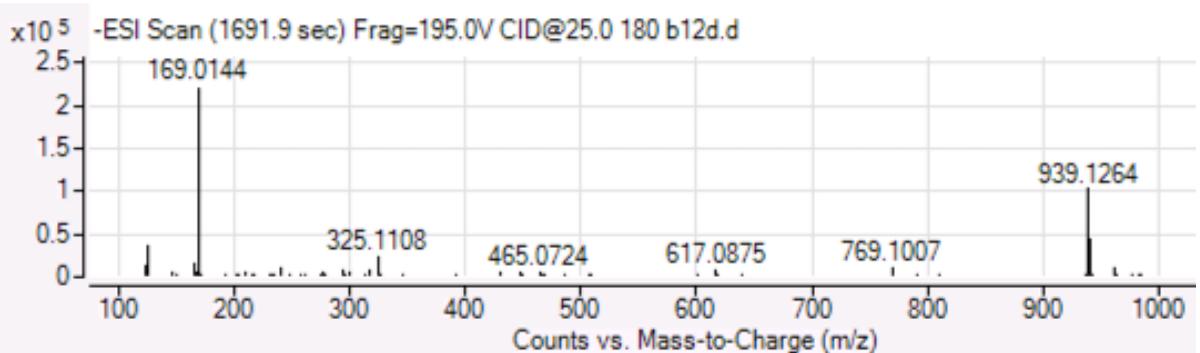


Peak 40: 1650 seconds BP 273.001 = unknown compound

Possibly the tail of peak at 1645 sec

17,544  
68,100  
13,149  
40  
1650 sec  
273.0014

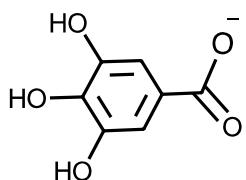
# Peak 41: 1692 seconds BP 169.011 = Penta-galloyl-glucose



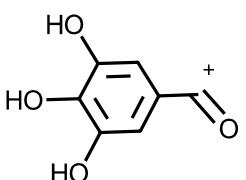
Monoisotopic Mass = 939.111 u  
Molecular Formula =  $C_{41}H_{31}O_{26}^-$

939.1056  
769.0837  
617.0715  
465.0641  
169.0111

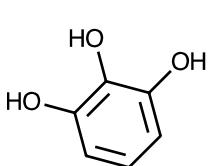
(2S,3S,4S,5S)-3,4,5-Tris(3,4,5-trihydroxybenzoyloxy)-5-[(3,4,5-trihydroxybenzoyloxy)methyl]tetrahydro-2H-pyran-2-yl 3,4-dihydroxy-5-oxybenzoate



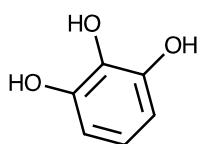
Monoisotopic Mass = 169.014 u



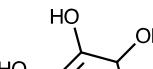
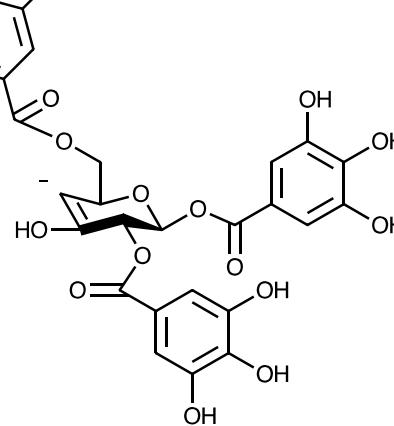
Monoisotopic Mass = 153.018 u



Monoisotopic Mass = 465.067 u



Monoisotopic Mass = 617.078 u



Monoisotopic Mass = 769.089 u

34,072

216,816

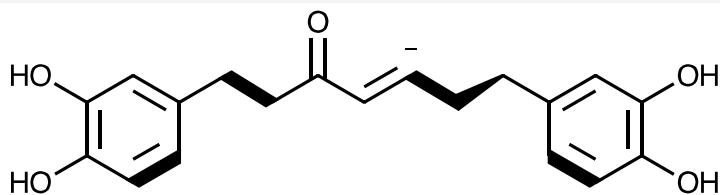
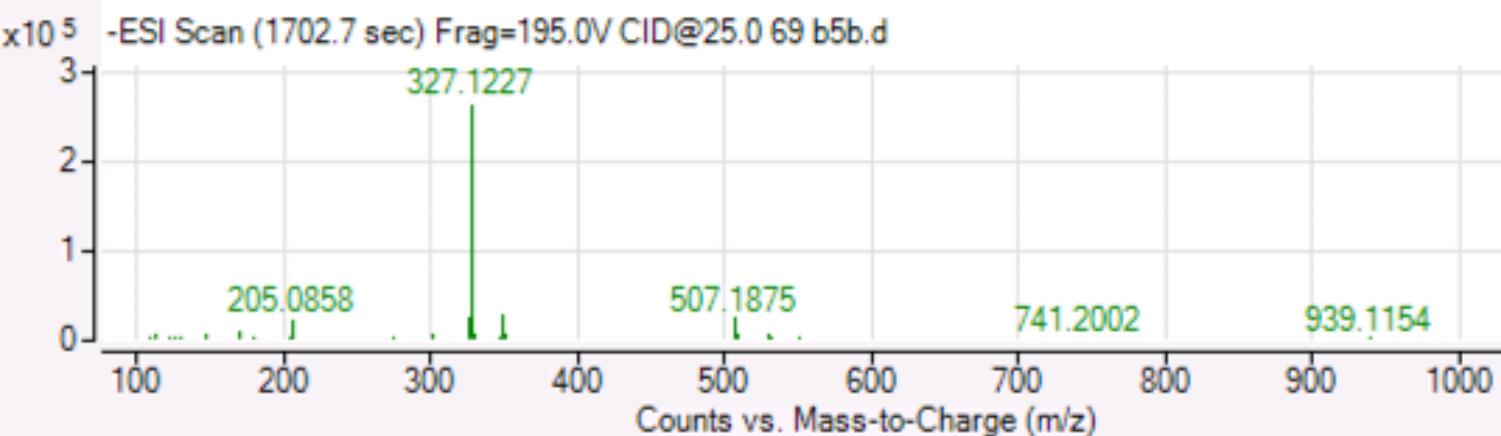
29,219

41

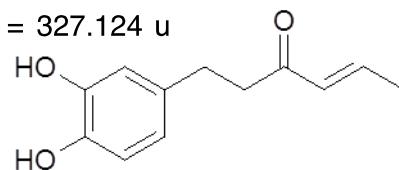
1692 sec

169.0114

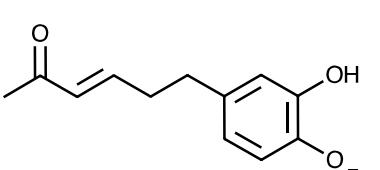
Peak 42: 1701 seconds BP 327.115 = Hirsutanonol-5-O-B-D-glucopyranoside (HOG)



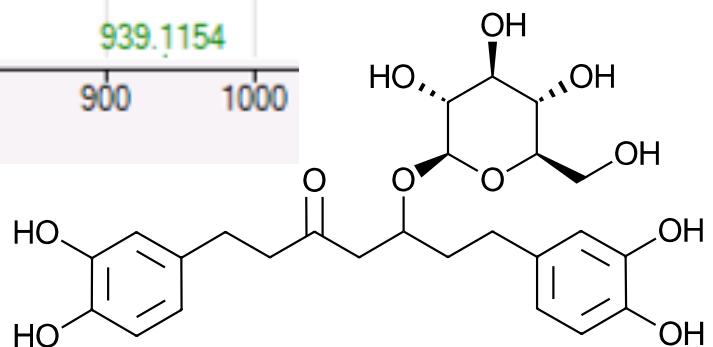
Monoisotopic Mass = 327.124 u



m/z- =205.0870  
C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>

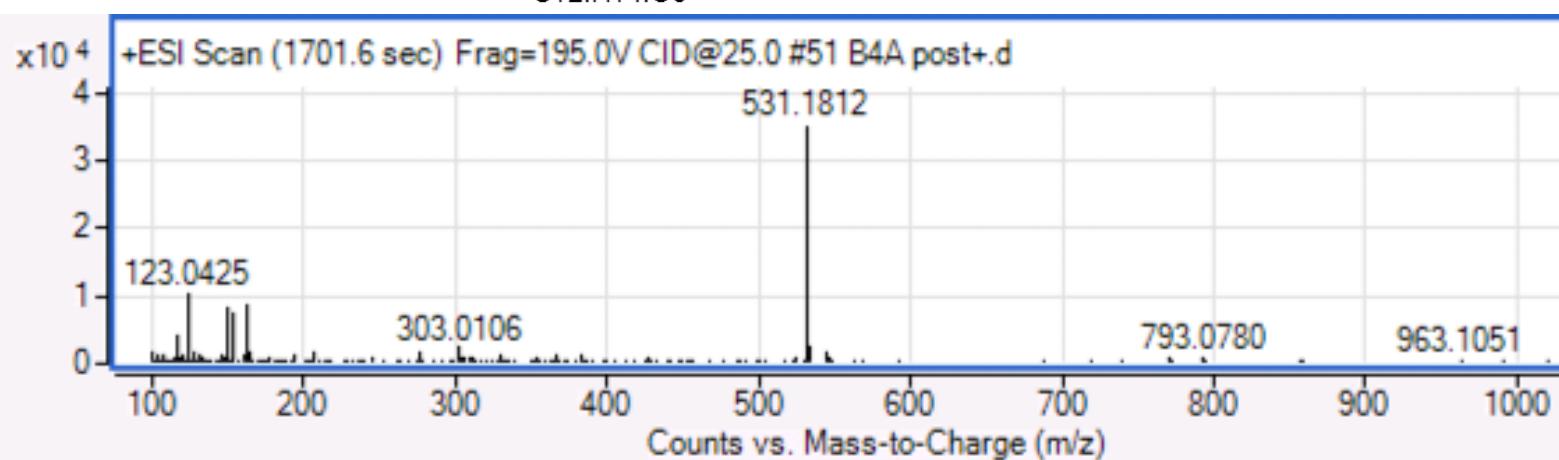


Monoisotopic Mass = 205.087 u

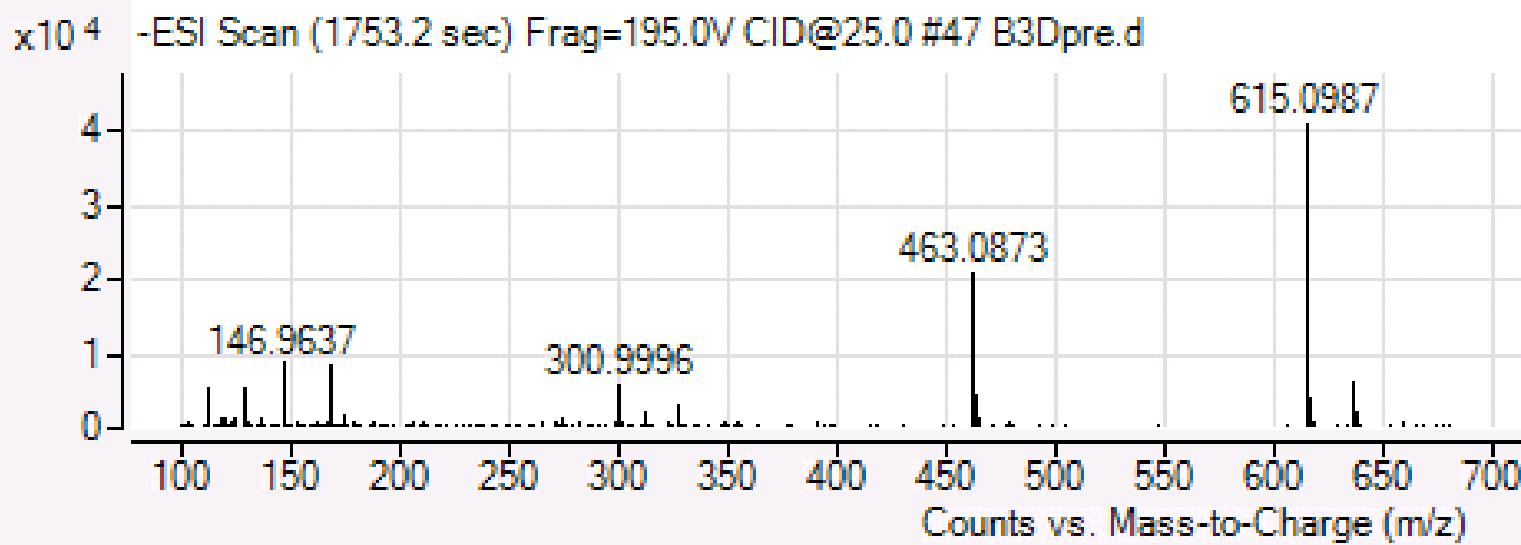


**106. hirsutanonol-5-O-B-D-glucopyranoside  
#7 Novakovic**

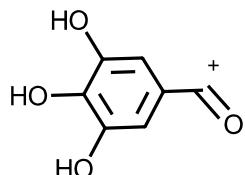
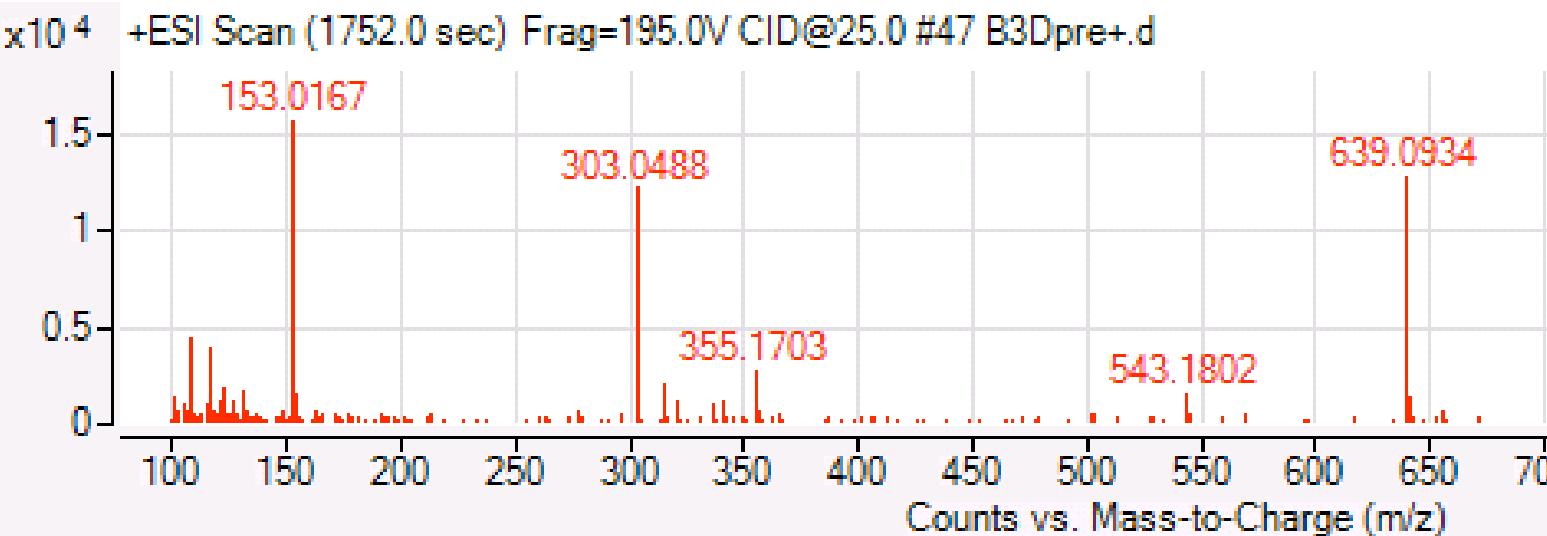
Molecular Formula = C<sub>25</sub>H<sub>31</sub>O<sub>11</sub>  
Monoisotopic Mass = 507.187 u



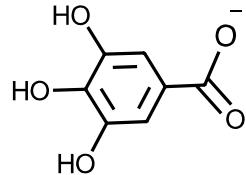
# Peak 43: 1750 seconds BP 615.093 = unknown compound



615.087  
 463.077  
 300.991  
 19,178  
 50,174  
 10,732  
 43  
 1750 sec  
 615.093

