

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 5, +TOF MS<sup>2</sup> (50 - 1000) from 5.213 min  
Precursor: 553.1 Da, CE: 35.0

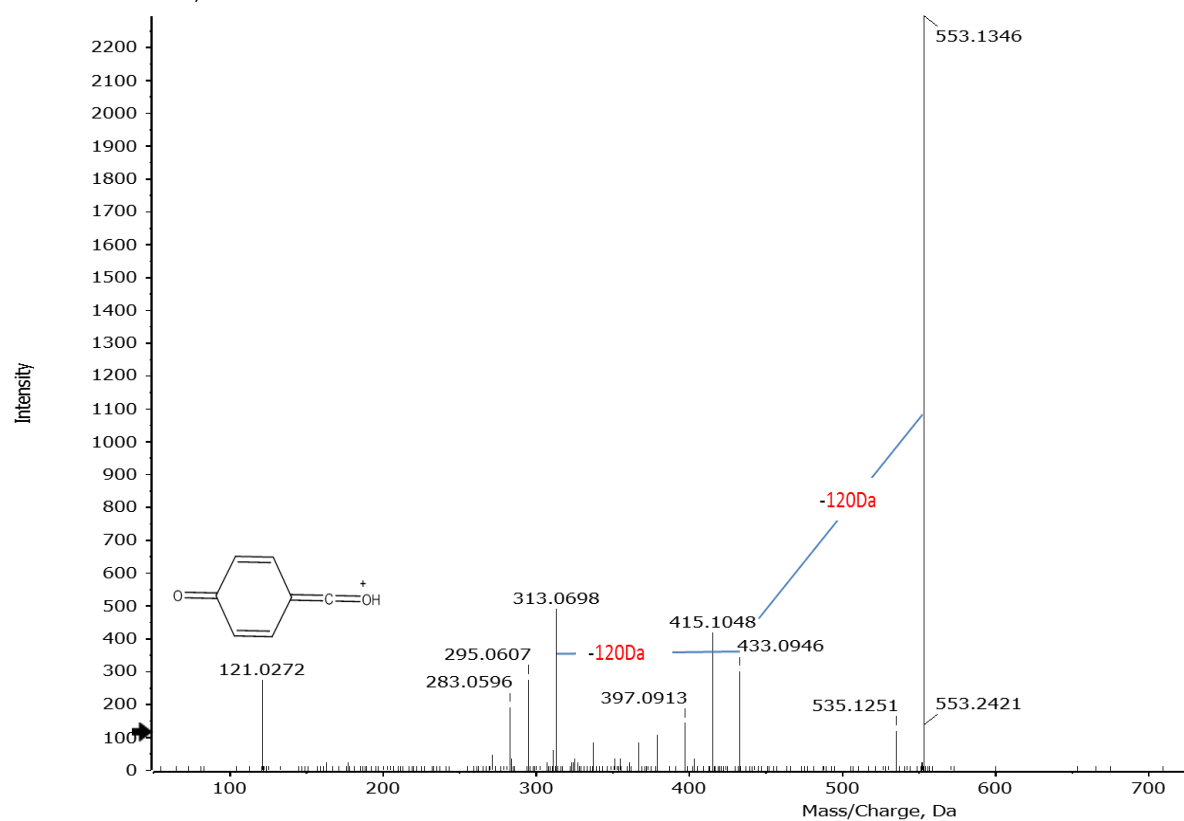
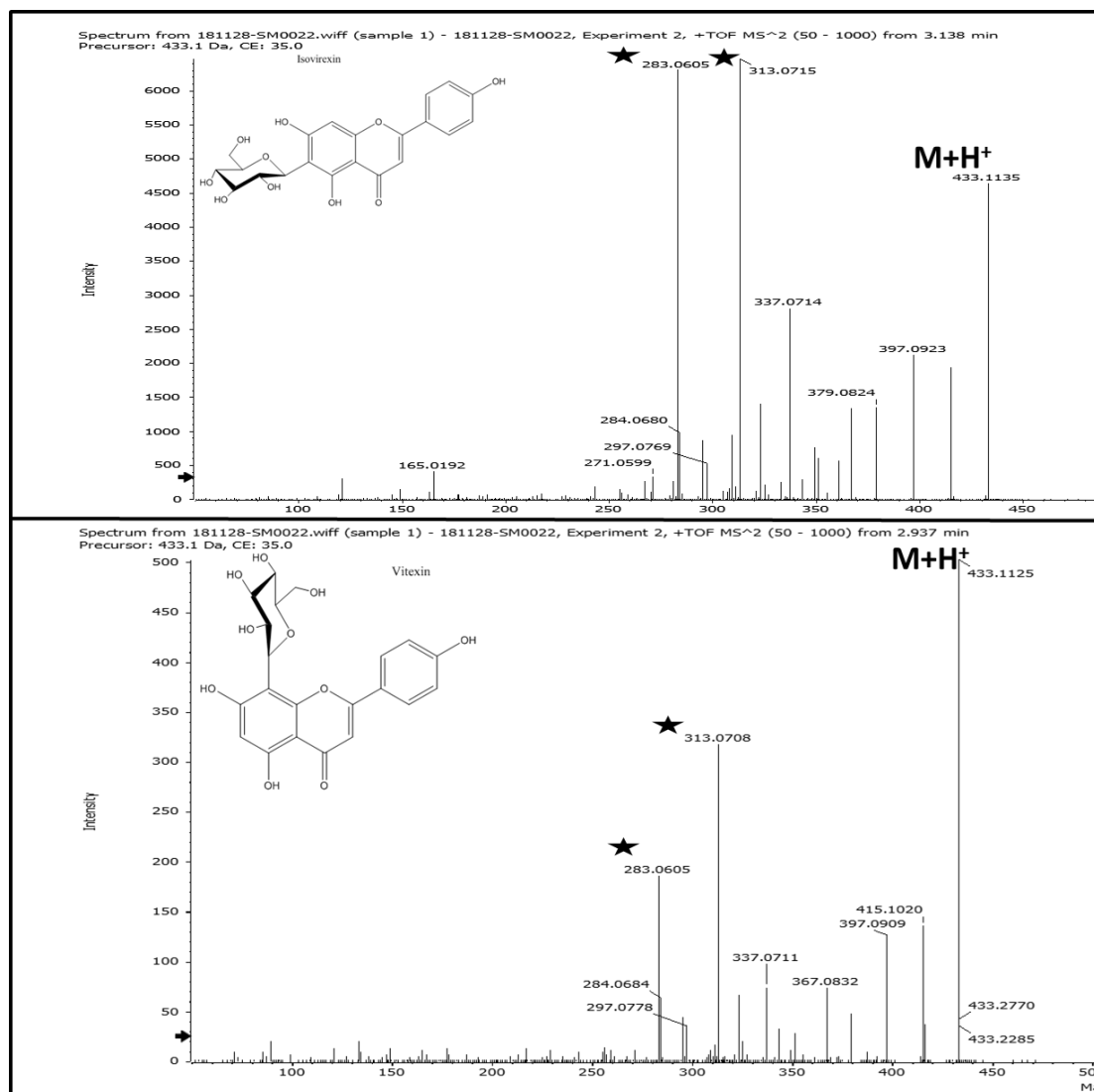
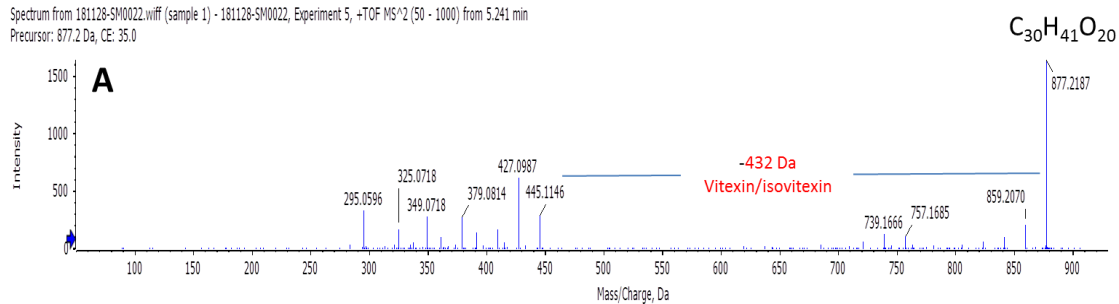


Figure S1. MS/MS spectrum of peak 29: Vitexin-p-hydroxybenzoate.

