Supplemental Table 1. Keefover-Ring *et al.* - Phenylpropanoid glycosides of *Mimulus guttatus* (yellow monkeyflower)

Supplemental Table 1a. ^{1}H and ^{13}C NMR spectroscopic data for compounds **1**-**4** in CD_3OD from the foliage of *Mimulus guttatus*. H-C designations confirmed with HSQC. Multiplet, and *J* (Hz) within parenthesis. See Figure 1 for carbon designations

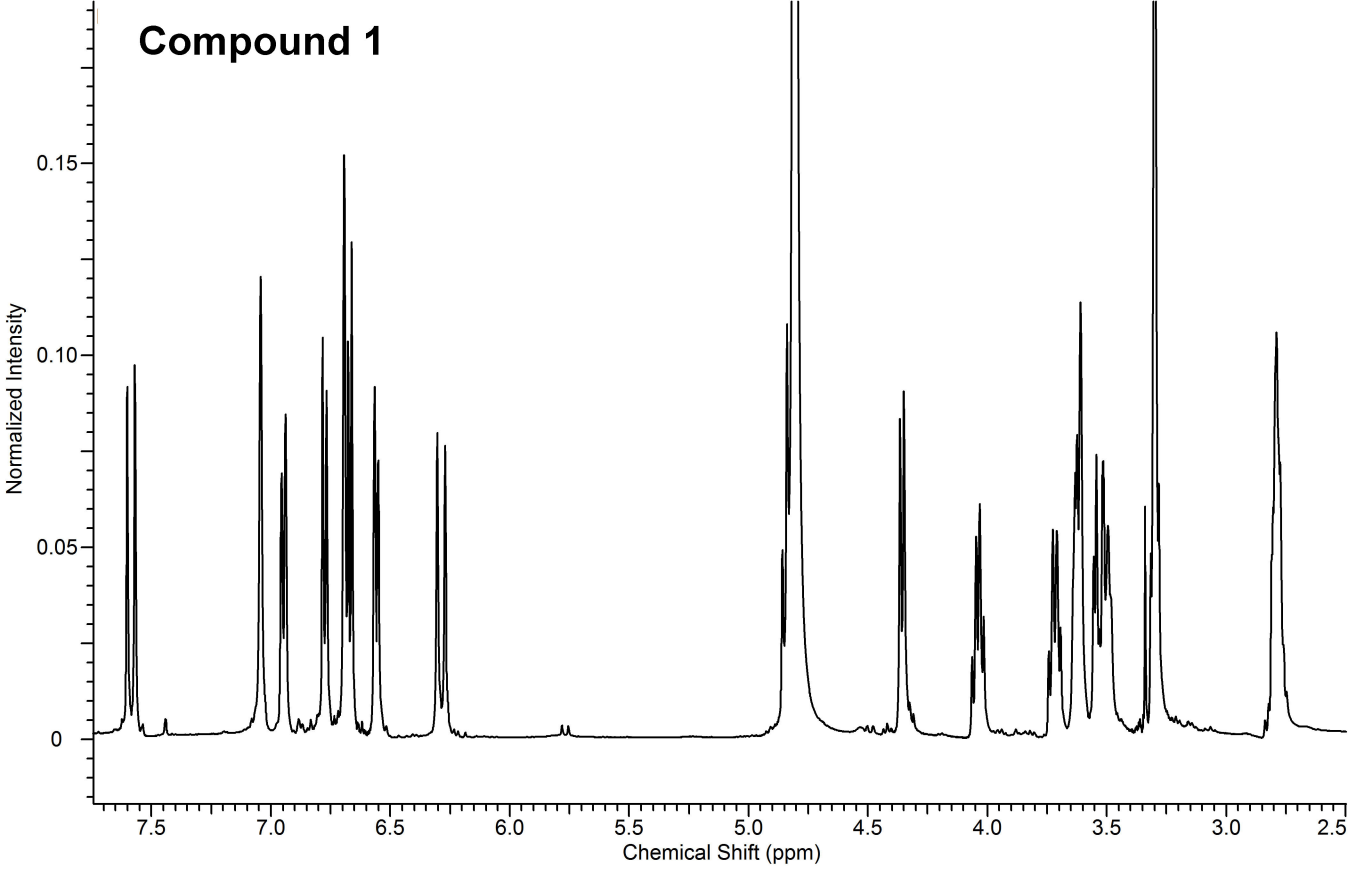
C-	**1** - Calceolarioside A		**2** - Calceolarioside B		**3** - Conandroside		**4** - Verbascoside	
no.	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C
Hydroxyphenylethyl moiety								
1		131.5		131.4		131.4		131.5
2	6.69 (*d*, 1.8)	117.1	6.66 (*d*, 1.8)	117.1	6.69 (*d*, 1.8)	117.1	6.69 (*d*, 1.8)	117.1
3		146.1		146.1		146.1		146.1
4		144.7		144.7		144.7		144.7
5	6.67 (*d*, 8.0)	116.3	6.62 (*d*, 8.0)	116.3	6.67 (*d*, 8.0)	116.3	6.67 (*d*, 8.0)	116.3
6	6.56 (*dd*, 1.8, 8.0)	121.3	6.53 (*dd*, 1.8, 8.0)	121.2	6.56 (*dd*, 1.8, 8.0)	121.3	6.56 (*dd*, 1.8, 8.0)	121.3
7	2.79 (*m*)	36.6	2.77 (*m*)	36.7	2.79 (*m*)	36.5	2.79 (*m*)	36.6
8	3.72 (*m*); 4.04 (*m*)	72.2	3.95 (*m*), 3.70 (*m*)	72.4	3.72 (*m*); 4.03 (*m*)	72.2	3.72 (*m*); 4.04 (*m*)	72.3
Glucosyl moiety								
1'	4.36 (*d*, 7.7)	104.4	4.32 (*d*, 7.9)	104.5	4.41 (*d*, 8.0)	103.9	4.37 (*d*, 8.0)	104.2
2'	3.30 (obs. by CHD_2OD)	75.2	3.20 (*t*, 8.3)	75.1	3.47 (*dd*, 8.0, 8.9)	75.7	3.38 (*t*, 8.5)	76.2
3'	3.62 (*m*)	75.8	3.36 (*m*)	77.9	3.83 (*t*, 9.3)	85.2	3.81 (*t*, 9.2)	81.6
4'	4.85 (*t*, 9.4)	72.5	3.35 (*m*)	71.7	4.91 (*t*, 9.2)	70.9	4.91 (*t*, 9.3)	70.6
5'	3.50 (*t*, 9.3)	76.1	3.51 (*m*)	75.5	3.53 (*m*)	76.0	3.53 (*m*)	76.1
6'	3.54 (*m*); 3.62 (*m*)	62.5	4.49 (*dd*, 8.0, 1.9), 4.33 (m)	64.6	3.54 (*m*); 3.62 (*m*)	62.3	3.53 (*m*); 3.62 (*m*)	62.4