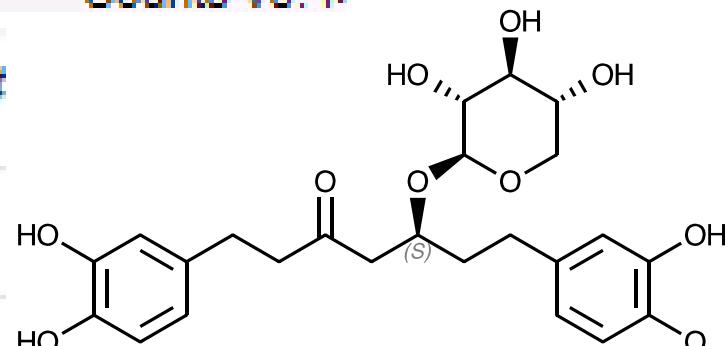
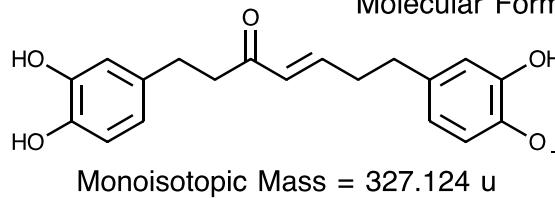
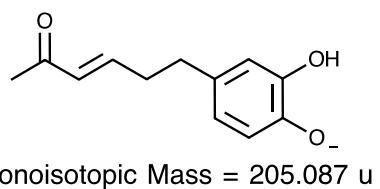
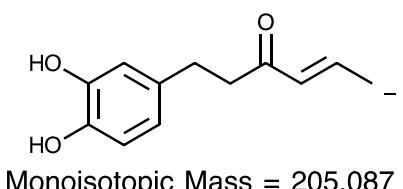
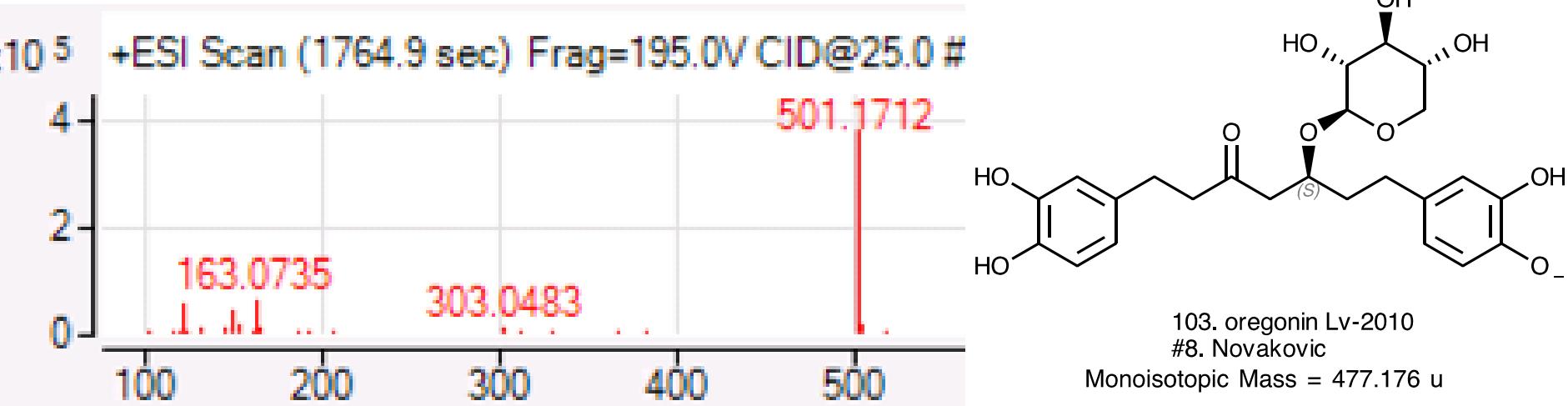
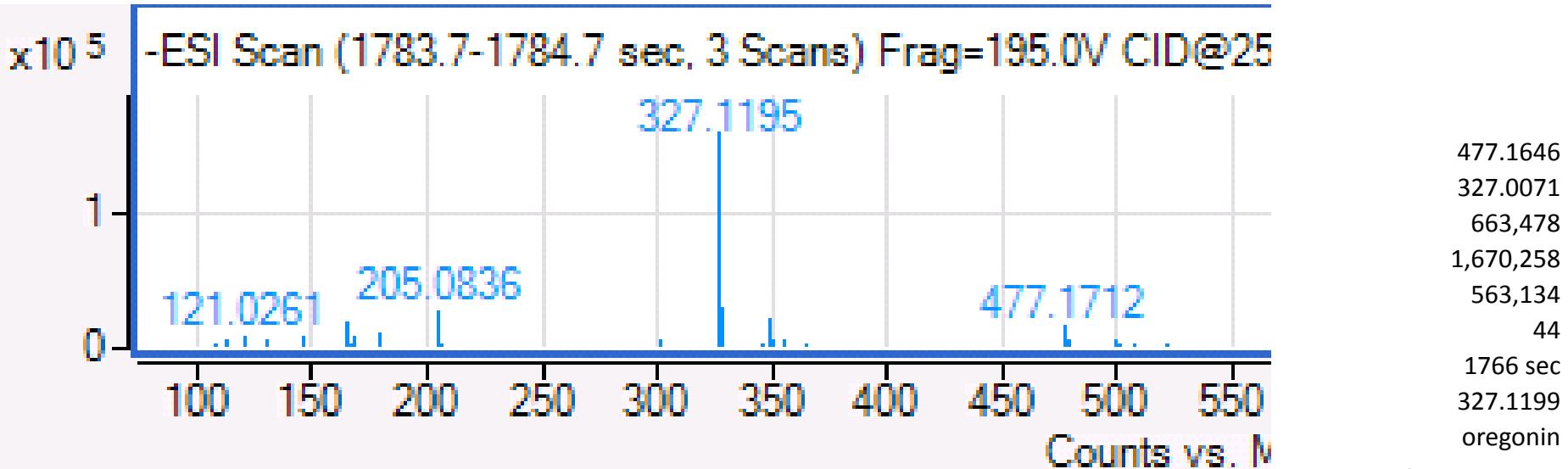


Monoisotopic Mass = 153.018 u

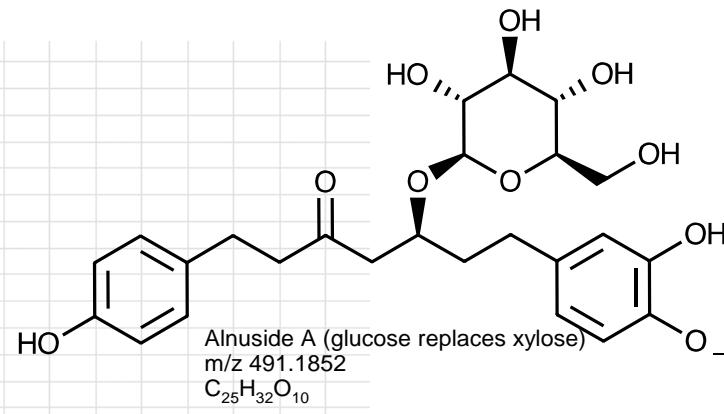
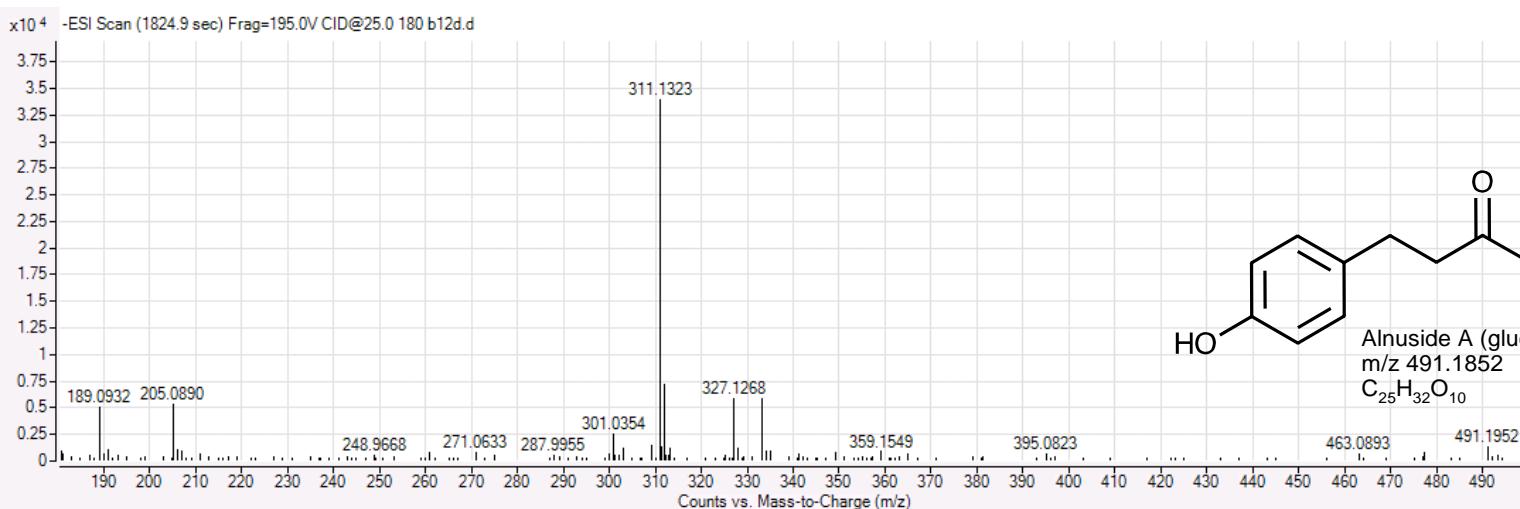


Monoisotopic Mass = 169.014 u

# Peak 44: 1766 seconds BP 327.1199 = Oregonin



# Peak 45: 1826 seconds BP 311.126 = Alnuside A-glycoside



491.185

311.123

7,974

33,965

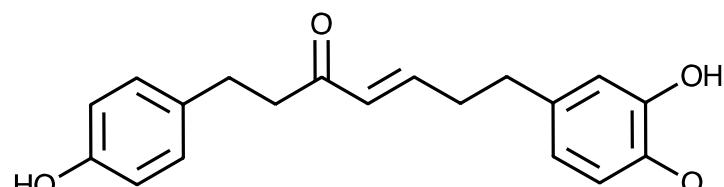
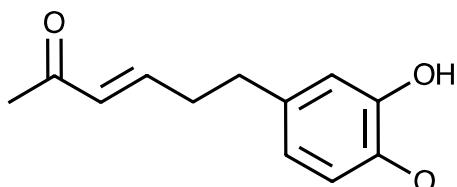
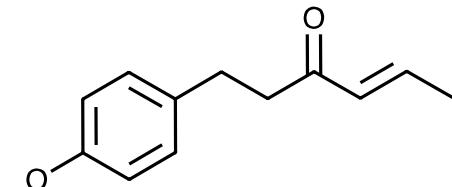
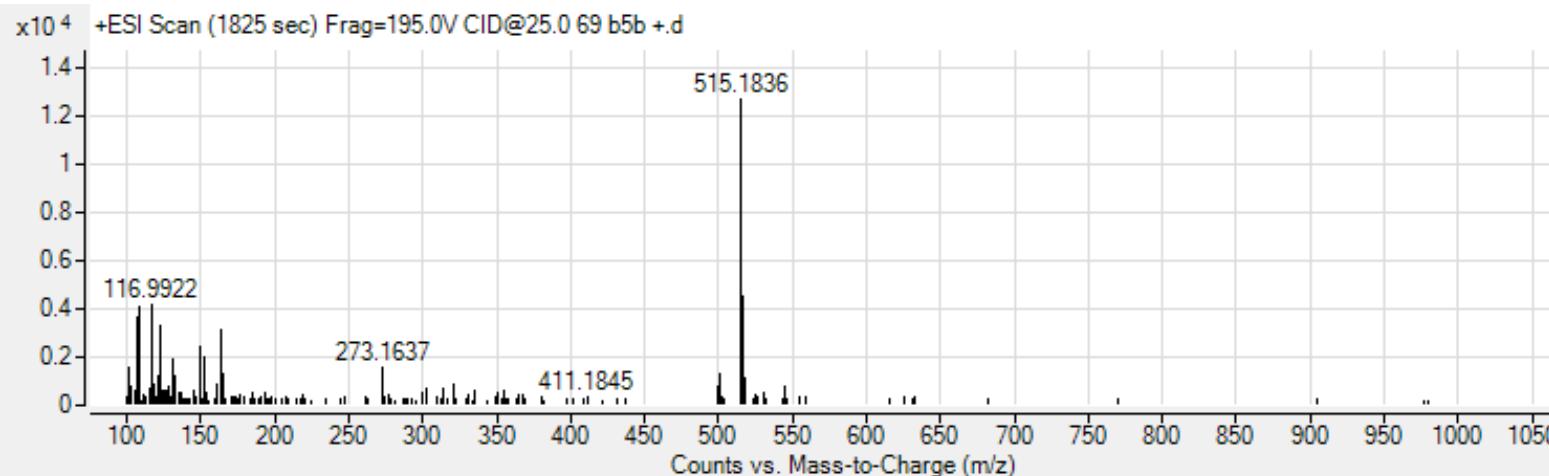
6,713

45

1826 sec

311.126

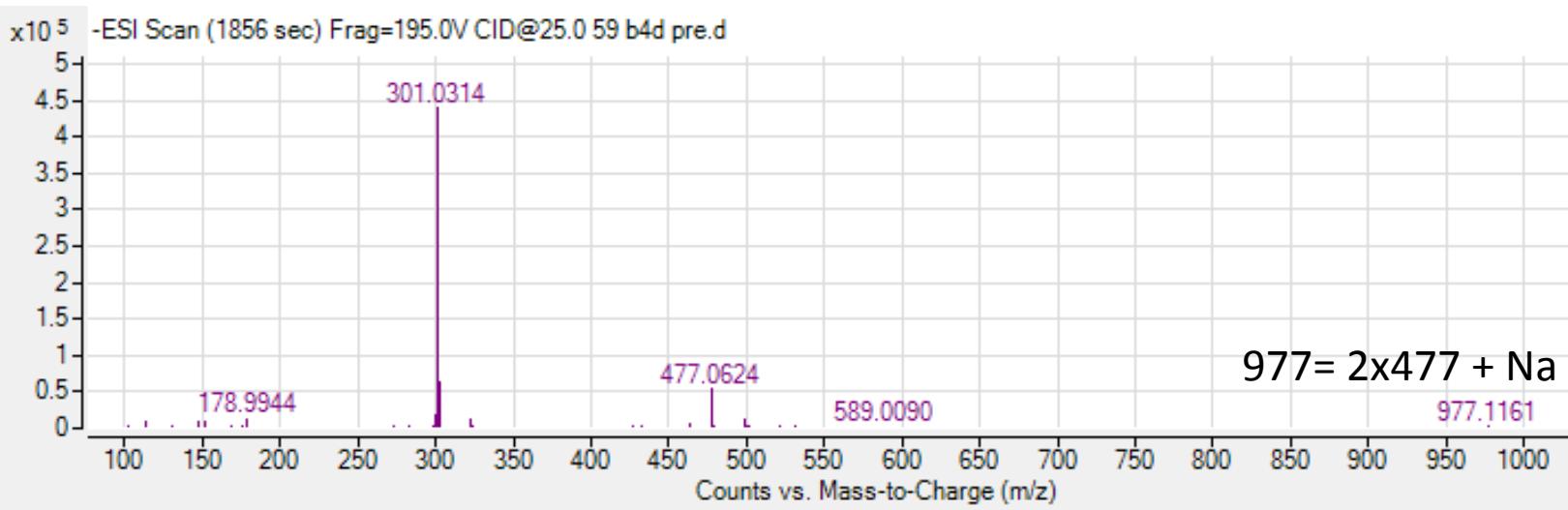
Alnuside A with  
glucose replacing  
xylose



Monoisotopic Mass = 189.092 u Monoisotopic Mass = 205.087 u

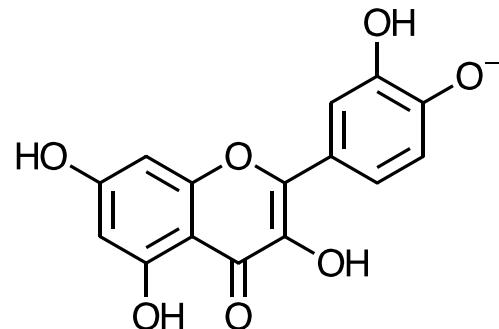
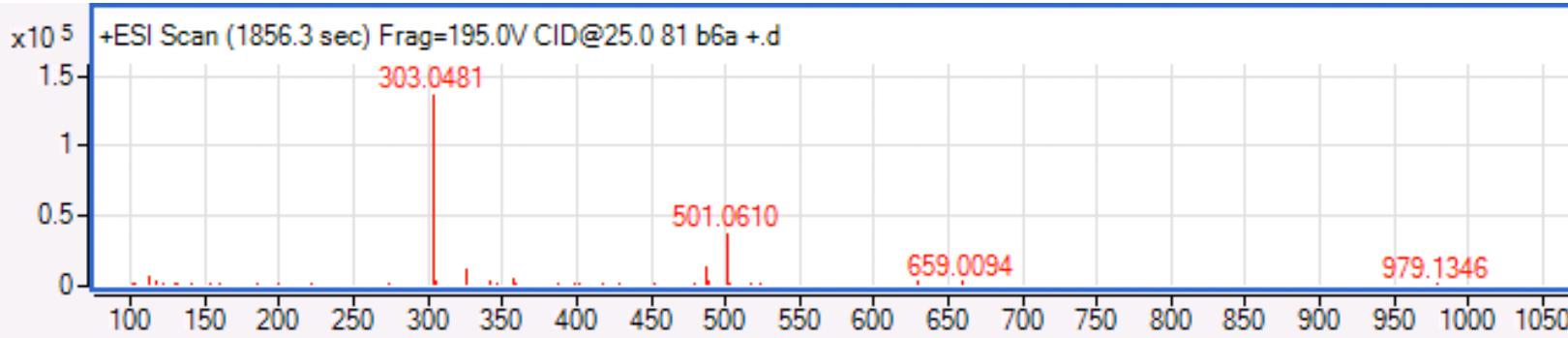
Monoisotopic Mass = 311.129 u