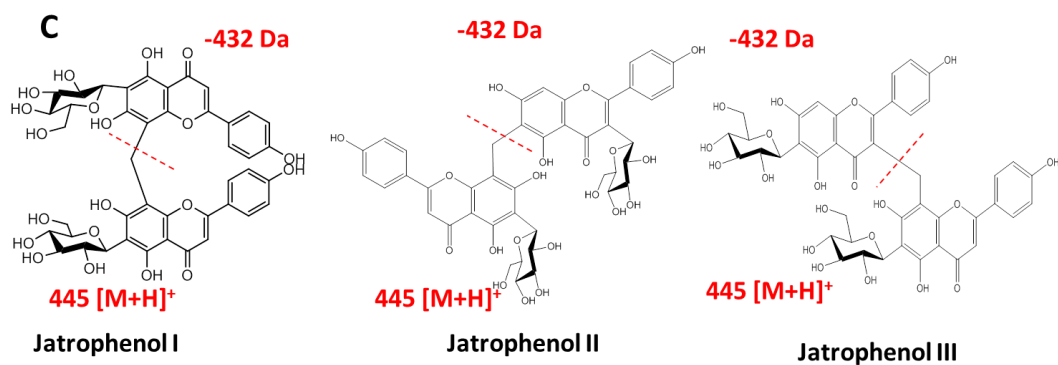
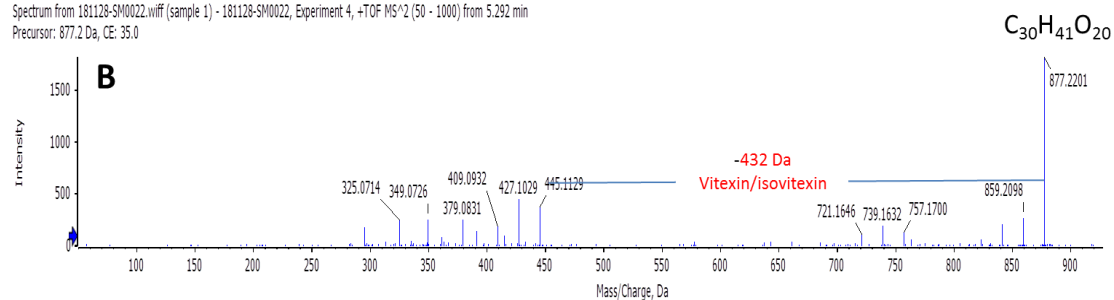


**Figure S2.** Fragmentation pattern highlighting different fragmentation of the two structural isomer vitexin and isovitaxin based on the intensity of 313 and 283 fragment ions.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 5, +TOF MS<sup>2</sup> (50 - 1000) from 5.241 min  
Precursor: 877.2 Da, CE: 35.0

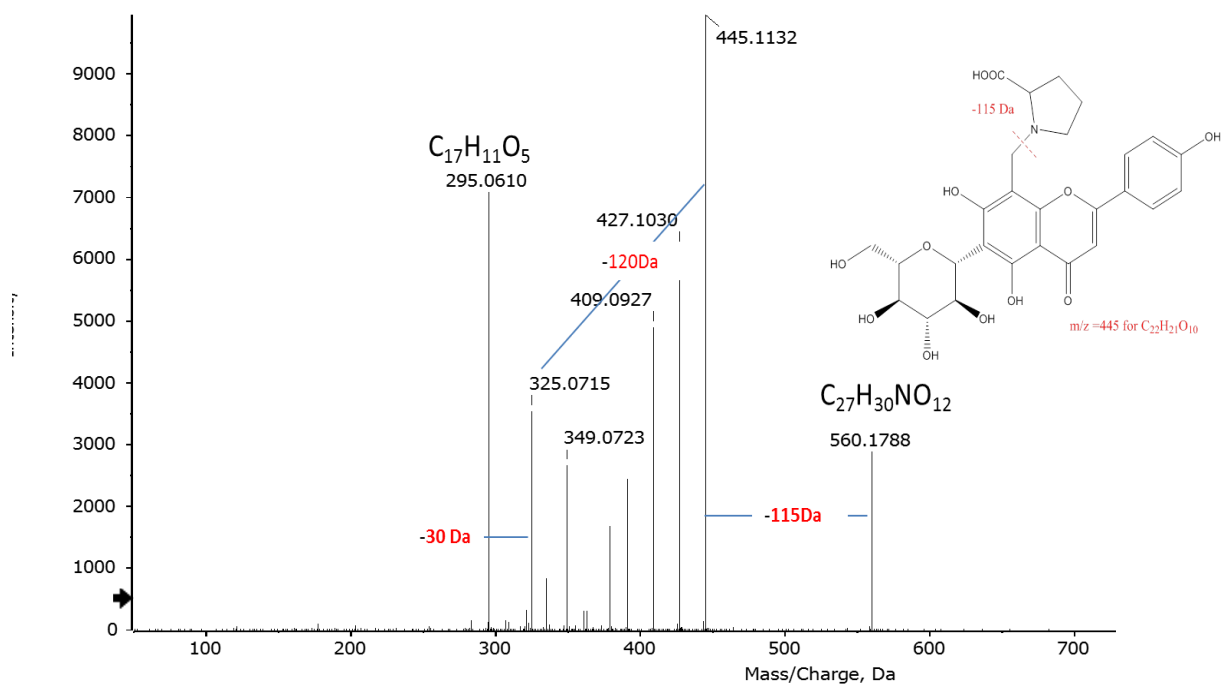


Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 4, +TOF MS<sup>2</sup> (50 - 1000) from 5.292 min  
Precursor: 877.2 Da, CE: 35.0



**Figure S3.** MS/MS spectrum of peaks 30 and 32: Jatrophanol I/II/III.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 8, +TOF MS<sup>2</sup> (50 - 1000) from 3.706 min  
Precursor: 560.2 Da, CE: 35.0



**Figure S4.** MS/MS spectrum of peak 35: Proline methylisovitexin.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 4, +TOF MS<sup>2</sup> (50 - 1000) from 6.215 min  
Precursor: 736.2 Da, CE: 35.0