Outer sugar moiety								
1"					4.43 (*d*, 7.9)	106.9	5.18 (*d*, 8.0)	103.0
2"					3.14 (*dd*, 7.9, 8.6)	74.9	3.91 (*t*, 8.6)	72.4
3"					3.26 (*t*, 9.0)	77.6	3.57 (*m*)	72.1
4"					3.33 (*m*)	71.0	3.28 (*t*, 9.6)	73.8
5"					3.06 (*dd*, 10.8, 10.4); 3.63 (*m*)	67.3	3.56 (*m*)	70.4
6"							1.08 (*d*, 6.2)	18.5
Hydroxycinnamic acid moiety								
1"'		127.7		127.7		127.7		127.6
2"'	7.04 (*d*, 1.8)	115.2	7.02 (*d*, 1.8)	115.0	7.05 (*d*, 1.7)	115.1	7.04 (*d*, 1.8)	115.2
3"'		146.8		146.8		146.9		146.9
4"'		149.7		149.7		149.7		149.9
5"'	6.77 (*d*, 8.1)	116.5	6.76 (*d*, 8.2)	116.5	6.77 (*d*, 8.2)	116.5	6.77 (*d*, 8.1)	116.5
6"'	6.95 (*dd*, 1.8, 8.1)	123.1	6.88 (*dd*, 1.8, 8.2)	123.2	6.95 (*dd*, 1.7, 8.2)	123.0	6.94 (*dd*, 1.8, 8.1)	123.2
β	7.59 (*d*, 15.9)	147.6	7.55 (*d*, 15.9)	147.2	7.56 (*d*, 15.9)	147.2	7.58 (*d*, 15.9)	148.0
α	6.29 (*d*, 15.9)	114.7	6.28 (*d*, 15.9)	114.8	6.25 (*d*, 15.9)	115.1	6.26 (*d*, 15.9)	114.7
C=O		168.6		169.2		168.4		168.3