# Peak 46: 1856 seconds BP 301.031 = Quercetin glucuronide

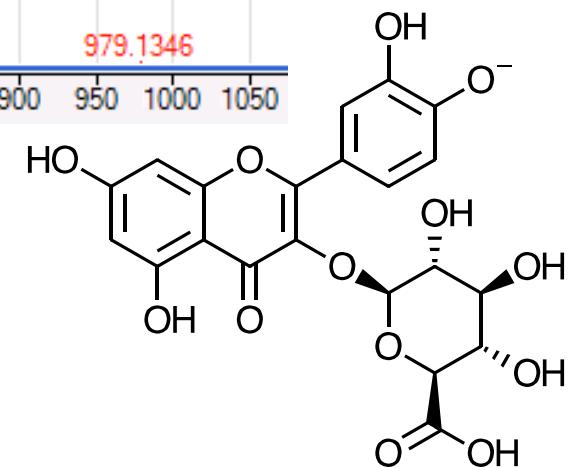


477.0624  
301.0314  
410,595  
811,755  
158,595  
46

1856 sec  
301.031  
Quercitin-  
glucuronide

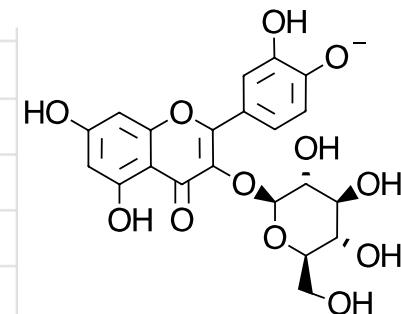
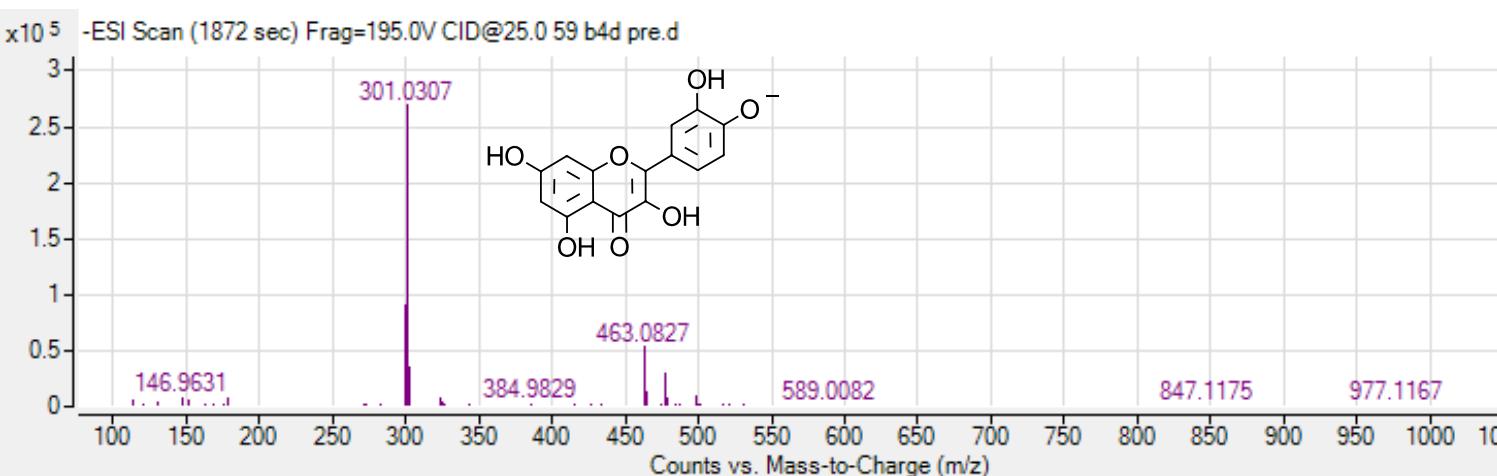


Monoisotopic Mass = 301.035 u

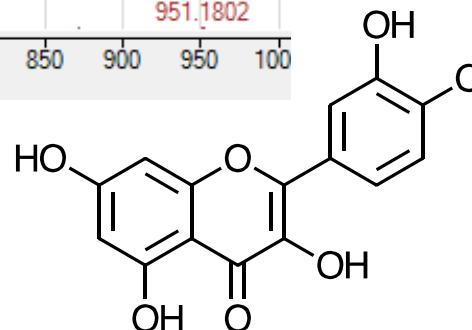
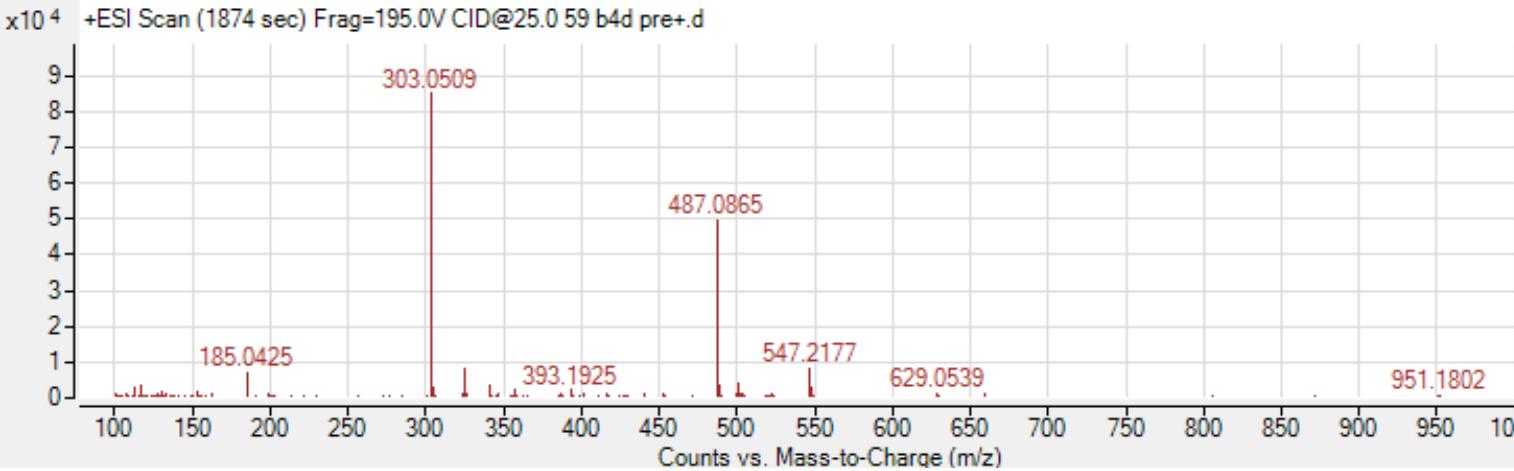


Monoisotopic Mass = 477.067 u

# Peak 47: 1873 seconds BP 463.083 = Quercetin glycoside



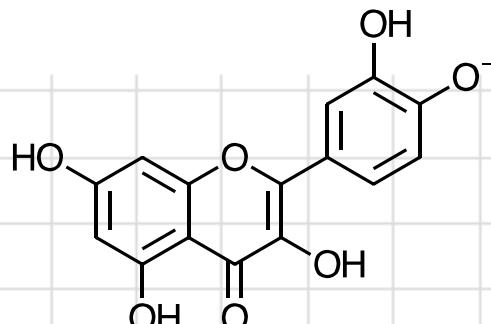
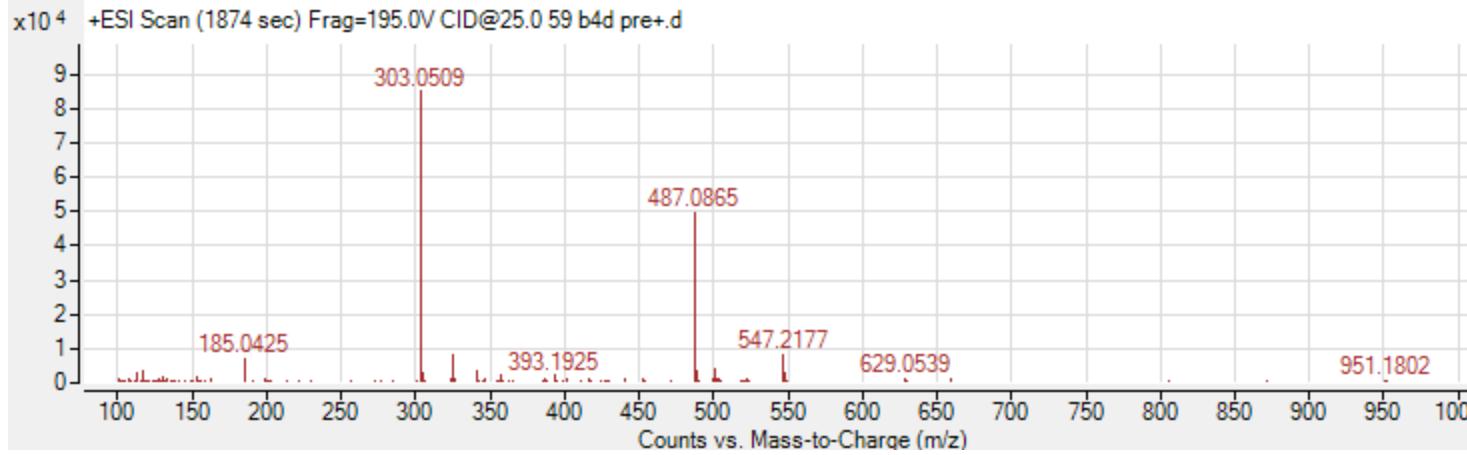
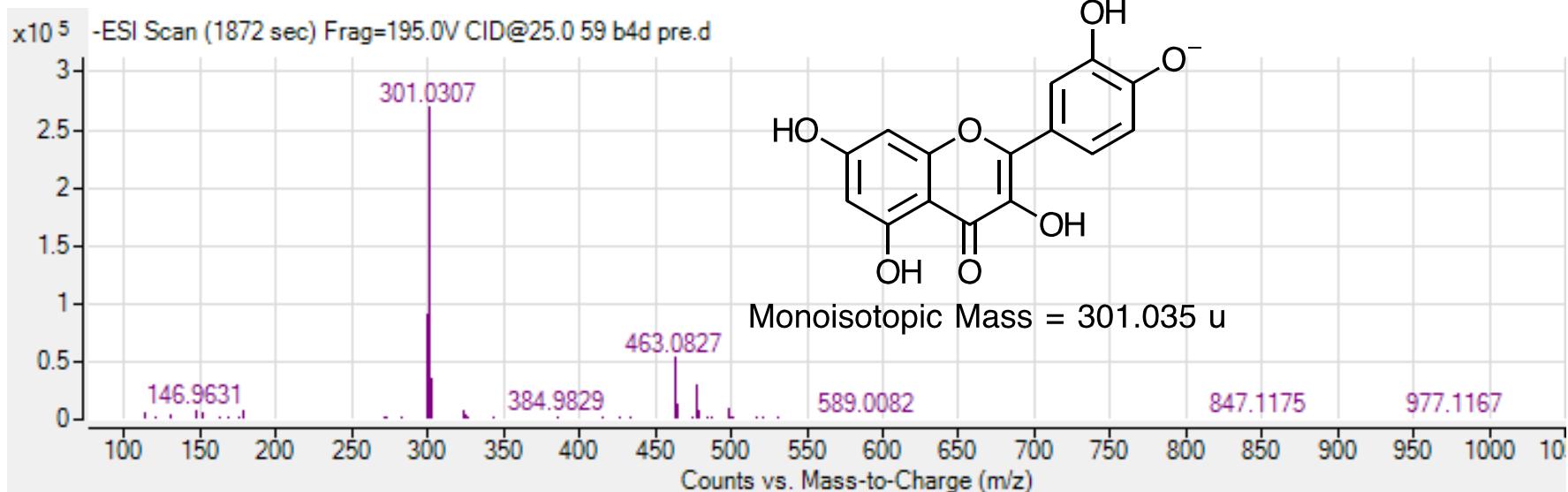
Quercetin3-O-glucoside  
m/z 463.0882  
C<sub>21</sub>H<sub>20</sub>O<sub>12</sub>



Monoisotopic Mass = 301.035 u

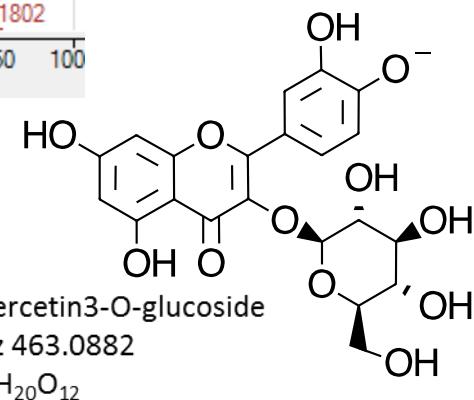
463.0827  
301.0307  
39,725  
293,768  
42,512  
47  
1873 sec  
463.0831  
Quercitin-  
glucoside

# Peak 47: 1873 seconds BP 463.083 = Quercetin glycoside

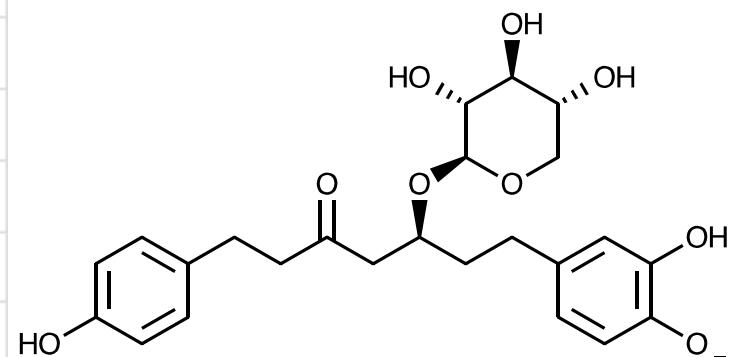
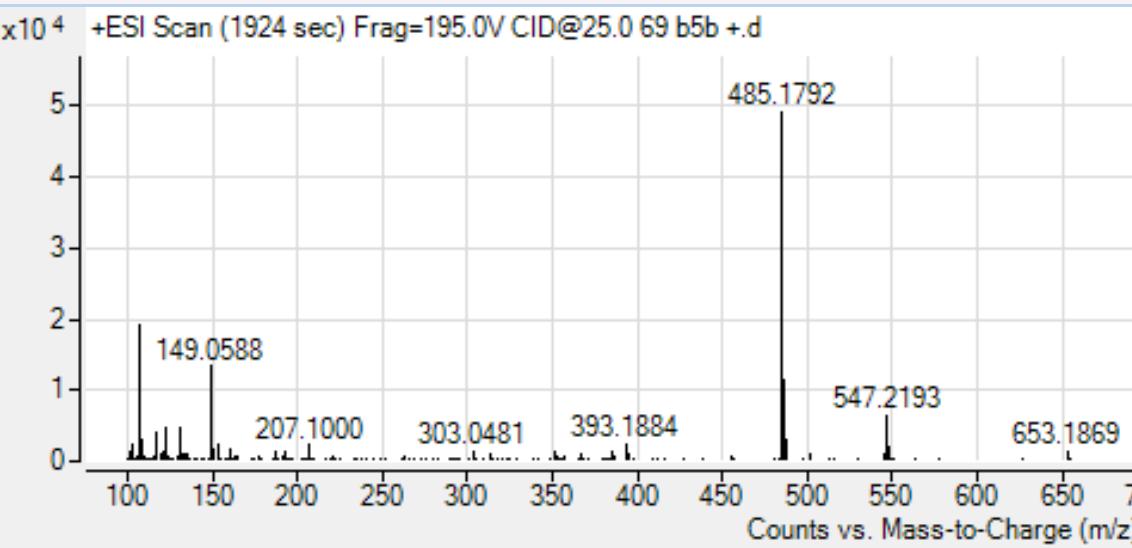
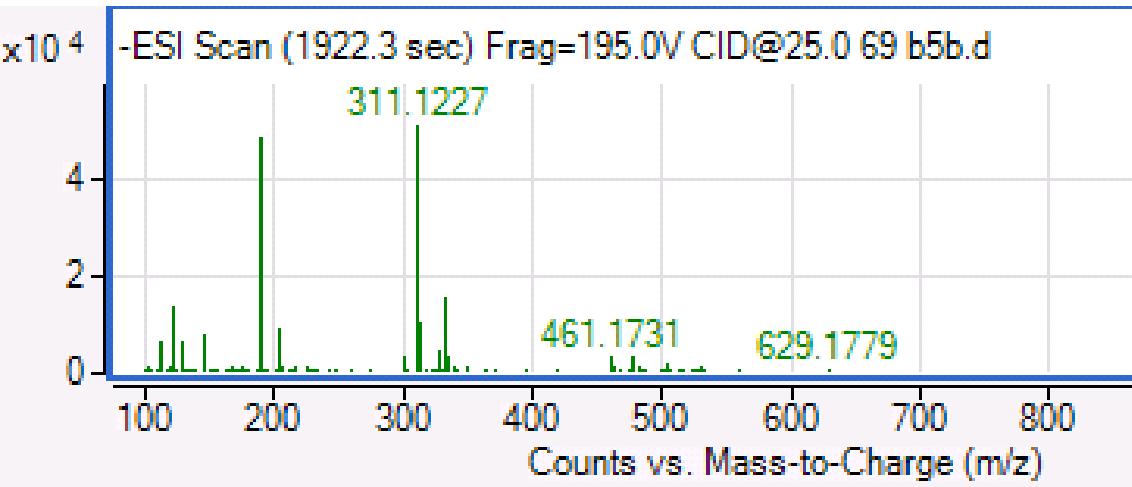


Monoisotopic Mass = 301.035 u

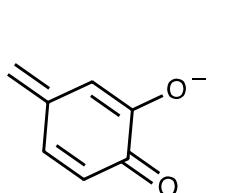
463.0827  
301.0307  
39,725  
293,768  
42,512  
47  
1873 sec  
463.0831