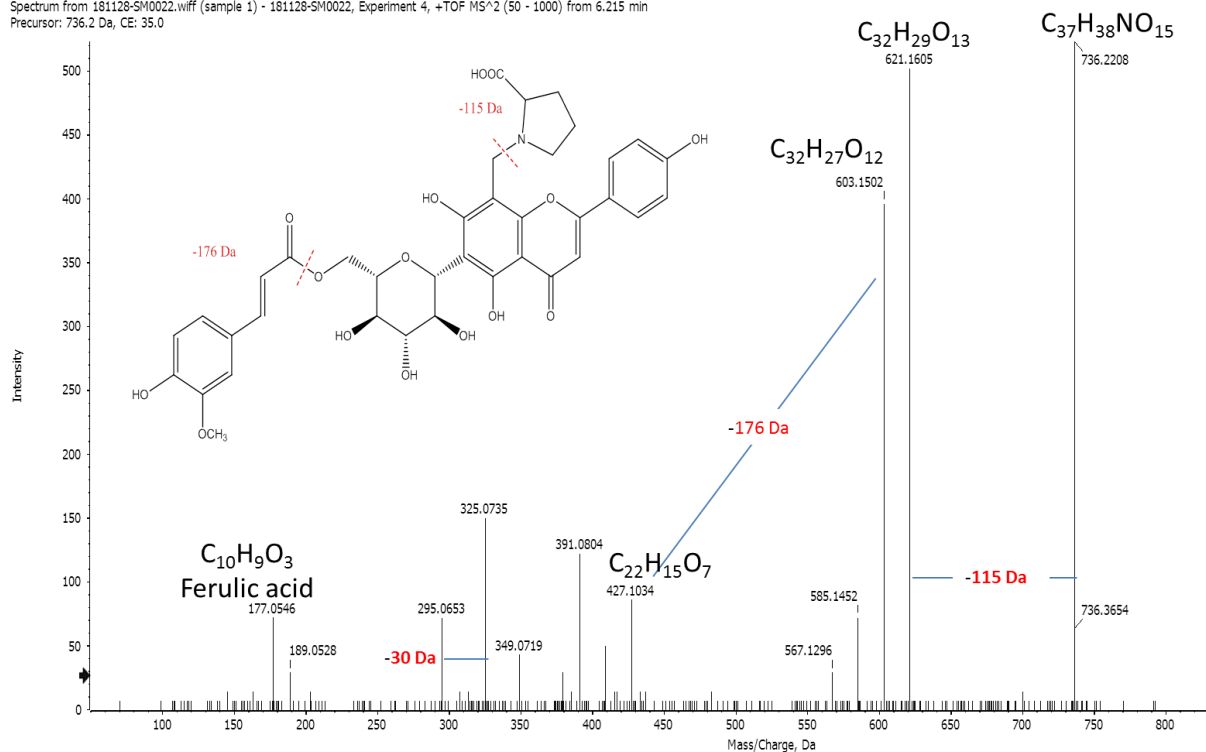


Figure S5. MS/MS spectrum of peak 35: Methylisovitexin proline ferulate.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 4, +TOF MS<sup>2</sup> (50 - 1000) from 4.396 min  
Precursor: 433.1 Da, CE: 35.0

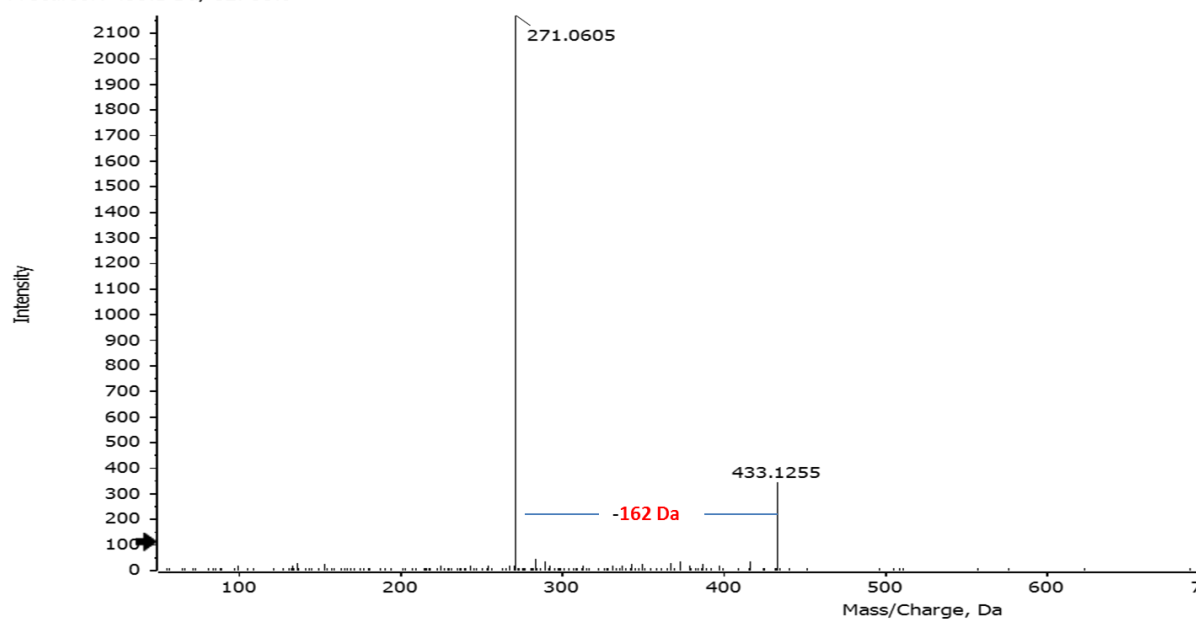


Figure S6. MS/MS spectrum of peak 26: Apigenin-O-hexoside.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 9, +TOF MS<sup>2</sup> (50 - 1000) from 4.253 min  
Precursor: 579.2 Da, CE: 35.0

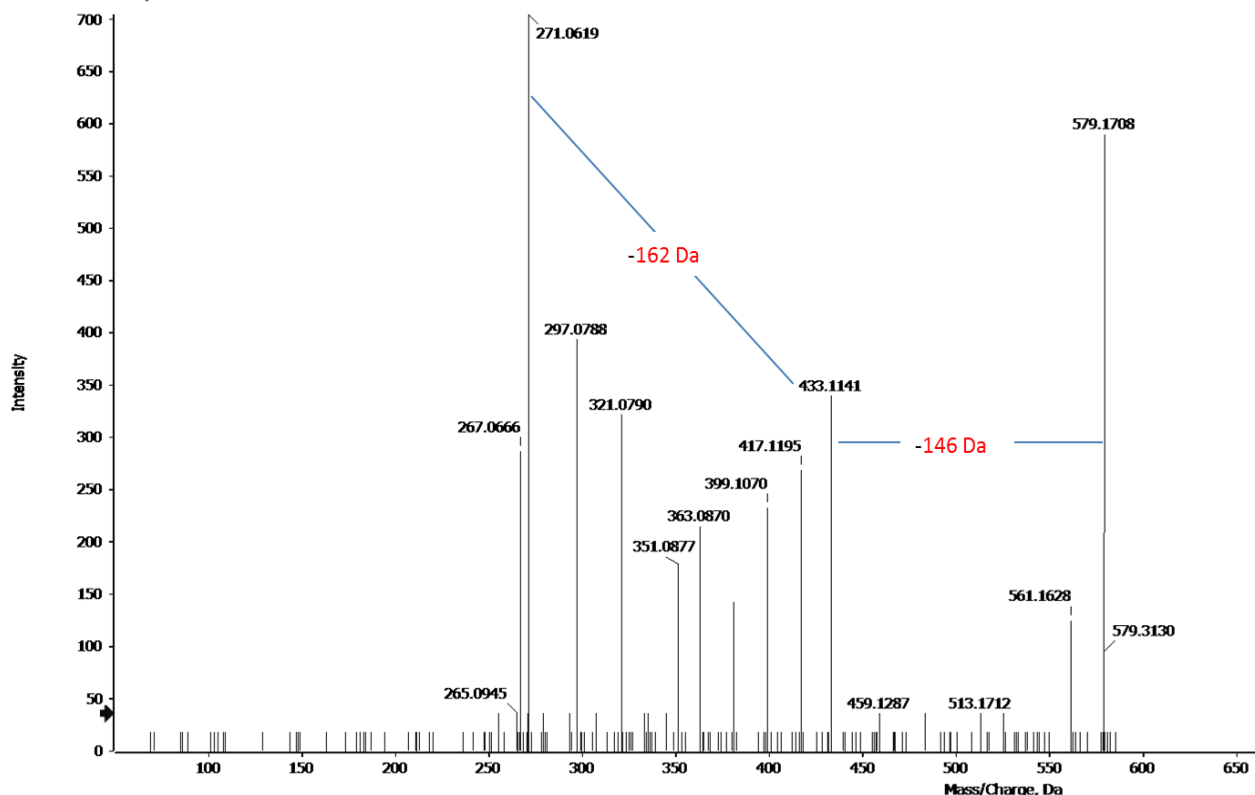


Figure S7. MS/MS spectrum of peak 25: Apigenin-O-hexoside-O-rhamnoside.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 7, +TOF MS<sup>2</sup> (50 - 1000) from 9.543 min  
Precursor: 722.5 Da, CE: 35.0

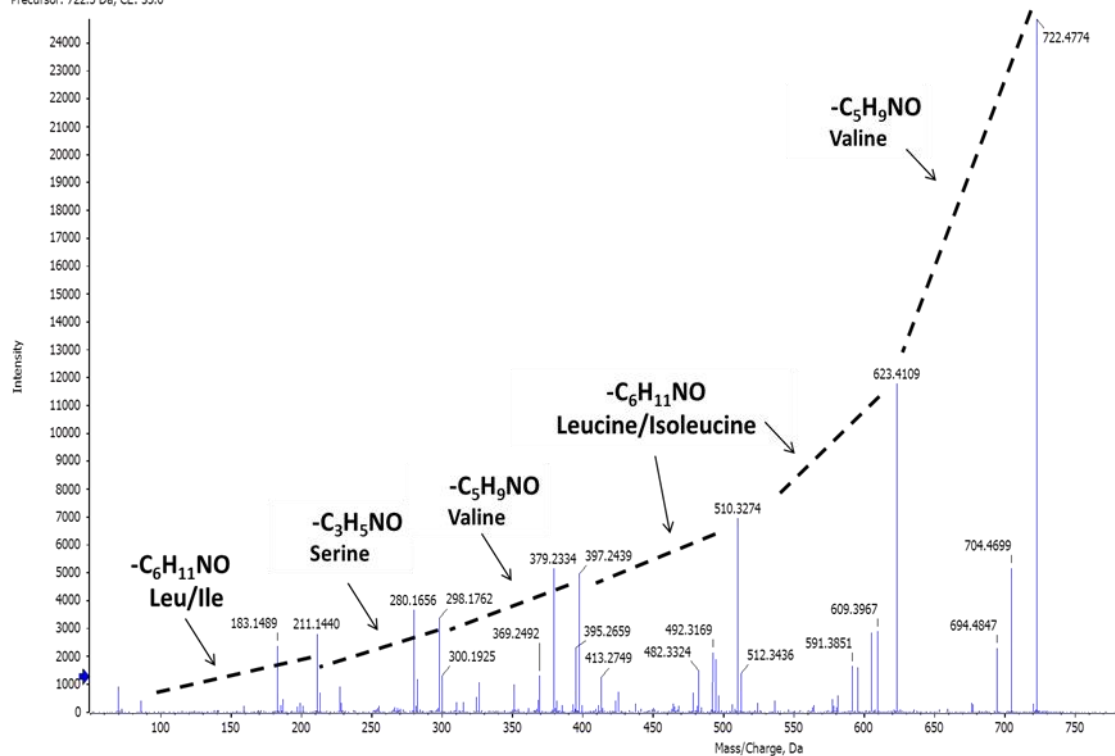


Figure S8. MS/MS spectrum of peak 43: A cycloheptapeptide.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 3, +TOF MS<sup>2</sup> (50 - 1000) from 9.591 min  
Precursor: 809.5 Da, CE: 35.0

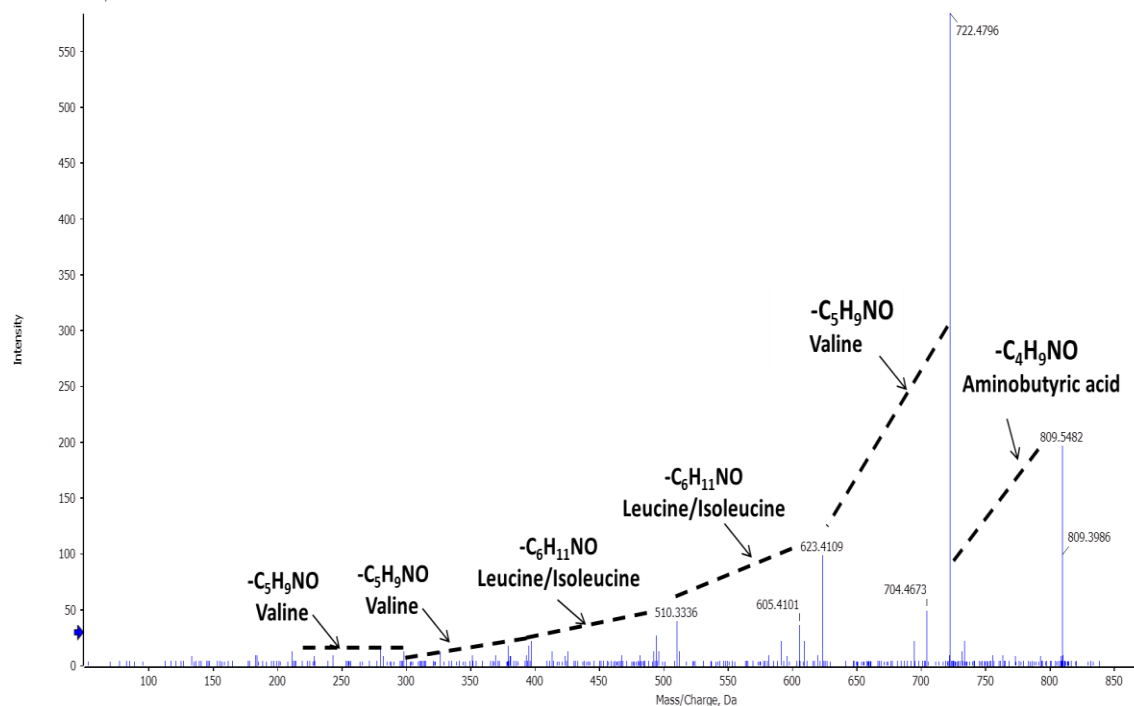


Figure S9. MS/MS spectrum of peak 45: A cyclooctapeptide.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 8, +TOF MS<sup>2</sup> (50 - 1000) from 9.616 min  
Precursor: 767.5 Da, CE: 35.0