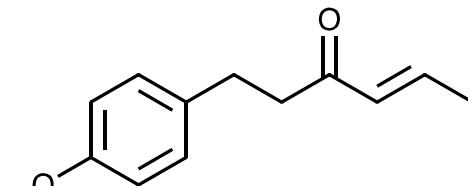
# Peak 48: 1924 seconds BP 311.124 = Alnuside A (xyloside)



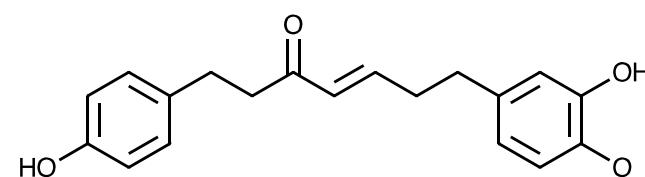
Monoisotopic Mass = 461.182 u  
89. alnuside A (Kuroyanagi 2005)



Monoisotopic Mass = 121.029 u



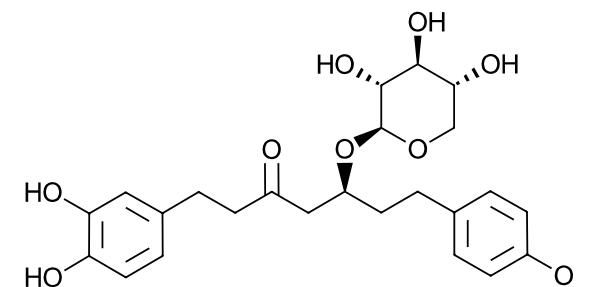
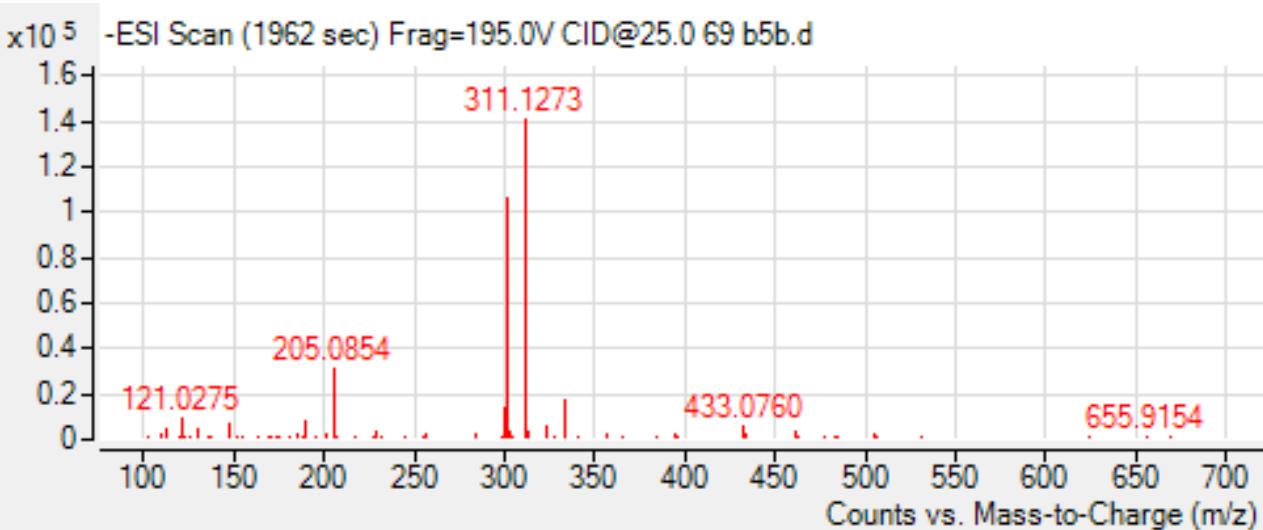
Monoisotopic Mass = 189.092 u



Monoisotopic Mass = 311.129 u

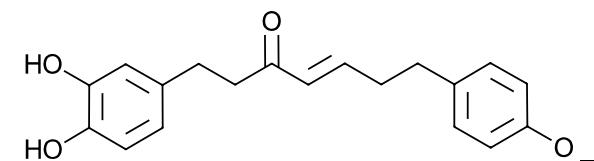
461.209  
311.151  
205.104  
11,986  
78,792  
12,377  
48  
1924 sec  
311.124  
Alnuside A

# Peak 49: 1960 seconds BP 300.9953 = Alnuside B

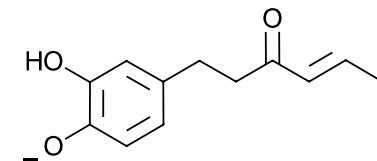


#4. Novakovic

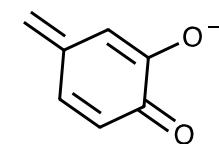
Monoisotopic Mass = 461.182 u



Monoisotopic Mass = 311.129 u



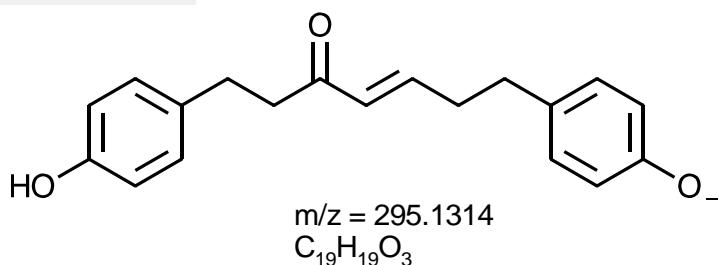
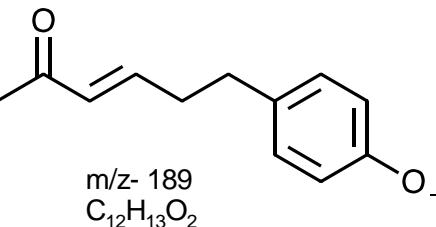
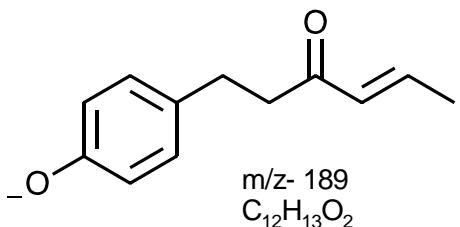
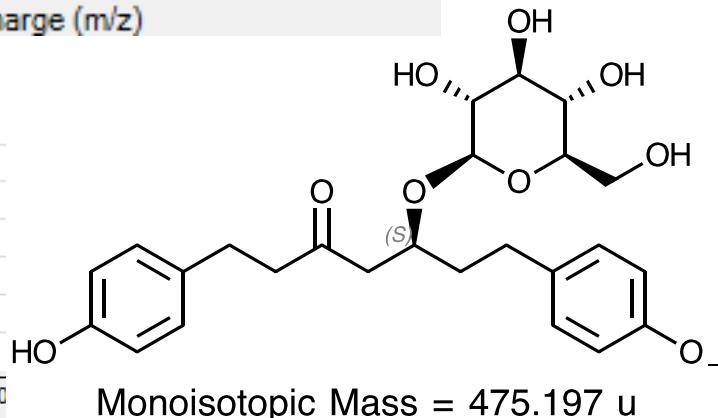
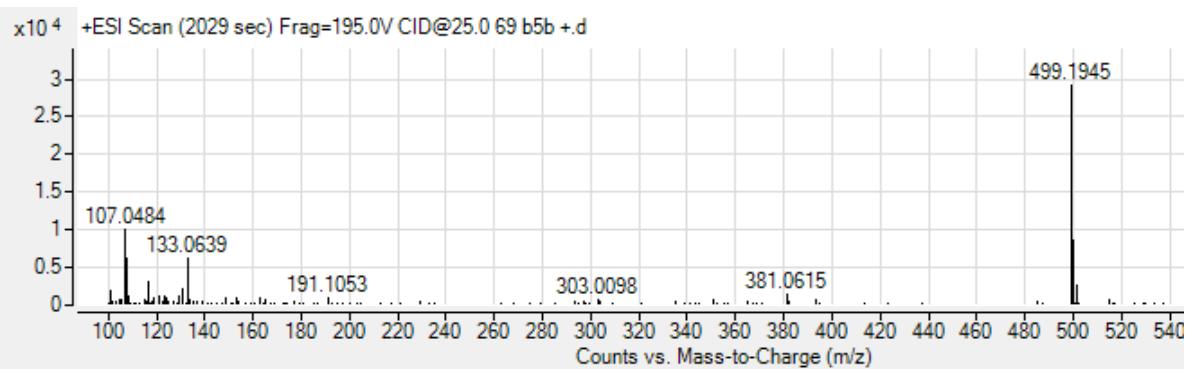
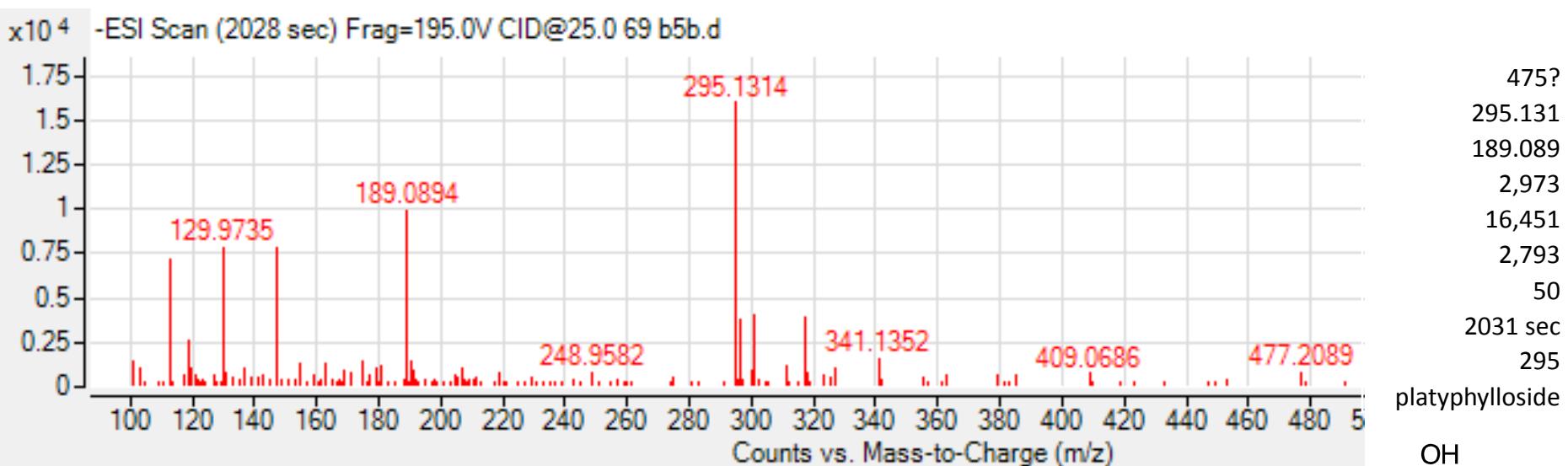
Monoisotopic Mass = 205.087 u



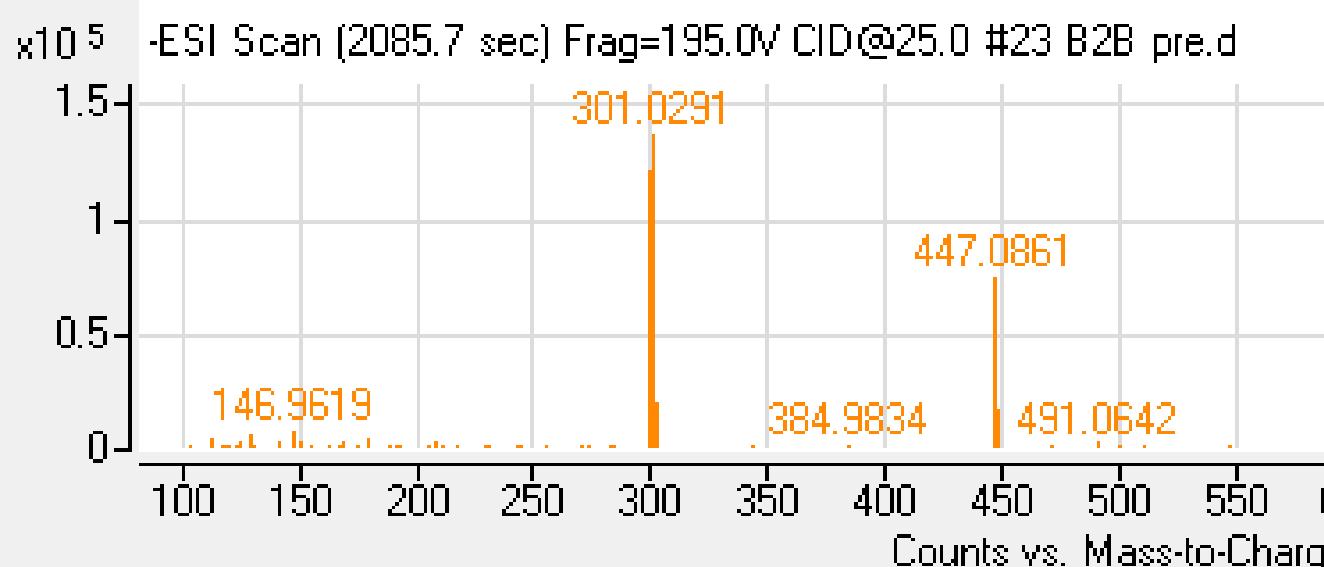
Monoisotopic Mass = 121.029 u

Samples with large amounts of Alnuside A have this peak 40 seconds later (485 peak belongs to the DAH, 457 goes with flavonoid + xylose???)

# Peak 50: 2031 seconds BP 295.0 = Platiphyllonol xyloside

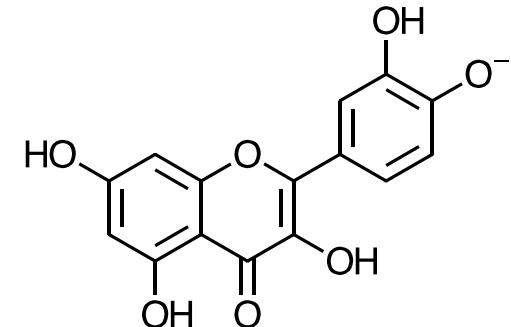
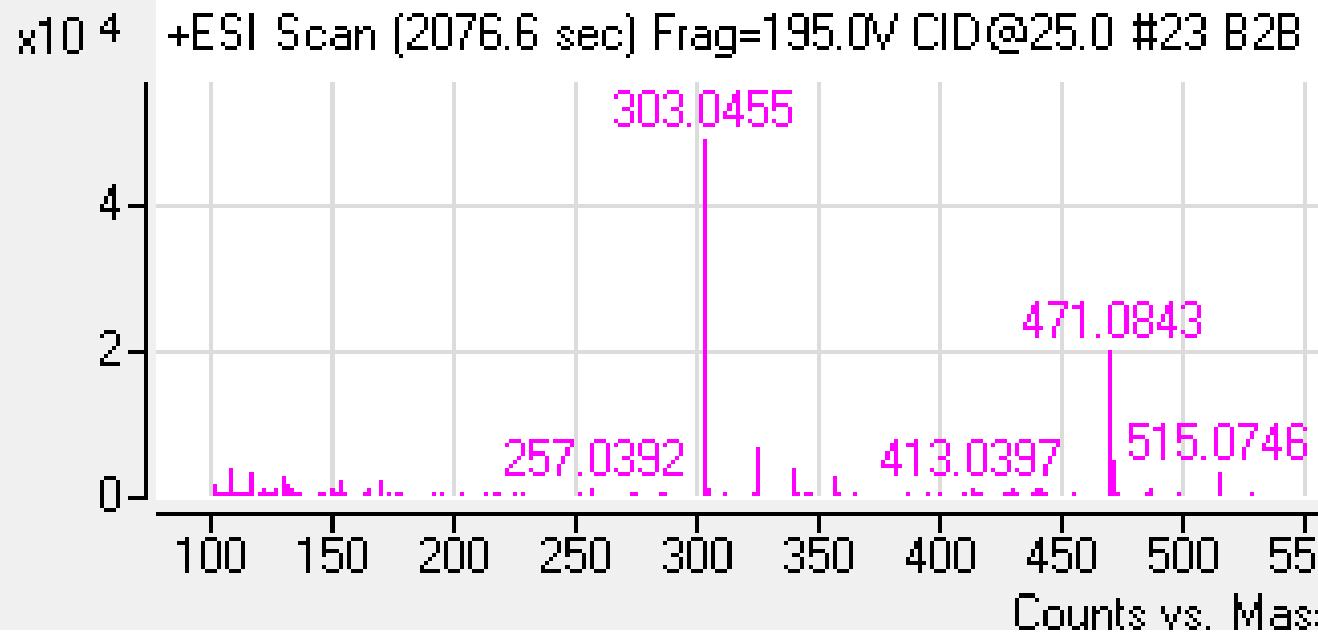
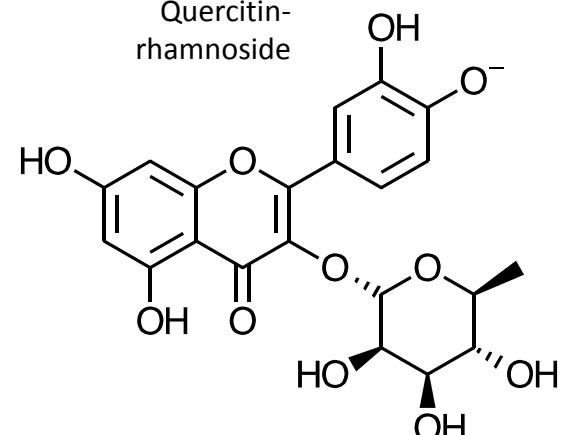