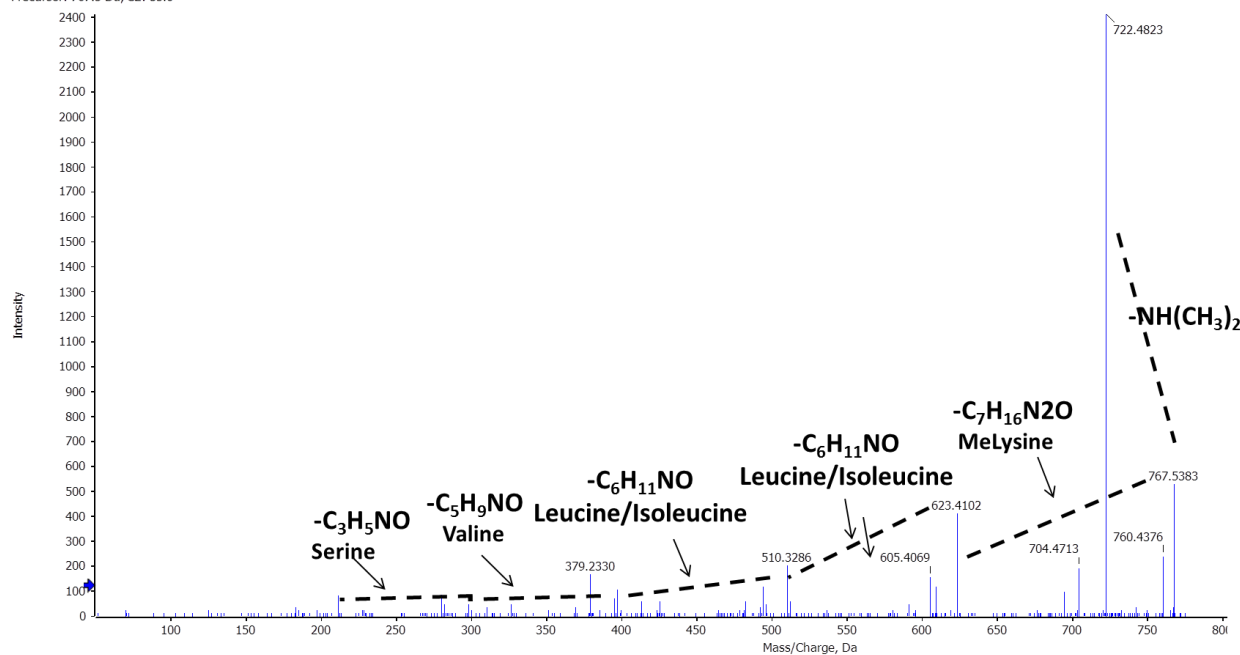
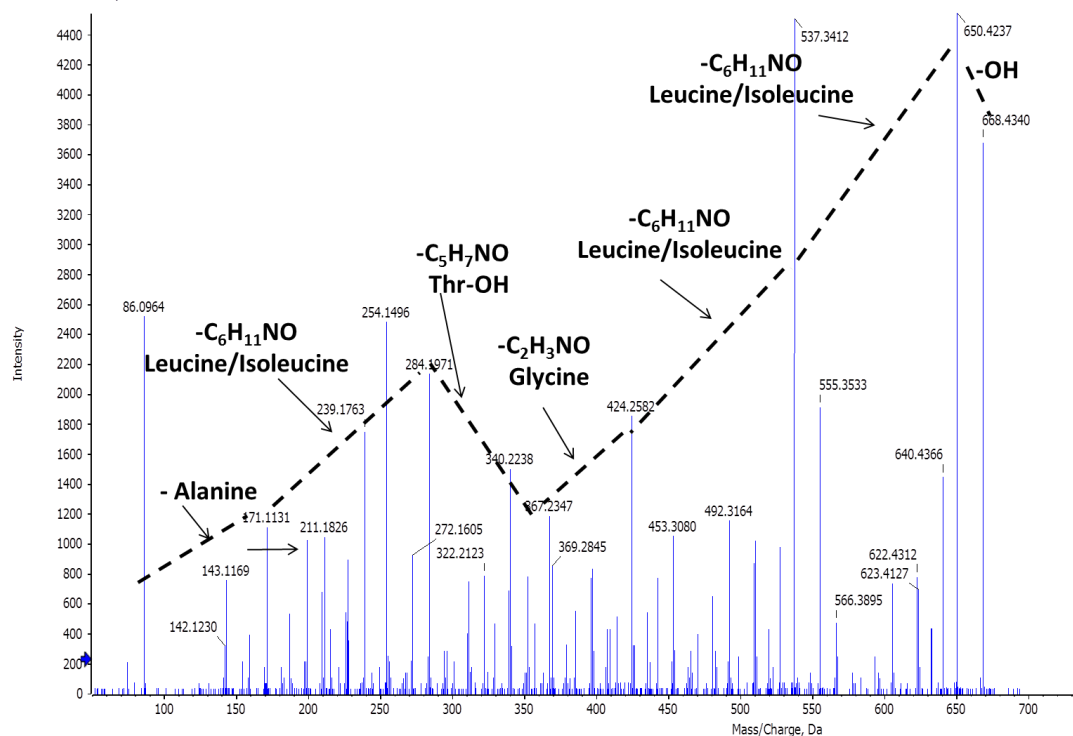


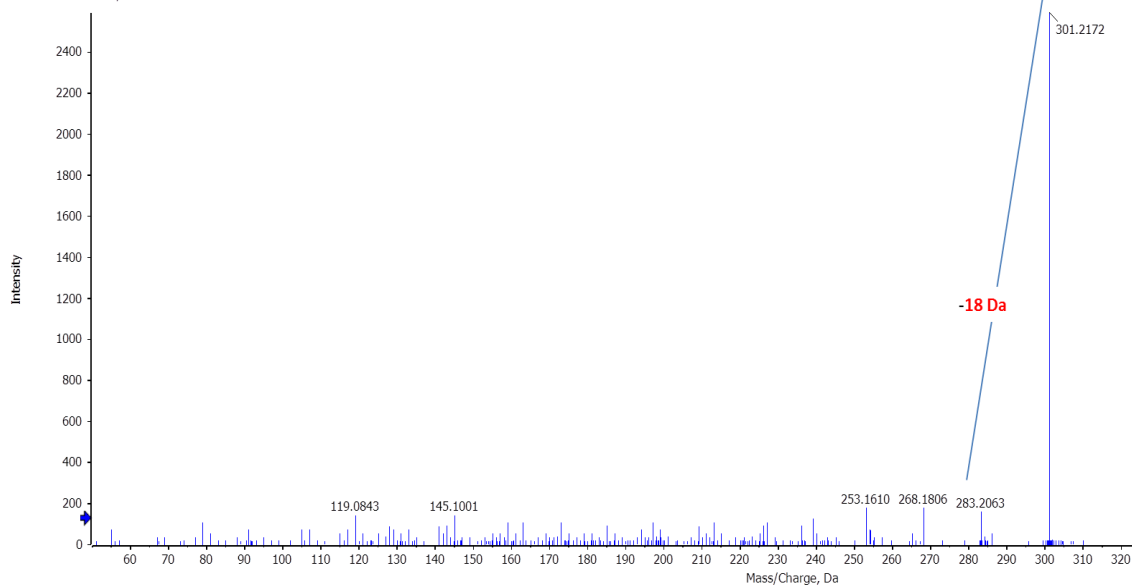
Figure S10. MS/MS spectrum of peak 46: A cycloheptapeptide.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 6, +TOF MS<sup>2</sup> (50 - 1000) from 10.554 min  
Precursor: 668.4 Da, CE: 46.5



**Figure S11.** MS/MS spectrum of peak 46: A cycloheptapeptide.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 2, +TOF MS<sup>2</sup> (50 - 1000) from 11.364 min  
Precursor: 301.2 Da, CE: 35.0



**Figure S12.** MS/MS spectrum of peak 59: Spruceanol.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 3, +TOF MS<sup>2</sup> (50 - 1000) from 11.952 min  
Precursor: 275.2 Da, CE: 35.0

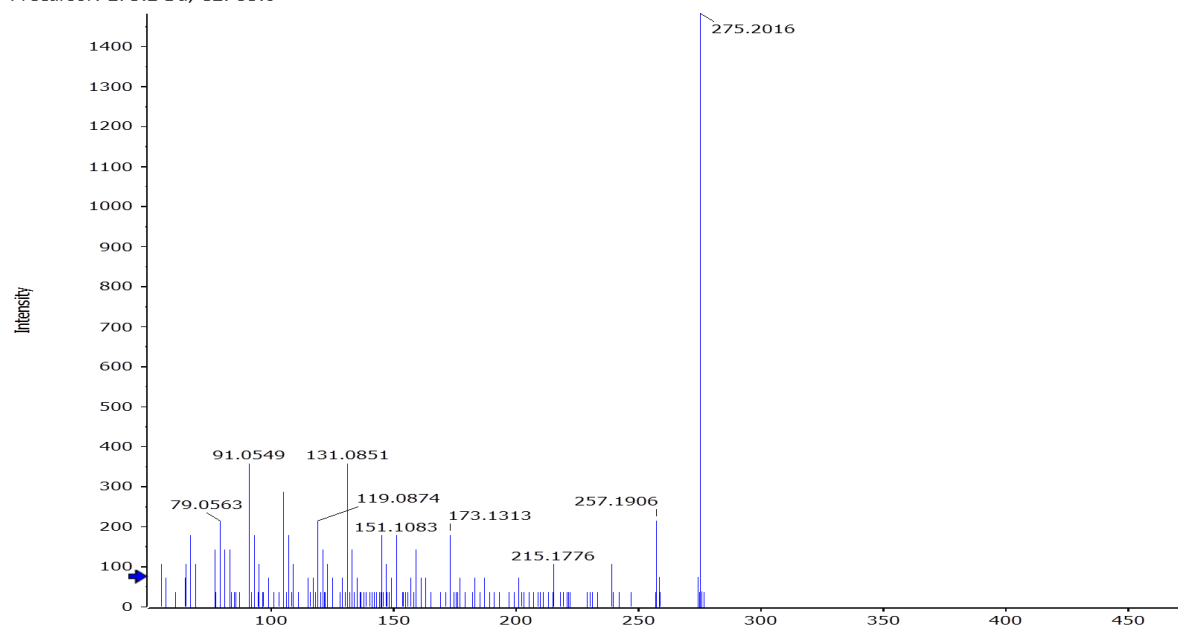


Figure S13. MS/MS spectrum of peak 61.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 2, +TOF MS<sup>2</sup> (50 - 1000) from 12.420 min  
Precursor: 411.2 Da, CE: 35.0

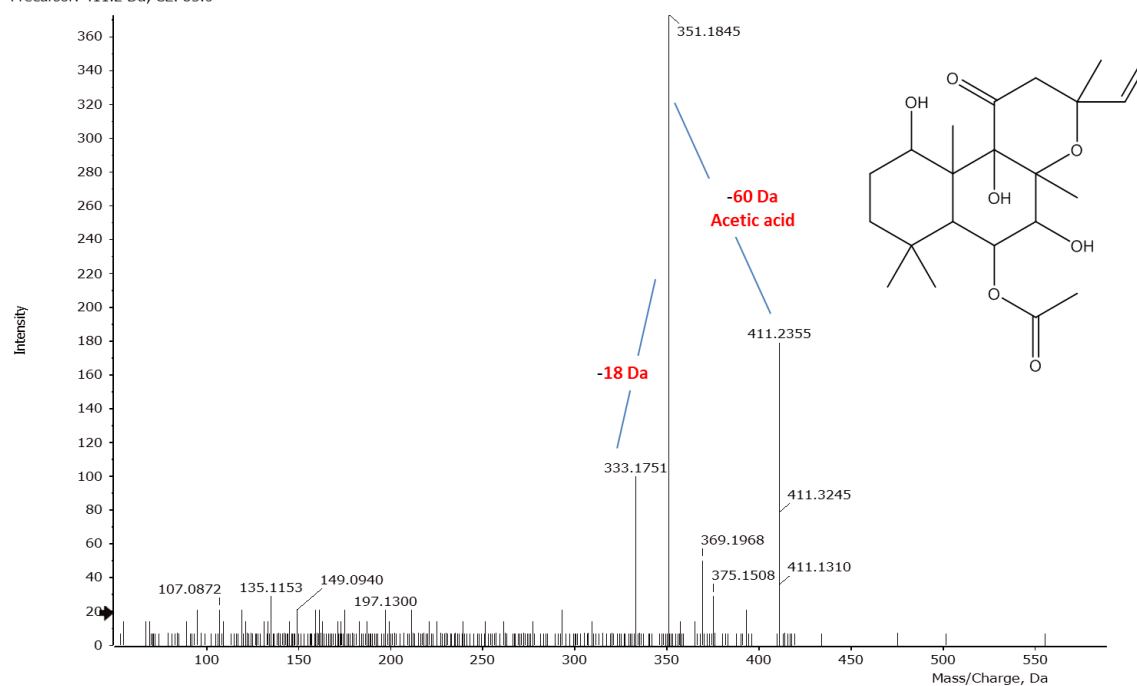
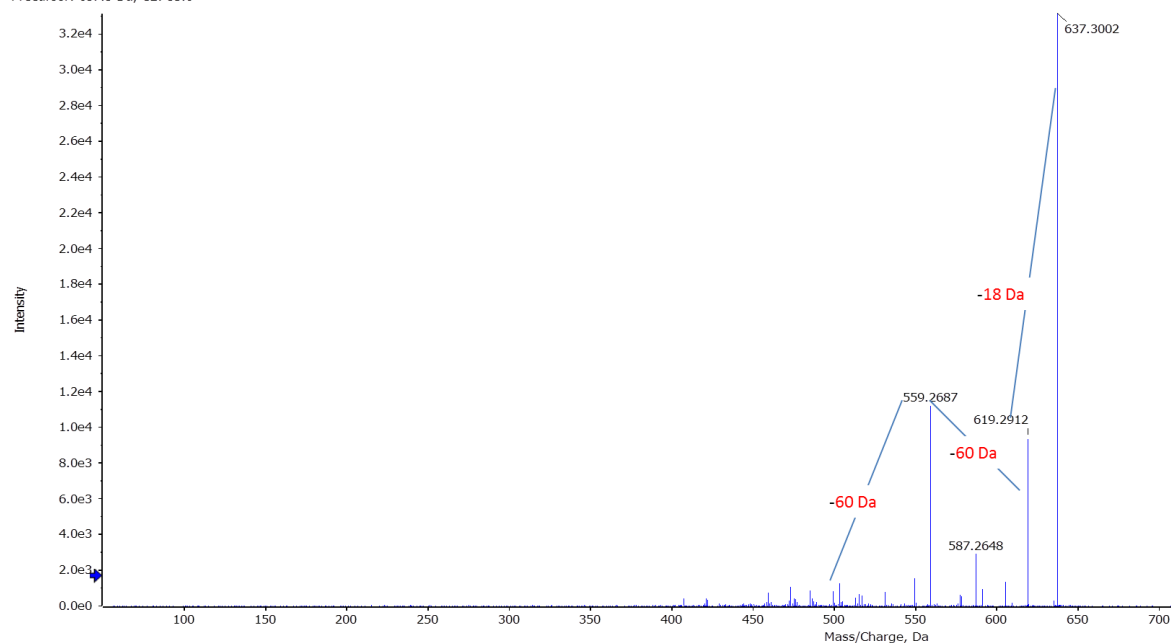


Figure S14. MS/MS for peak 67: Isoforskolin.