# Peak 51: 2075 seconds BP 301.03 = Quercetin rhamnoside

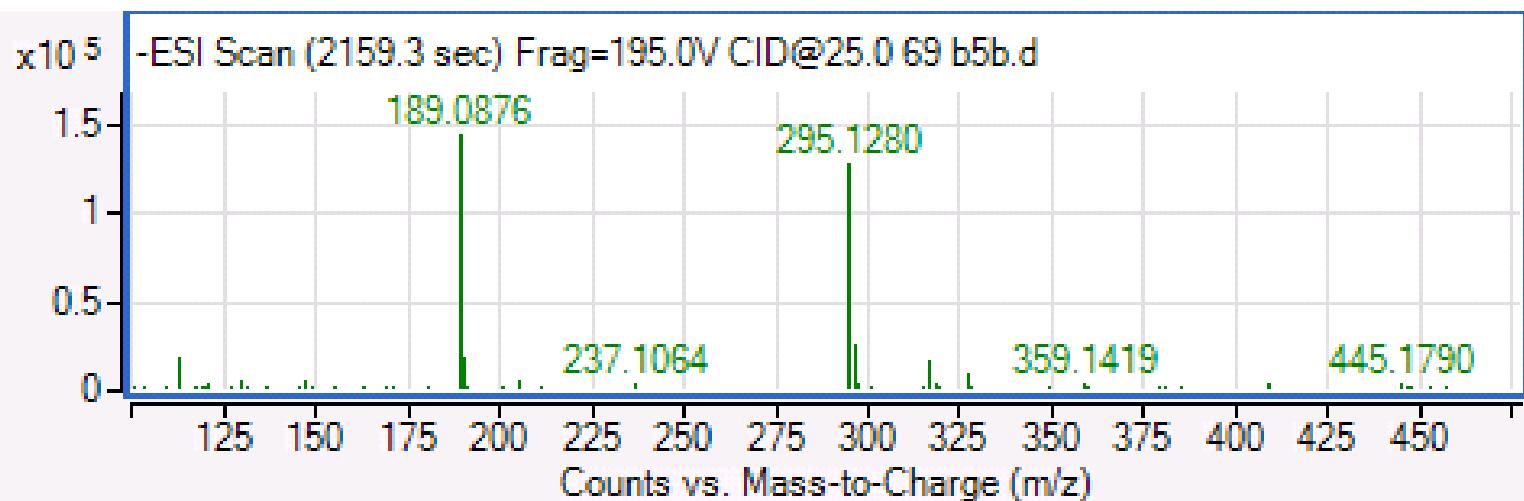


447.0861  
301.0291  
122,604  
259,407  
50,319  
51  
2075 sec  
301.0296

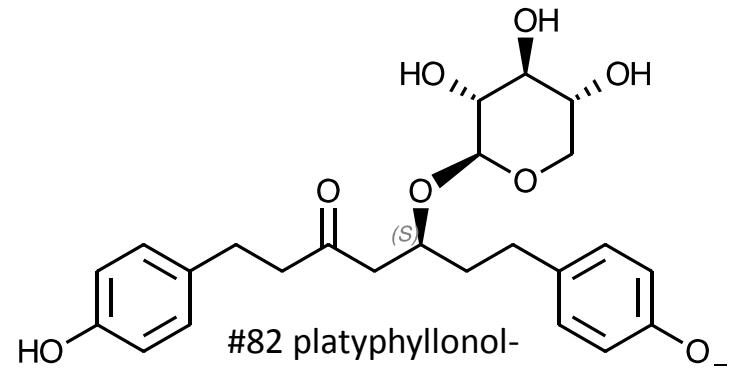
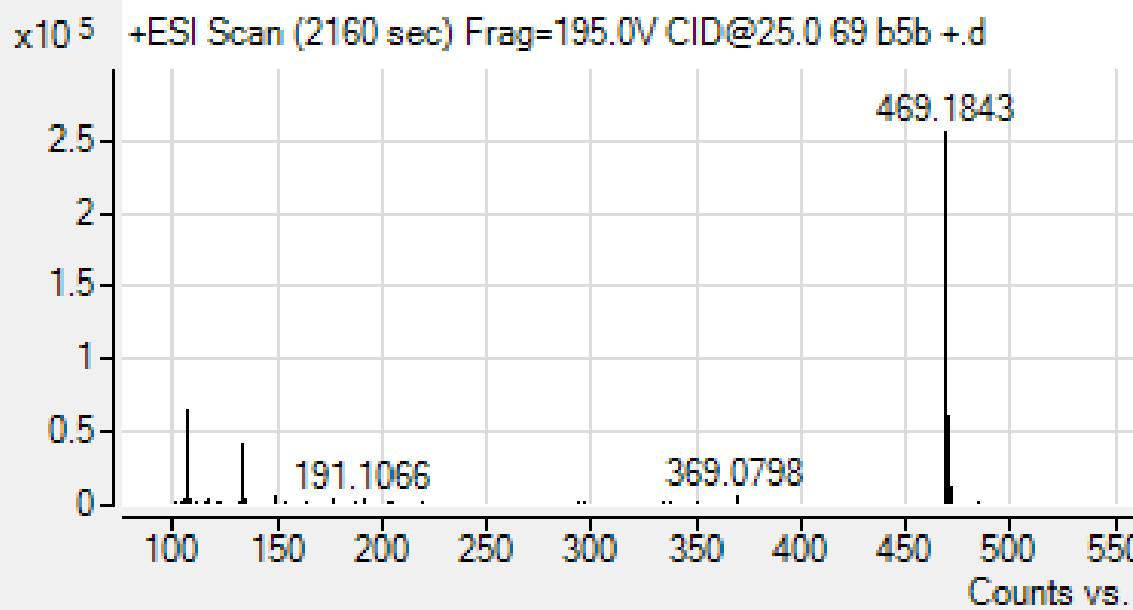
Quercitin-  
rhamnoside



# Peak 52: 2160 seconds BP 189.082= Platyphyllonol-xyloside



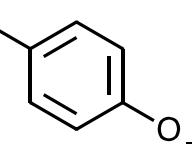
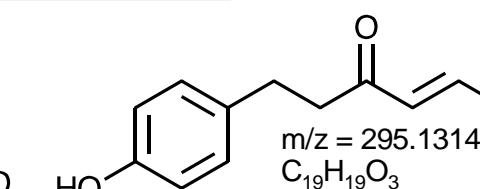
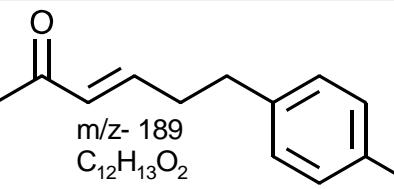
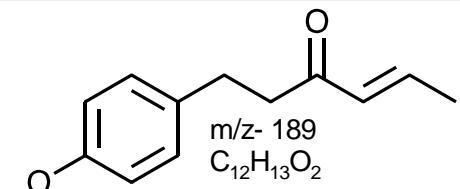
445.1785  
295.1283  
189.0876  
49,696  
297,270  
46,565  
52  
2160 sec  
189.0819



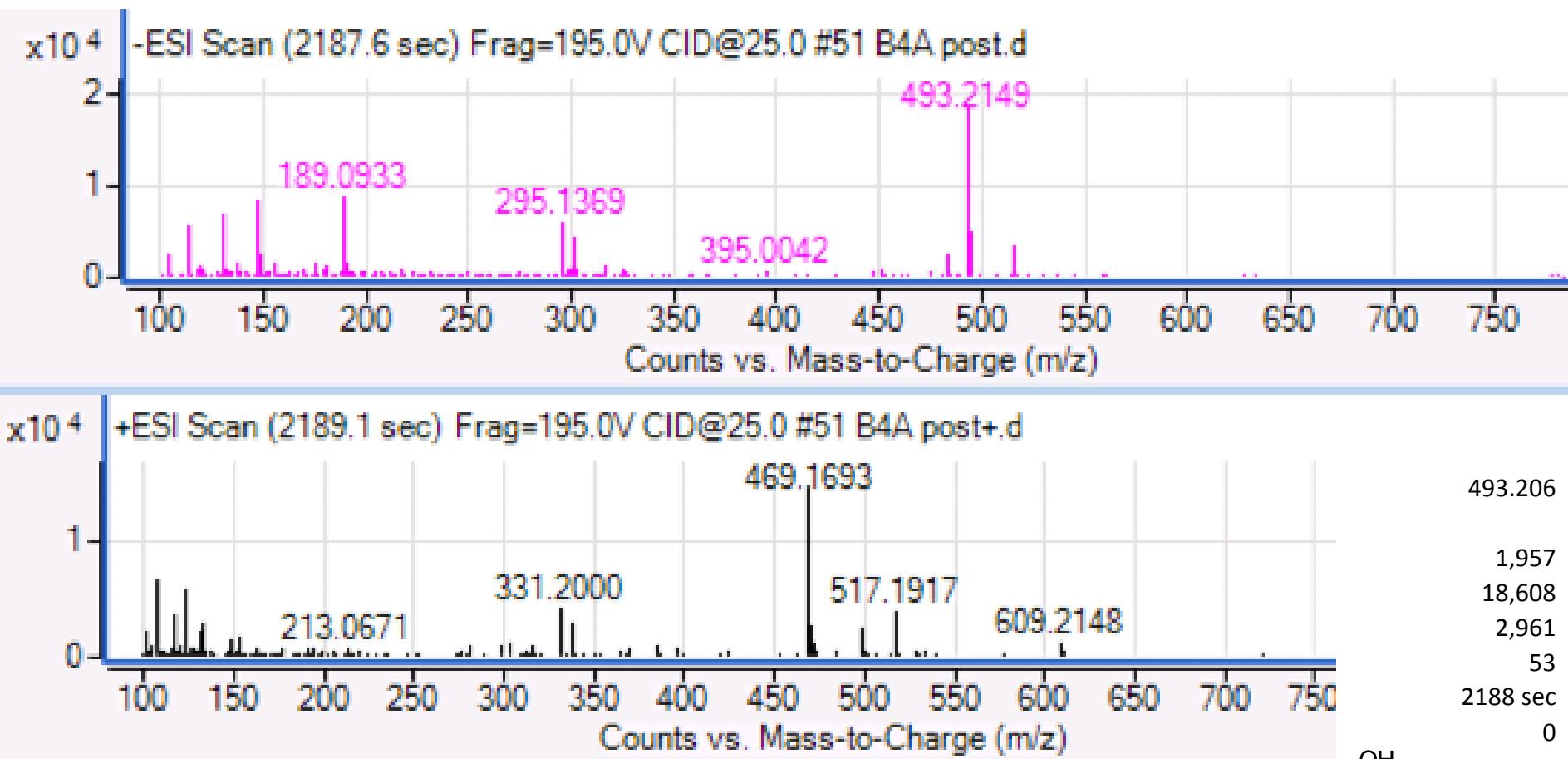
MW 445.1738 ppm +1.123  
MW 469.1843 (+Na) ppm +1.01

$C_{24}H_{30}O_8$

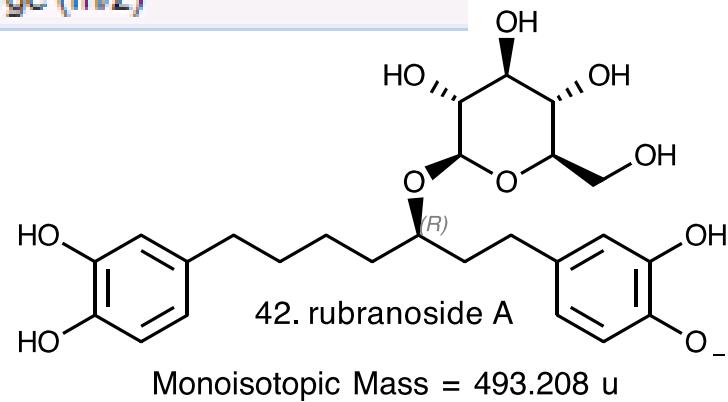
#2 Novakovic 2014



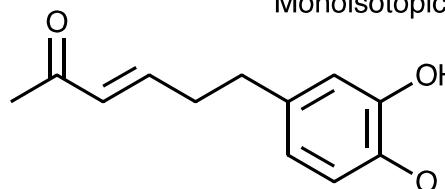
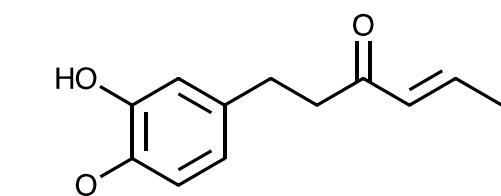
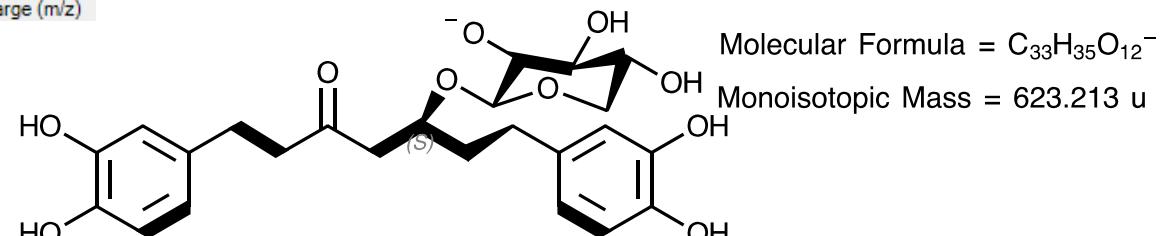
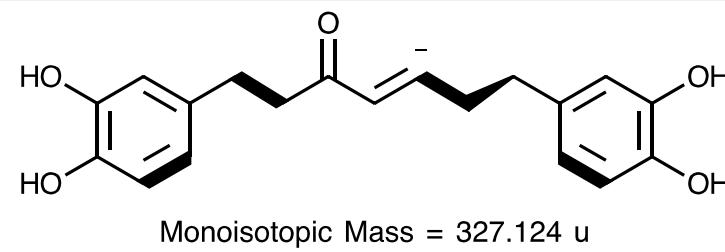
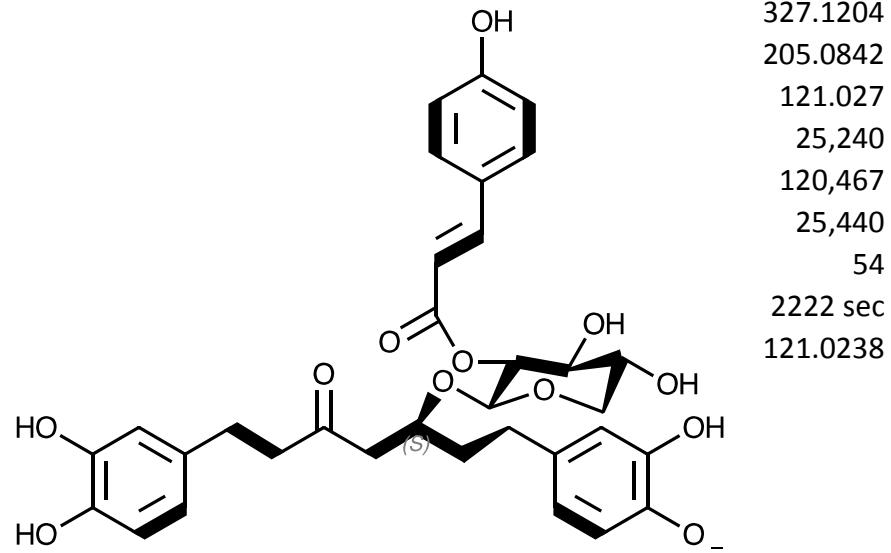
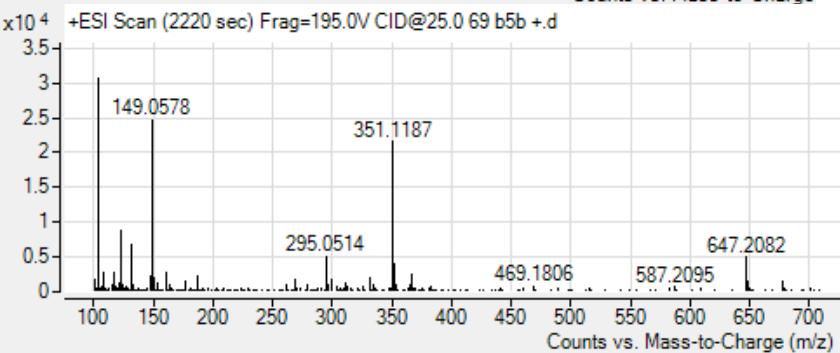
# Peak 53: 2188 seconds BP = Rubranoside A



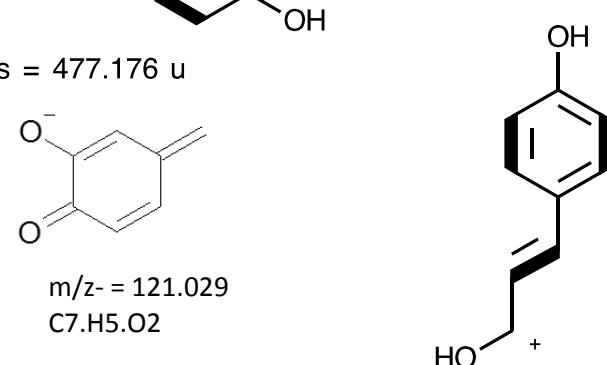
Probably not, 189 fragment suggests 1-OH on left side, lack of 205 rules out Rubranoside A so maybe aglycone.