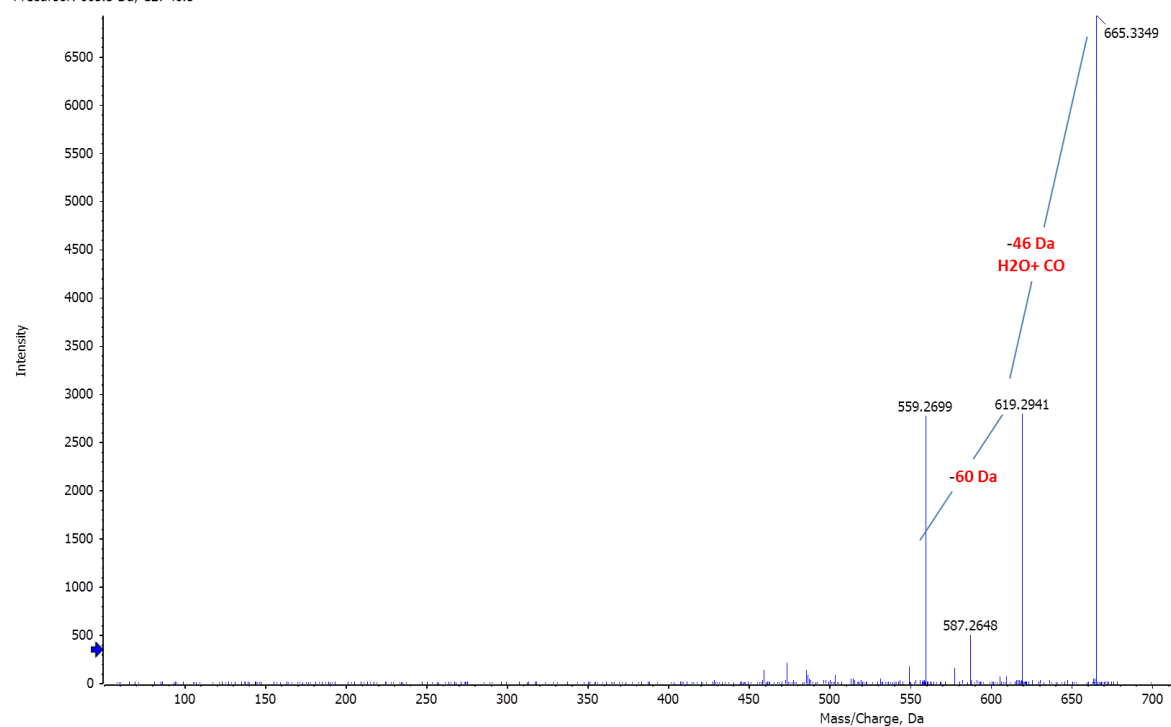


Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 3, +TOF MS<sup>2</sup> (50 - 1000) from 20.410 min  
Precursor: 637.3 Da, CE: 35.0



**Figure S15.** MS/MS for peak 114: Premyrsinol/peditithin derivatives.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 6, +TOF MS<sup>2</sup> (50 - 1000) from 21.962 min  
Precursor: 665.3 Da, CE: 46.5



**Figure S16.** MS/MS of peak 125: Premyrsinol/peditithin derivative.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 4, +TOF MS<sup>2</sup> (50 - 1000) from 13.796 min  
Precursor: 557.3 Da, CE: 35.0

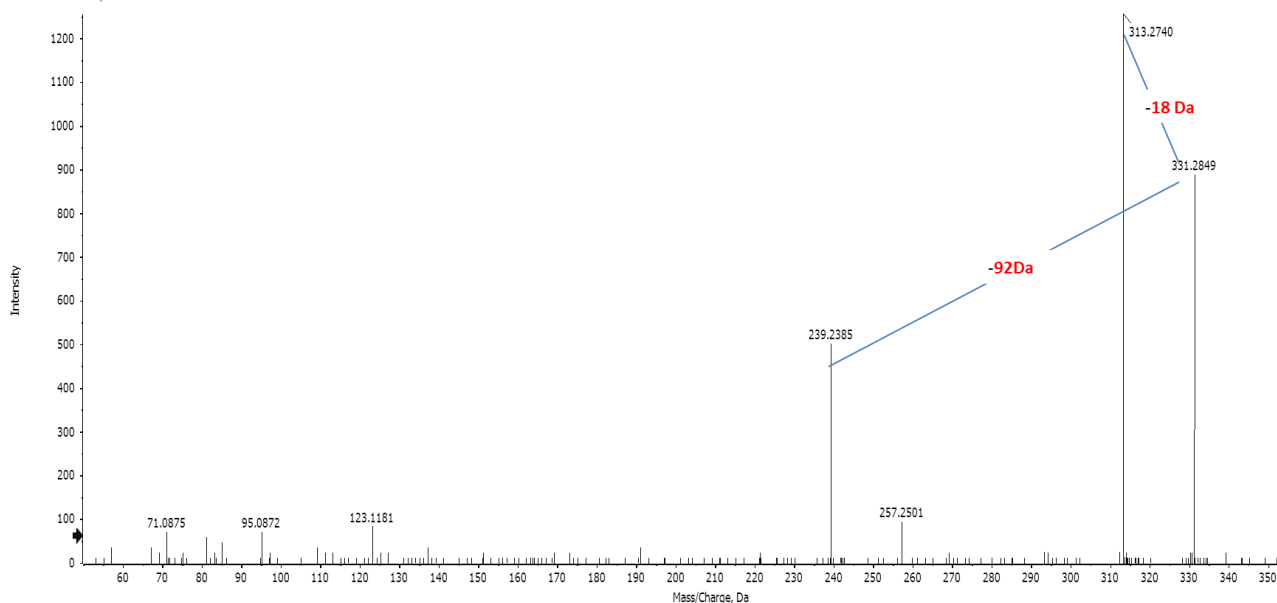


Figure S17. MS/MS of peak 82: Monopalmitin.

Spectrum from 181128-SM0022.wiff (sample 1) - 181128-SM0022, Experiment 15, +TOF MS<sup>2</sup> (50 - 1000) from 14.082 min  
Precursor: 467.3 Da, CE: 35.0