# Peak 54: 2222 seconds BP 121.024 = Oregonoyl A

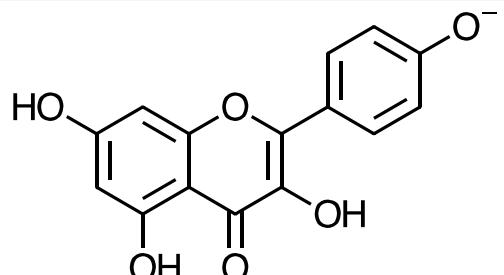
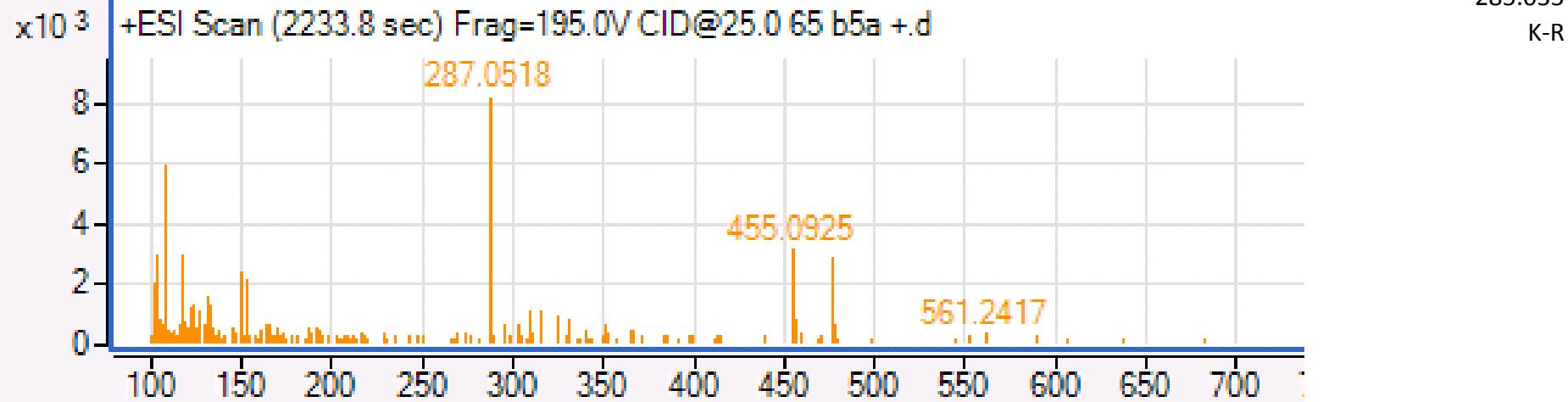
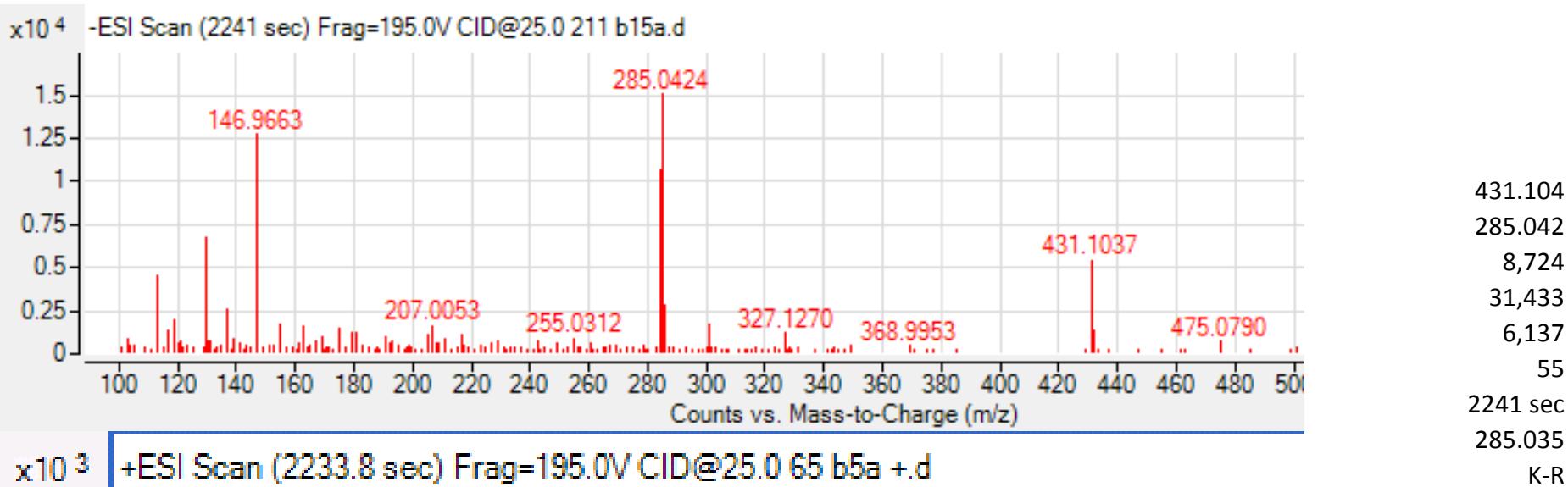


Hirsutanone 327 623 → 647 DAH suggests oregonoyl.  
hirsutanonol + xylose + coumaroyl (Lv2010#104)

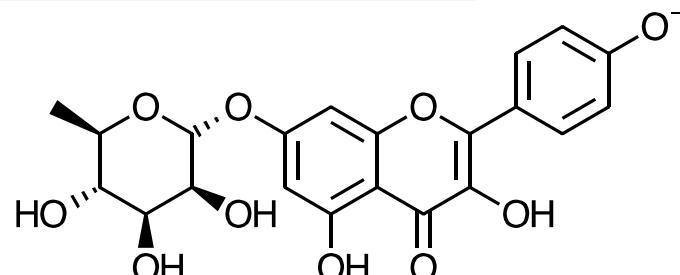


Monoisotopic Mass = 149.060 u

# Peak 55: 2241 seconds BP 285.035 = Kaempferol-rhamnoside

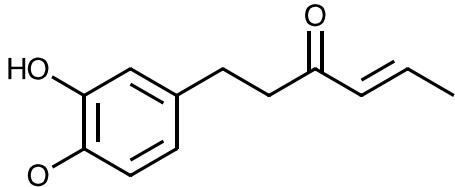
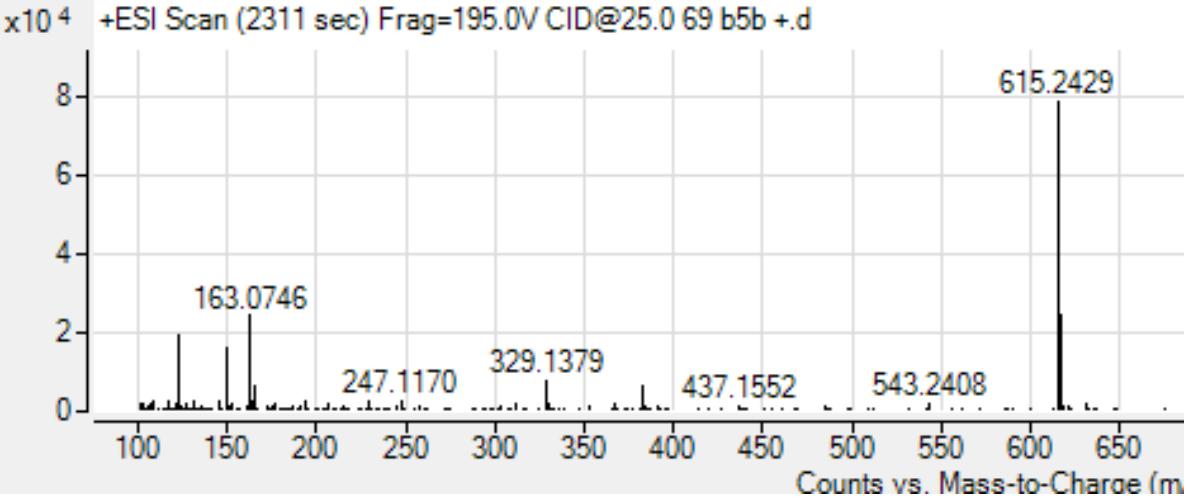
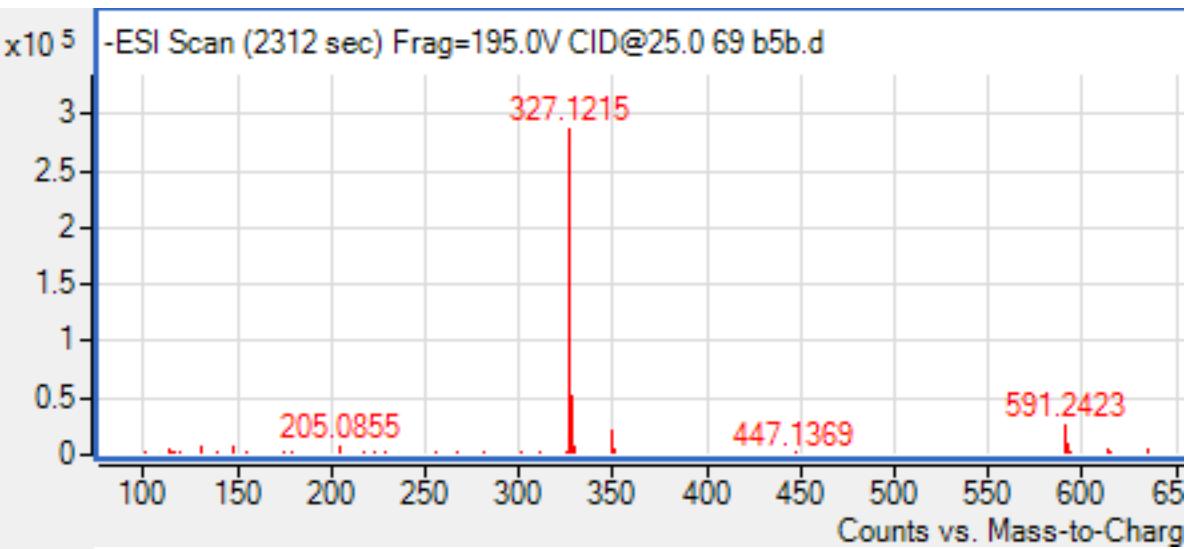


Monoisotopic Mass = 285.040 u

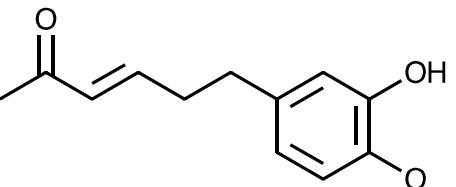


Monoisotopic Mass = 431.098 u

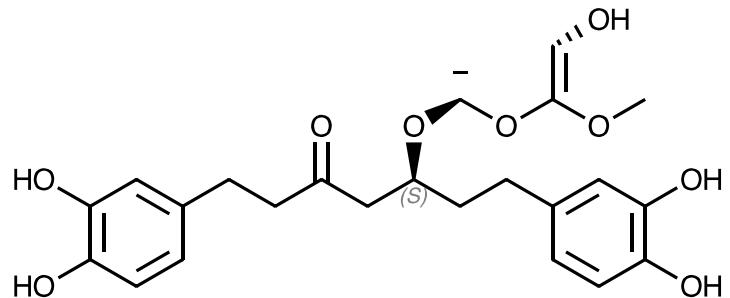
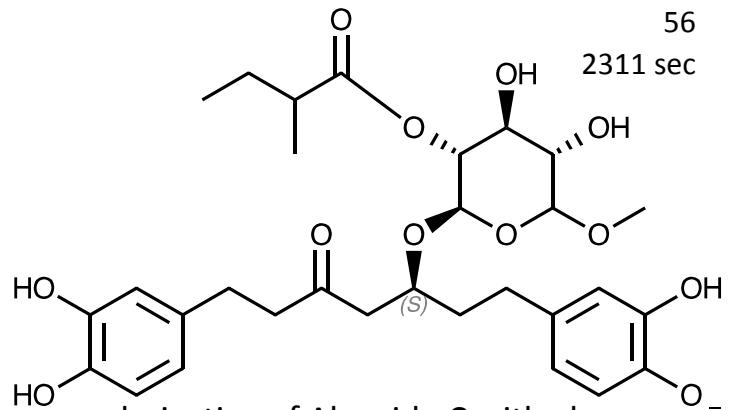
# Peak 56: 2311 seconds BP 327.115 = Alnuside C glycoside



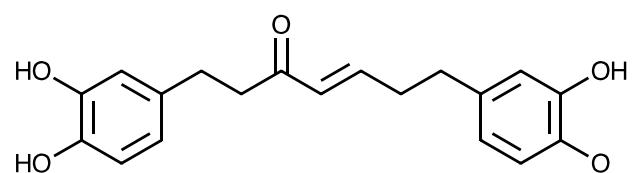
Monoisotopic Mass = 205.087 u



Monoisotopic Mass = 205.087 u

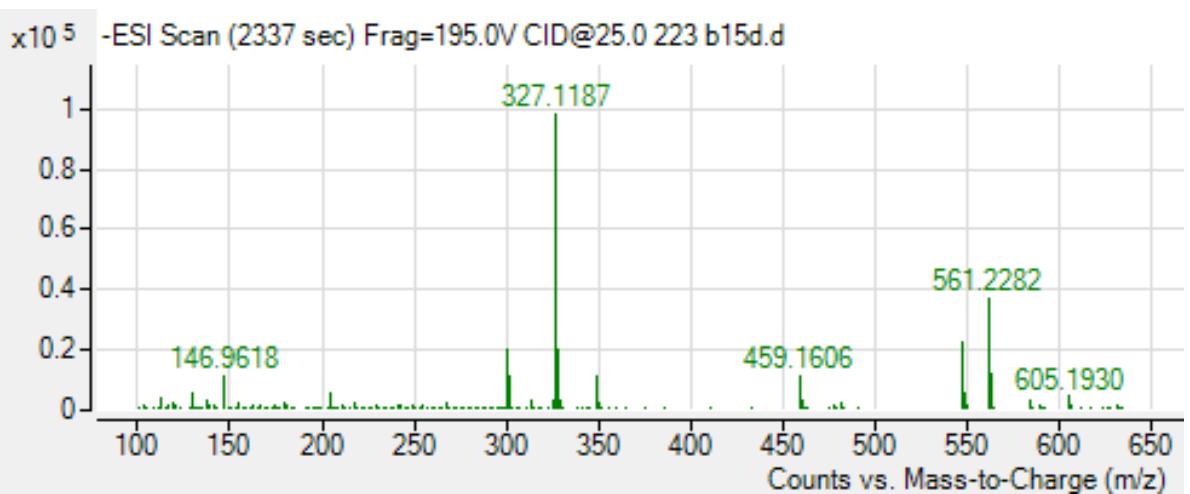


Monoisotopic Mass = 447.166 u



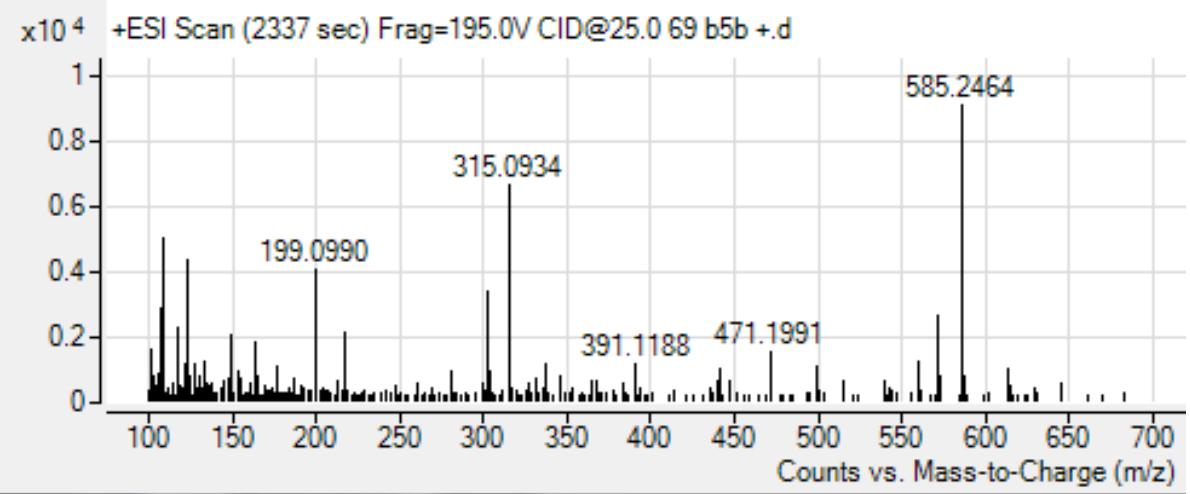
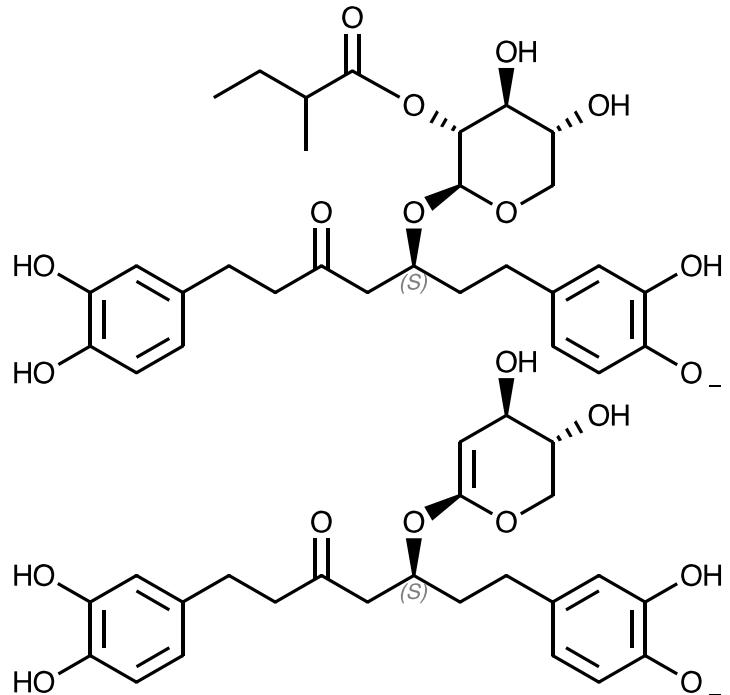
Monoisotopic Mass = 327.124 u

# Peak 57: 2338 seconds BP 327.203 = Alnuside C xyloside

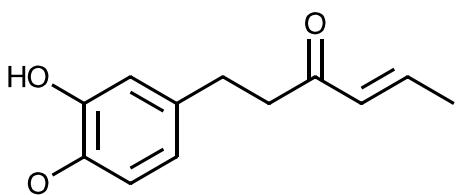


107. alnuside C (Kuroyanagi 2005)  
 (5S)-1,7-bis-(3,4-dihydroxyphenyl)-5-hydroxy-  
 3-heptanone-5-O-[2-(2-methyl-butenoyl)]-D-xylo  
 pyranoside

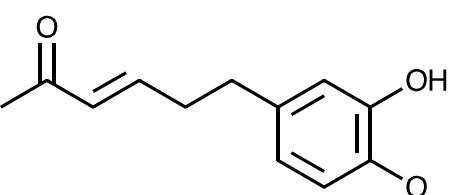
Molecular Formula =  $C_{29}H_{37}O_{11}^-$   
 Monoisotopic Mass = 561.234 u



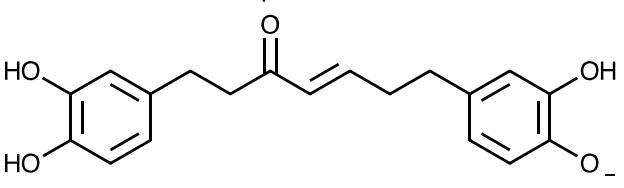
Monoisotopic Mass = 459.166 u



Monoisotopic Mass = 205.087 u



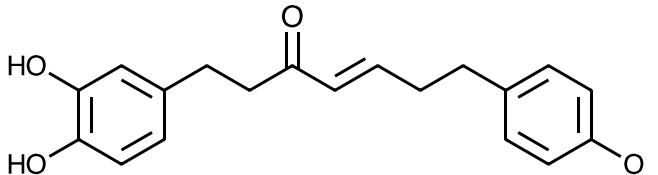
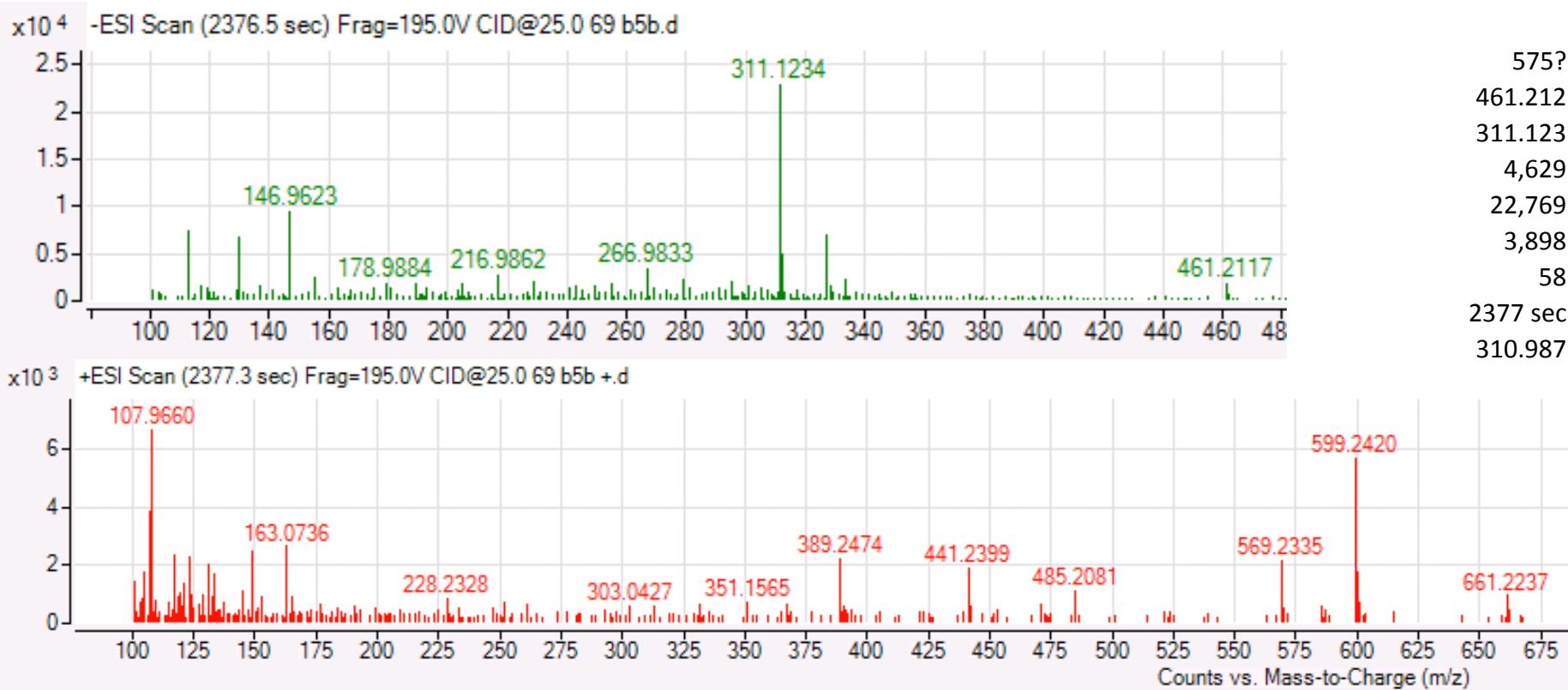
Monoisotopic Mass = 205.087 u



Monoisotopic Mass = 327.124 u

561.228  
 549?  
 459.161  
 327.119  
 9,052  
 98,501  
 12,360  
 57  
 2338 sec  
 327.203

Peak 58: 2377 seconds BP 310.987 =  
 1-(3,4-dihydroxyphenyl)-7-(4-hydroxyphenyl)-4-hepten-3-one



125. 1-(3,4-dihydroxyphenyl)-7-(4-hydroxyphenyl)-4-hepten-3-one

Molecular Formula = C<sub>19</sub>H<sub>19</sub>O<sub>4</sub><sup>-</sup>

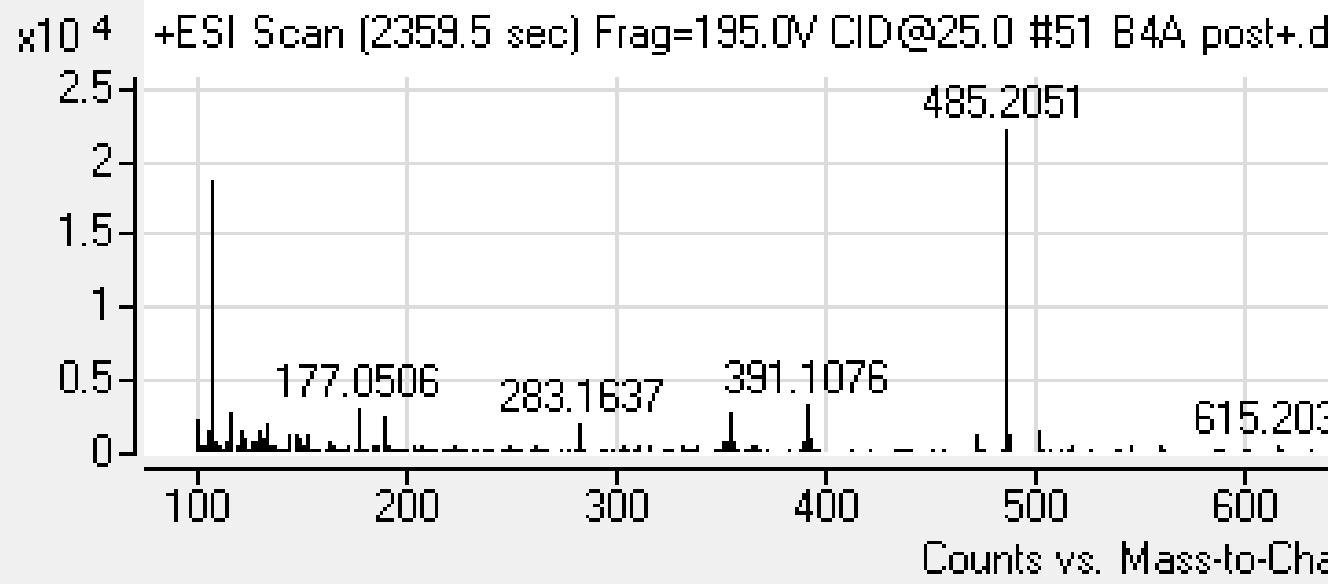
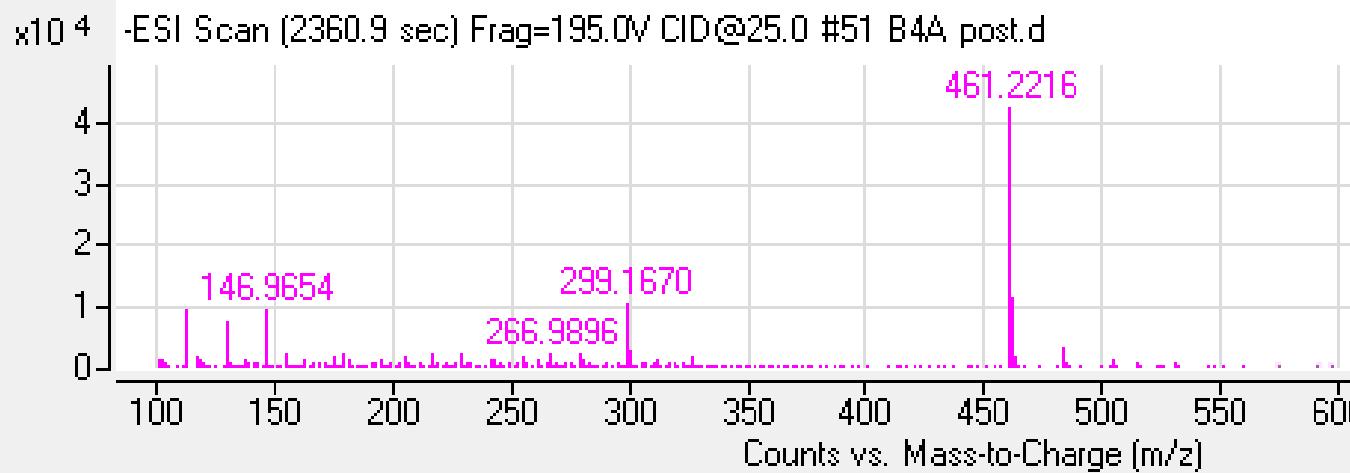
Monoisotopic Mass = 311.129 u

599 + peak may be beta-sitosterol glucoside (weak MS)

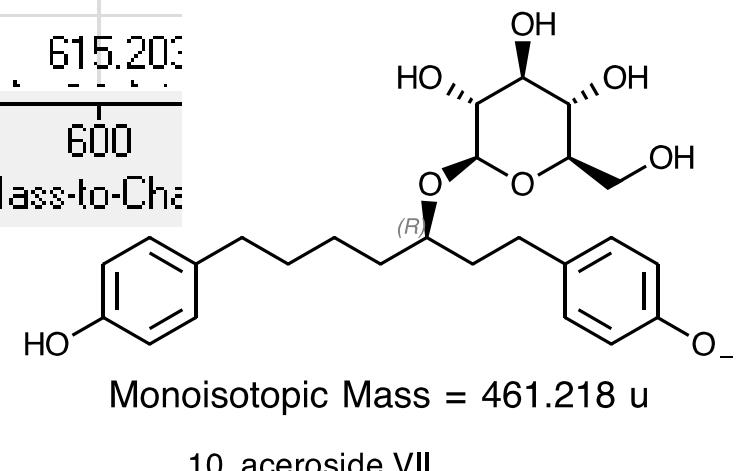
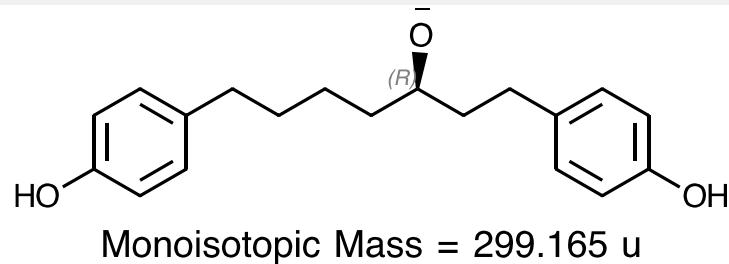
No good indication of + mode ion, probably this aglycone known  
 from *Alnus rubra* co-eluting with other compounds

Need more fragment info  
 Can't ID 311 from this

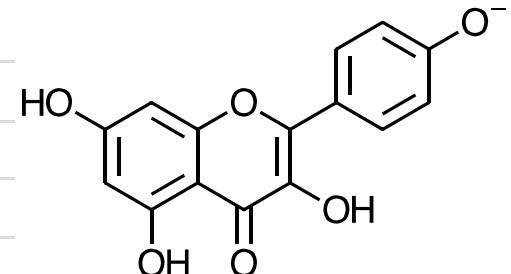
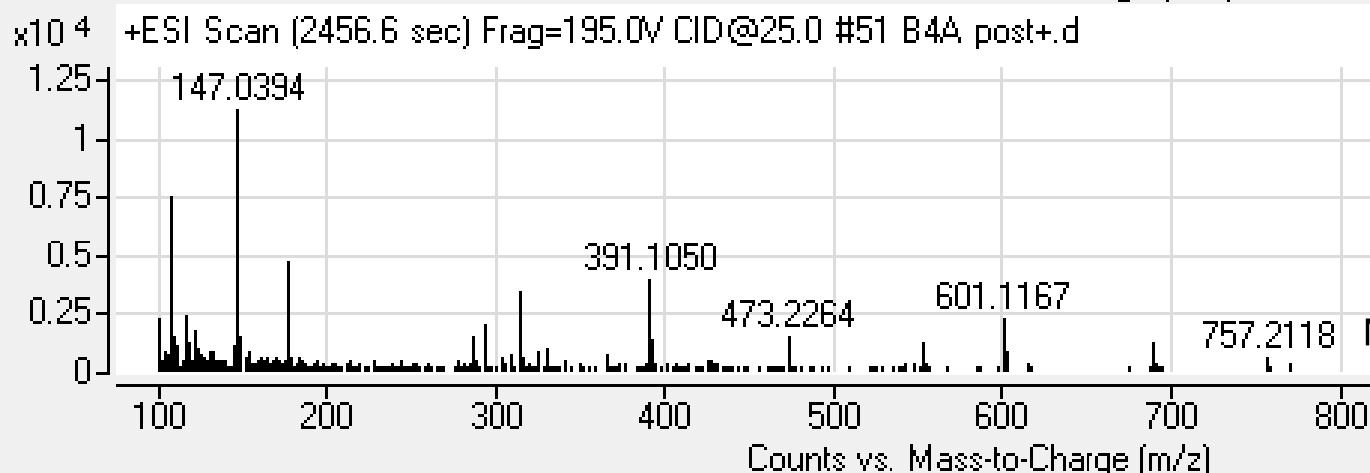
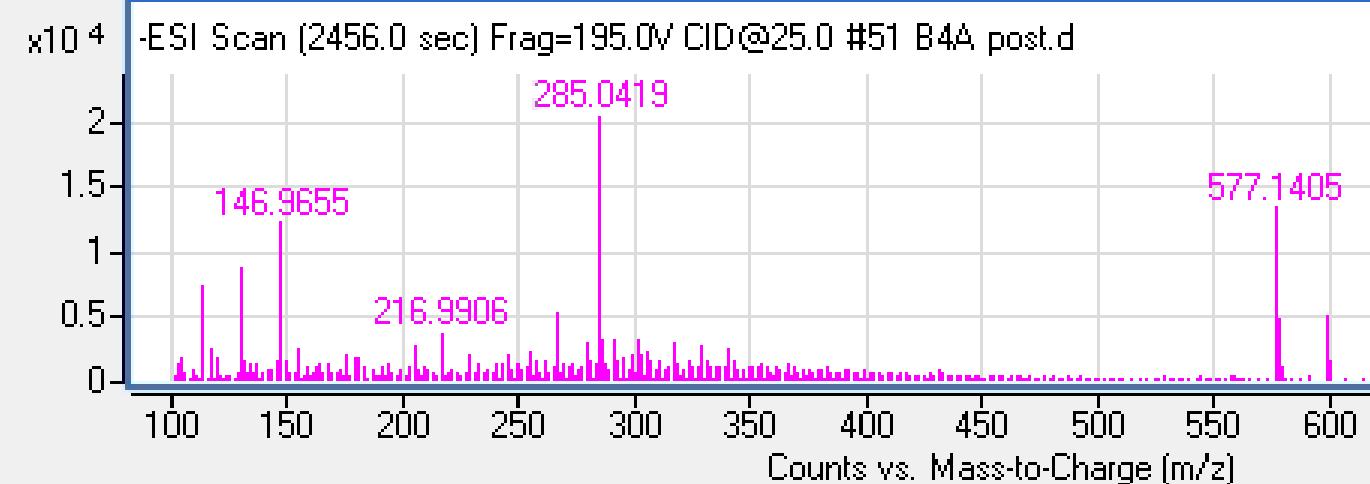
# Peak 59: 2385 seconds = Aceroside VII