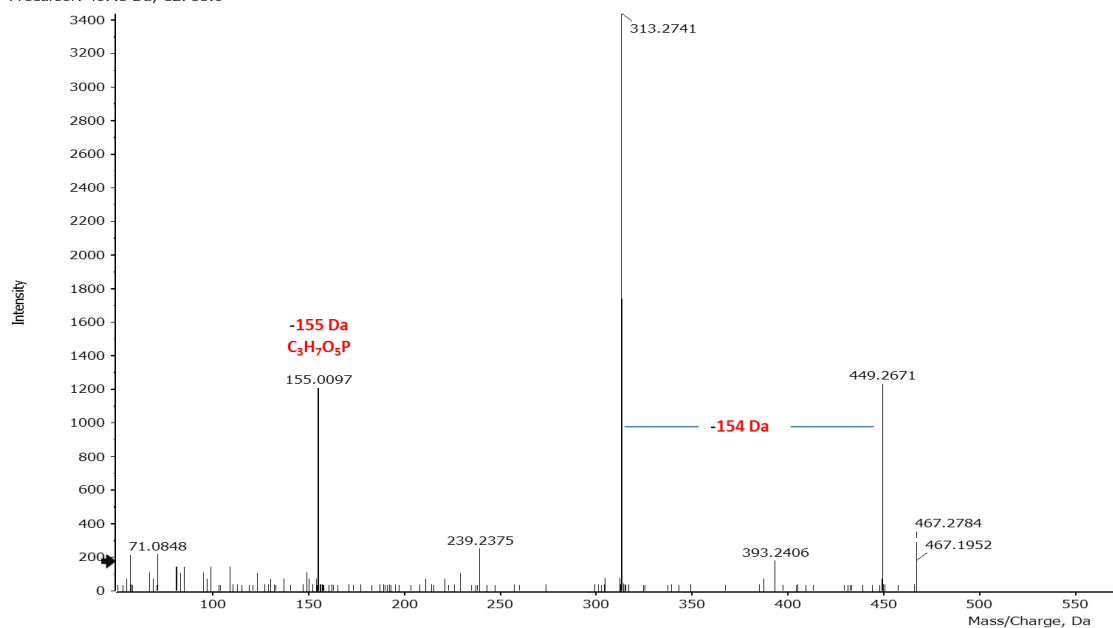
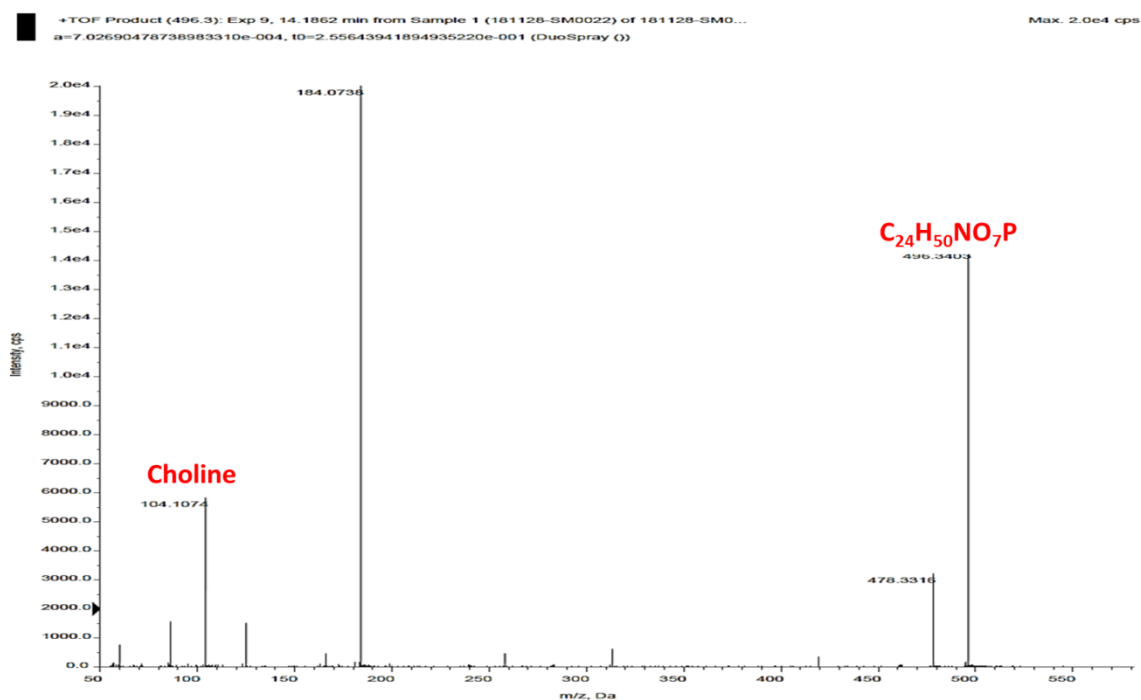


Figure S18. MS/MS of peak 84: Phosphatidic acid (10:0/9:0).



**Figure S19.** MS/MS of peak 86: Lysophosphatidylcholine (16:0/0:0).

**Table S1.** Analysis of high resolution MS/MS Q-TOF fragments for newly identified cyclic peptides.

Peak No.	<i>m/z</i>	Calculated formula	MS data		Neutral loss	Corresponding amino acid
			<i>m/z</i>	calculated formula		
43/45	722.4774	C <sub>36</sub> H <sub>64</sub> N <sub>7</sub> O <sub>8</sub>	623.4151	C <sub>31</sub> H <sub>55</sub> N <sub>6</sub> O <sub>7</sub>	-99 Da	Val
			510.3274	C <sub>25</sub> H <sub>44</sub> N <sub>5</sub> O <sub>6</sub>	-113 Da	Leu/Ile
			397.2439	C <sub>19</sub> H <sub>33</sub> N <sub>4</sub> O <sub>5</sub>	-113 Da	Leu/Ile
			298.1762	C <sub>14</sub> H <sub>24</sub> N <sub>3</sub> O <sub>4</sub>	-99 Da	Val
			211.1440	C <sub>11</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub>	-87 Da	Ser
46	809.5482	C <sub>40</sub> H <sub>73</sub> N <sub>8</sub> O <sub>9</sub>	722.4796	C <sub>36</sub> H <sub>64</sub> N <sub>7</sub> O <sub>8</sub>	-87 Da	ABA
			623.4109	C <sub>31</sub> H <sub>55</sub> N <sub>6</sub> O <sub>7</sub>	-99 Da	Val
			510.3336	C <sub>25</sub> H <sub>44</sub> N <sub>5</sub> O <sub>6</sub>	-113 Da	Leu/Ile
			397.2439	C <sub>19</sub> H <sub>33</sub> N <sub>4</sub> O <sub>5</sub>	-113 Da	Leu/Ile
			298.1762	C <sub>14</sub> H <sub>24</sub> N <sub>3</sub> O <sub>4</sub>	-99 Da	Val
47	767.5383	C <sub>38</sub> H <sub>71</sub> N <sub>8</sub> O <sub>8</sub>	211.1436	C <sub>11</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub>	-87 Da	Ser
			623.4102	C <sub>31</sub> H <sub>55</sub> N <sub>6</sub> O <sub>7</sub>	-144 Da	MeLys
			510.3286	C <sub>25</sub> H <sub>44</sub> N <sub>5</sub> O <sub>6</sub>	-113 Da	Leu/Ile
			397.2445	C <sub>19</sub> H <sub>33</sub> N <sub>4</sub> O <sub>5</sub>	-113 Da	Leu/Ile
			298.1805	C <sub>14</sub> H <sub>24</sub> N <sub>3</sub> O <sub>4</sub>	-99 Da	Val
55	668.4340	C <sub>32</sub> H <sub>58</sub> N <sub>7</sub> O <sub>8</sub>	211.1434	C <sub>11</sub> H <sub>19</sub> N <sub>2</sub> O <sub>2</sub>	-87 Da	Ser
			555.3528	C <sub>26</sub> H <sub>47</sub> N <sub>6</sub> O <sub>7</sub>	-113 Da	Leu/Ile
			442.2628	C <sub>20</sub> H <sub>36</sub> N <sub>5</sub> O <sub>6</sub>	-113 Da	Leu/Ile
			385.2413	C <sub>18</sub> H <sub>33</sub> N <sub>4</sub> O <sub>5</sub>	-57 Da	Gly
			284.1949	C <sub>14</sub> H <sub>24</sub> N <sub>3</sub> O <sub>4</sub>	-101 Da	Thr
			171.1119	C <sub>8</sub> H <sub>15</sub> N <sub>2</sub> O <sub>2</sub>	-113 Da	Lec/Ile
			86.0964	C <sub>5</sub> H <sub>12</sub> N	-85 Da	Ala

ABA : amino butyric acid, Ala : alanine, Gly : glycine, Ile : isoleucine, Leu: leucine, Lys : lysine, Ser : serine, Thr : threonine, Val : valine. Isoleucine and Leucine cannot be differentiated based on their high resolution mass.