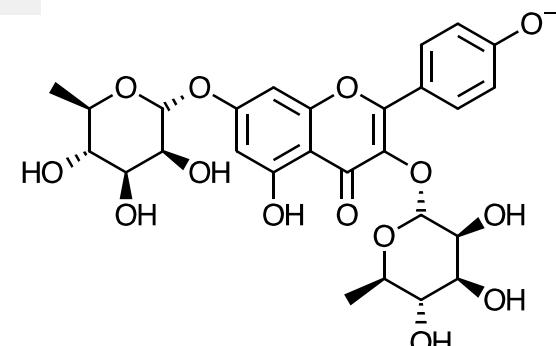
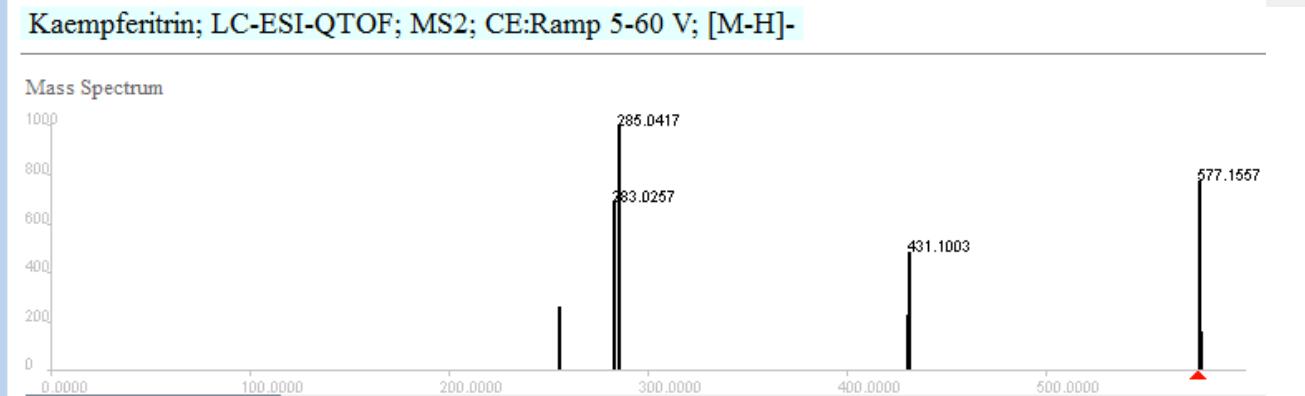
461.222  
299.167  
483  
41,816  
4,390  
59  
2385 sec



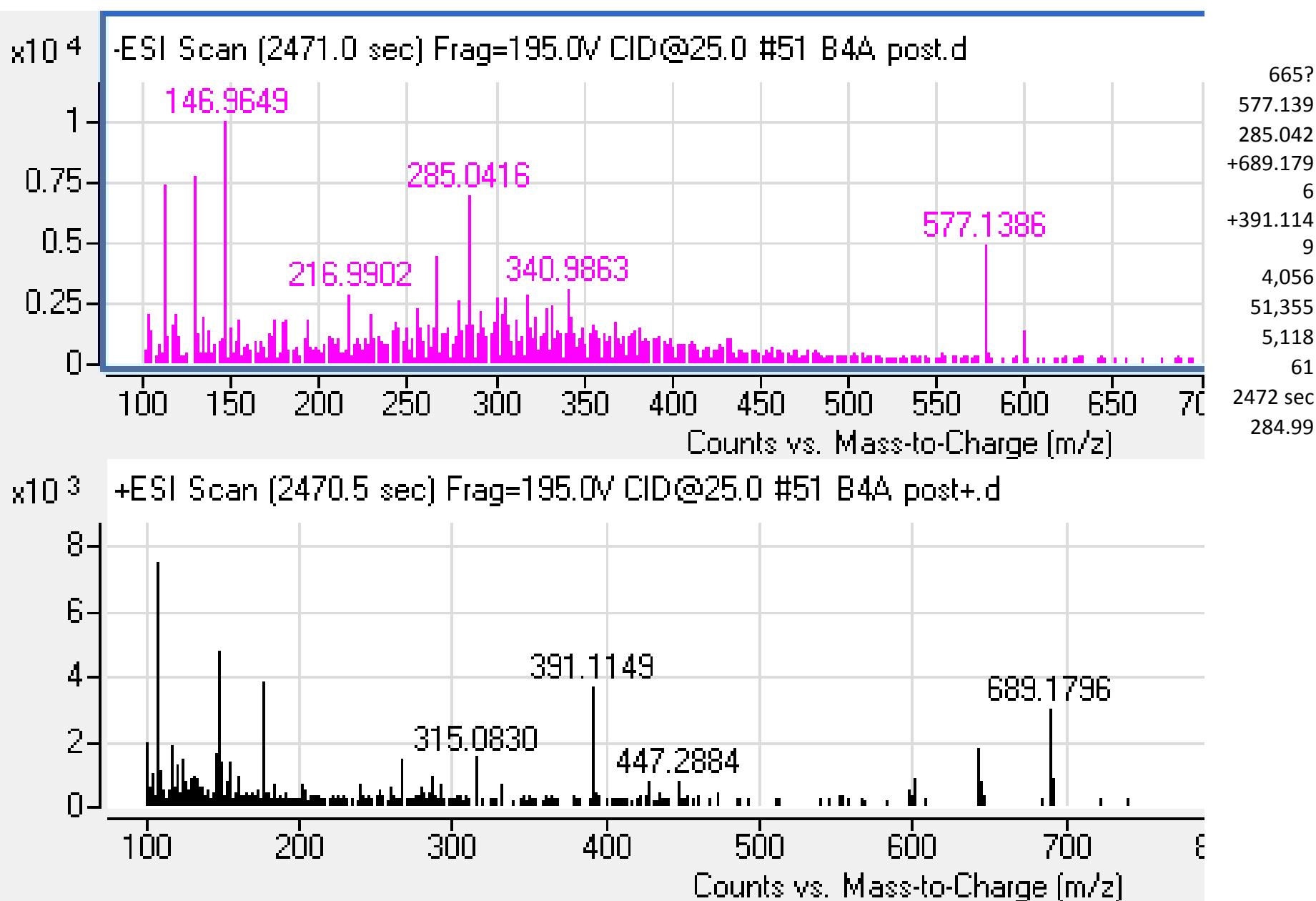
# Peak 60: 2461 seconds BP 285.03 = Kaempferitrin



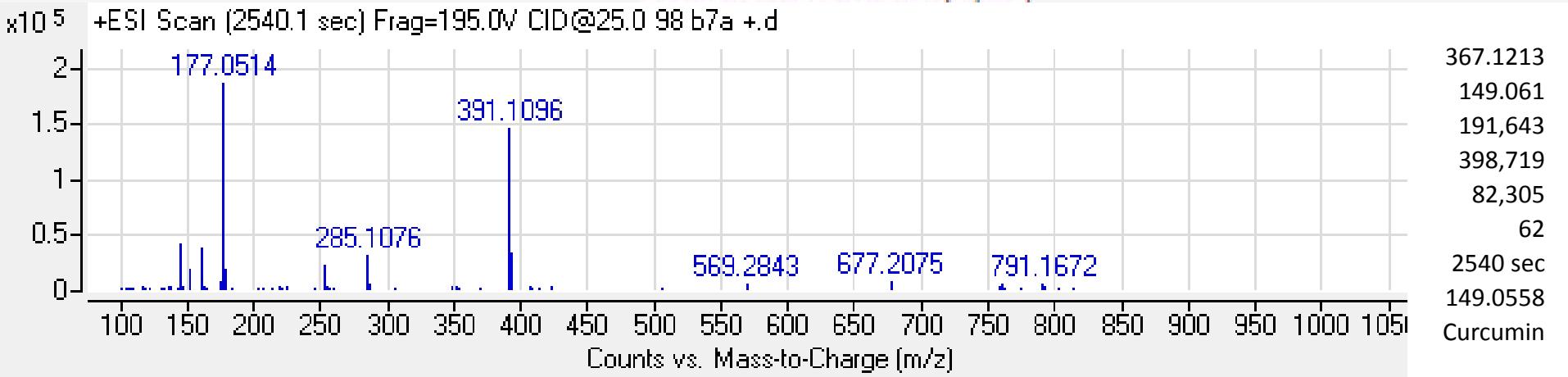
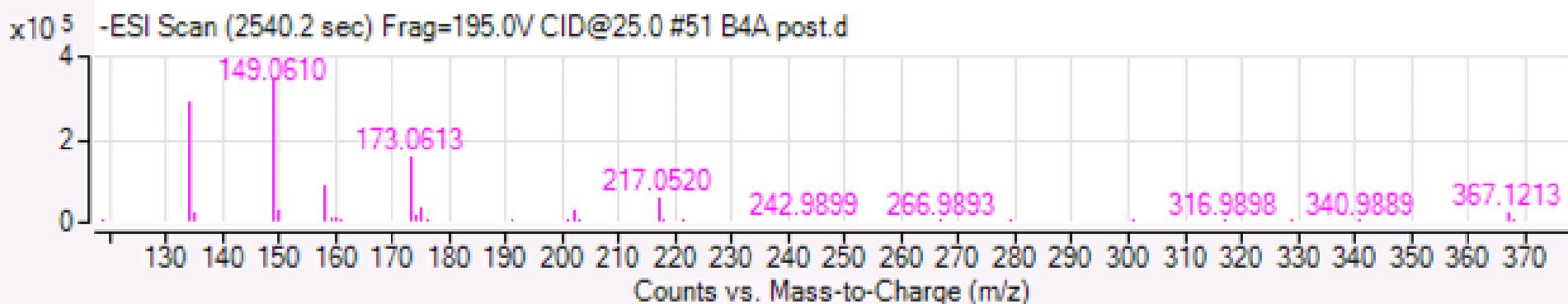
Kaempferitrin; LC-ESI-QTOF; MS2; CE:Ramp 5-60 V; [M-H]<sup>-</sup>



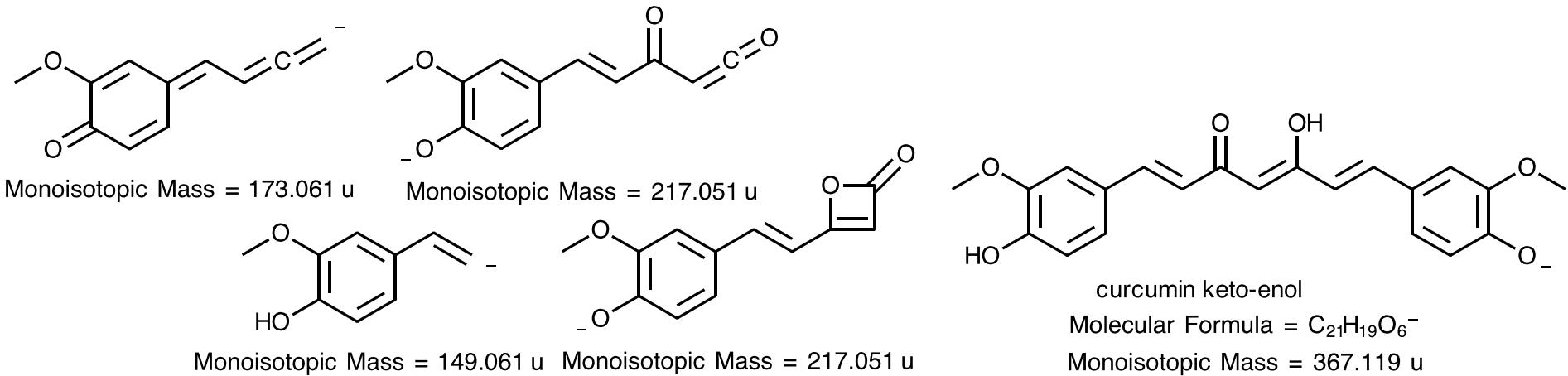
# Peak 61: 2472 seconds BP 284.99 = Manoyl derivative of Kaempferetin



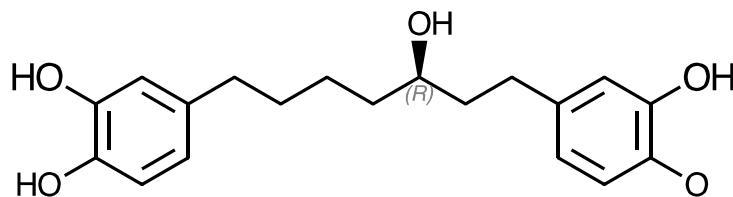
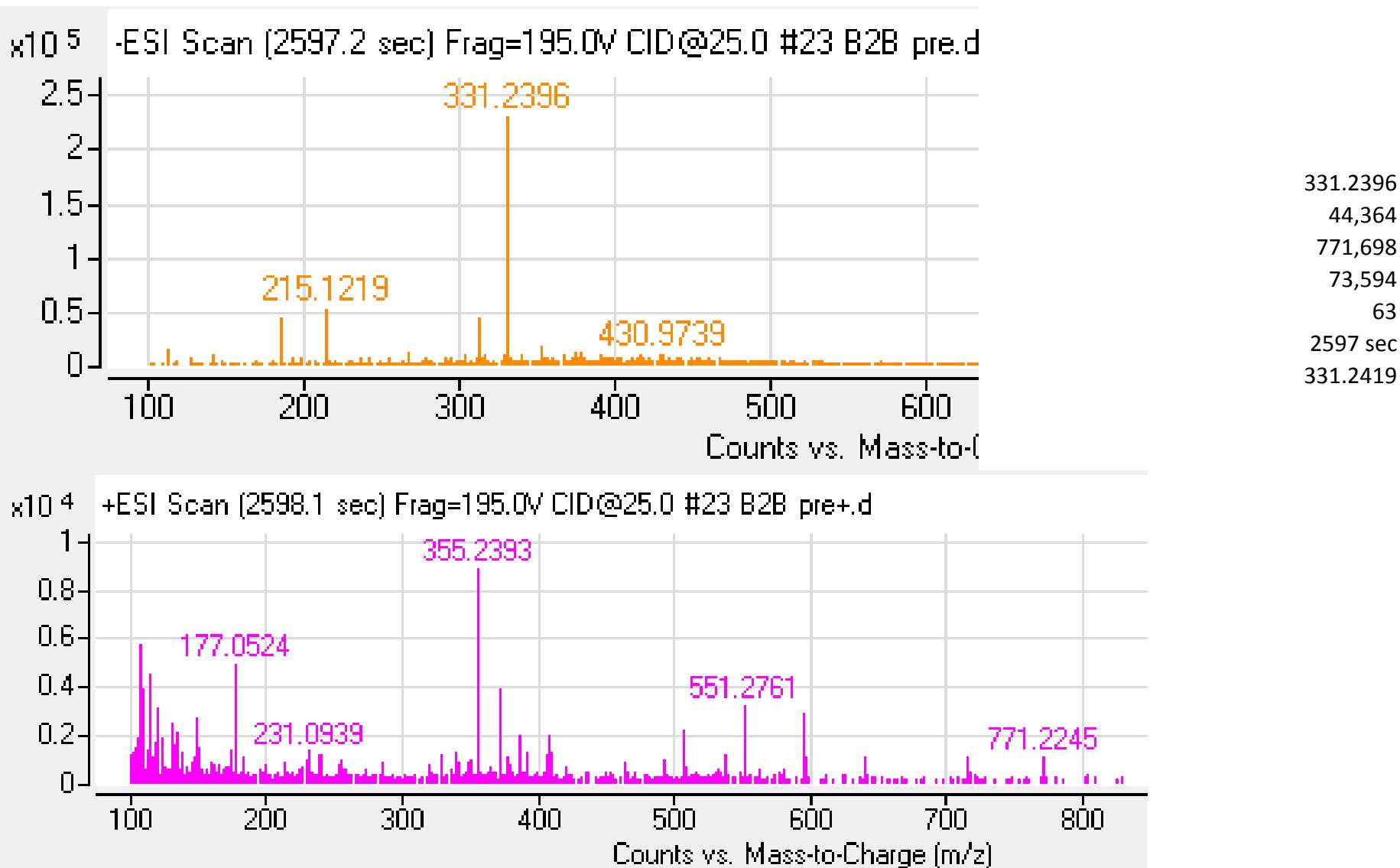
# Peak 62: 2540 seconds BP 149.056 = Curcumin



367.1213  
149.061  
191.643  
398.719  
82.305  
62  
2540 sec  
149.0558  
Curcumin



Peak 63: 2597 seconds BP 331.242 = (5R)-1,7-bis-(3,4-dihydroxyphenyl)=heptan-5-ol



#43 (5R)-1,7-bis-(3,4-dihydroxyphenyl)-heptan-5-ol  
Mass 331.155 Lv2010