Supplemental Table 1b. COSY and HMBC two-dimensional NMR spectroscopic data for compounds **1-4** in CD_3OD from the foliage of *Mimulus guttatus*. H-C designations confirmed with HSQC. Key HMBC correlations for structure elucidation in bold face. See Figure 1 for carbon designations. * = long range

C-	**1** - Calceolarioside A		**2** - Calceolarioside B		**3** - Conandroside		**4** - Verbascoside	
no.	COSY	HMBC	COSY	HMBC	COSY	HMBC	COSY	HMBC
Hydroxyphenylethyl moiety								
1								
2		36.6, 121.3, 144.7, 146.1		36.7, 121.2, 131.4, 144.7, 146.1		36.5, 121.3, 144.7, 146.1		36.6, 121.3, 144.7
3								
4								
5	6	117.1, 131.5, 144.7, 146.1	6	117.1, 121.2, 131.4, 144.7, 146.1	6	131.4, 144.7, 146.1	6	131.5, 144.7, 146.1
6	5	36.3, 117.1, 144.7, 146.1	5	36.7, 117.1, 144.7	5	36.5, 117.1, 131.4, 144.7, 146.1	5	36.6, 117.1, 144.7
7	8	72.2, 117.1, 121.3, 131.5	8	72.4, 117.1, 121.2, 131.4	8	72.2, 117.1, 121.3, 131.4	8	72.3, 117.1, 121.3, 131.5
8	7, 8	36.6, **104.4**, 131.5	7, 8	36.7, **104.5**, 131.4	7	36.5, **103.9**, 131.4	7, 8	36.6, **104.2**, 131.5
Central glucosyl moiety								
1'	2'	**72.2**, 76.1	2'	**72.4**, 77.9	2'	**72.2**, 76.0, 85.2	2'	**72.3**, 76.1, 81.6
2'	1', 3'	75.8, 104.4	1', 3'	77.9, 104.5	1', 3'	85.2, 103.9	1', 3'	81.6, 104.2
3'	2', 4'	72.5, 75.2	2', 4'	71.7, 75.1	2', 4'	70.9, 74.9, **106.9**	2', 4'	76.2, 70.6, **103.0**
4'	3', 5'	62.5, 76.1, **168.6**	5'	64.6, 75.5, 77.9	3', 5'	62.3, 76.0, 85.2, **168.4**	3', 5'	62.4, 76.1, 81.6, **168.3**
5'	4', 6'	62.5, 72.5, 76.1, 104.4	4', 6'	64.6, 71.7, 77.9, 104.5	4', 6'	62.3, 70.9, 76.0, 85.2, 103.9	4', 6'	62.4, 70.6, 76.1, 81.6, 104.2
6'	5'	72.5, 76.1	5', 6'	75.5, **169.2**	5', 6'	70.9	5', 6'	70.6, 76.1, 104.2

Outer sugar moiety								
1"					2"	67.3, **85.2**	2"	70.4, 72.4, **81.6**
2"					1", 3"	71.0, 77.6, 106.9	1", 3"	72.1, 73.8
3"					2", 4"	71.0, 75.7	2", 4"	72.1, 73.8, 70.4
4"					3", 5"	67.3, 77.6	3", 5"	18.5, 70.4, 72.1
5"					4"	71.0, 77.6, 106.9	6"	70.6, 73.8, 103.0
6"							5"	70.4, 73.8
Hydroxycinnamic acid moiety								
1"'								
2"'	6"'*	123.1, 146.8, 147.6, 149.7		123.2, 147.2, 149.7	6"'*	123.0, 146.9, 147.2, 149.7		123.2, 146.9, 148.0, 149.9
3"'								
4"'								
5"'	6"'	115.2, 123.1, 146.8, 149.7	6"'	115.0, 123.2, 127.7, 147.2, 149.7	6"'	123.0, 127.7, 146.9, 149.7	6"'	123.2, 127.6, 146.9, 149.9
6"'	5"'	115.2, 116.5, 147.6, 149.7	5"'	115.0, 116.5, 147.2, 149.7	2"'*, 5"'	115.1, 116.5, 147.2, 149.7	5"'	115.2, 148.0, 149.9
β	α	114.7, 115.2, 123.1, 127.7, 147.6, 168.6	α	115.0, 123.2, 127.7, 169.2	α	115.1, 123.0, 127.7, 168.4	α	115.2, 123.2, 127.6, 168.3
α	β	127.7, 147.6, 168.6	β	127.7, 169.2	β	127.7, 168.4	β	127.6, 168.3
C=O								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Normalized Intensity
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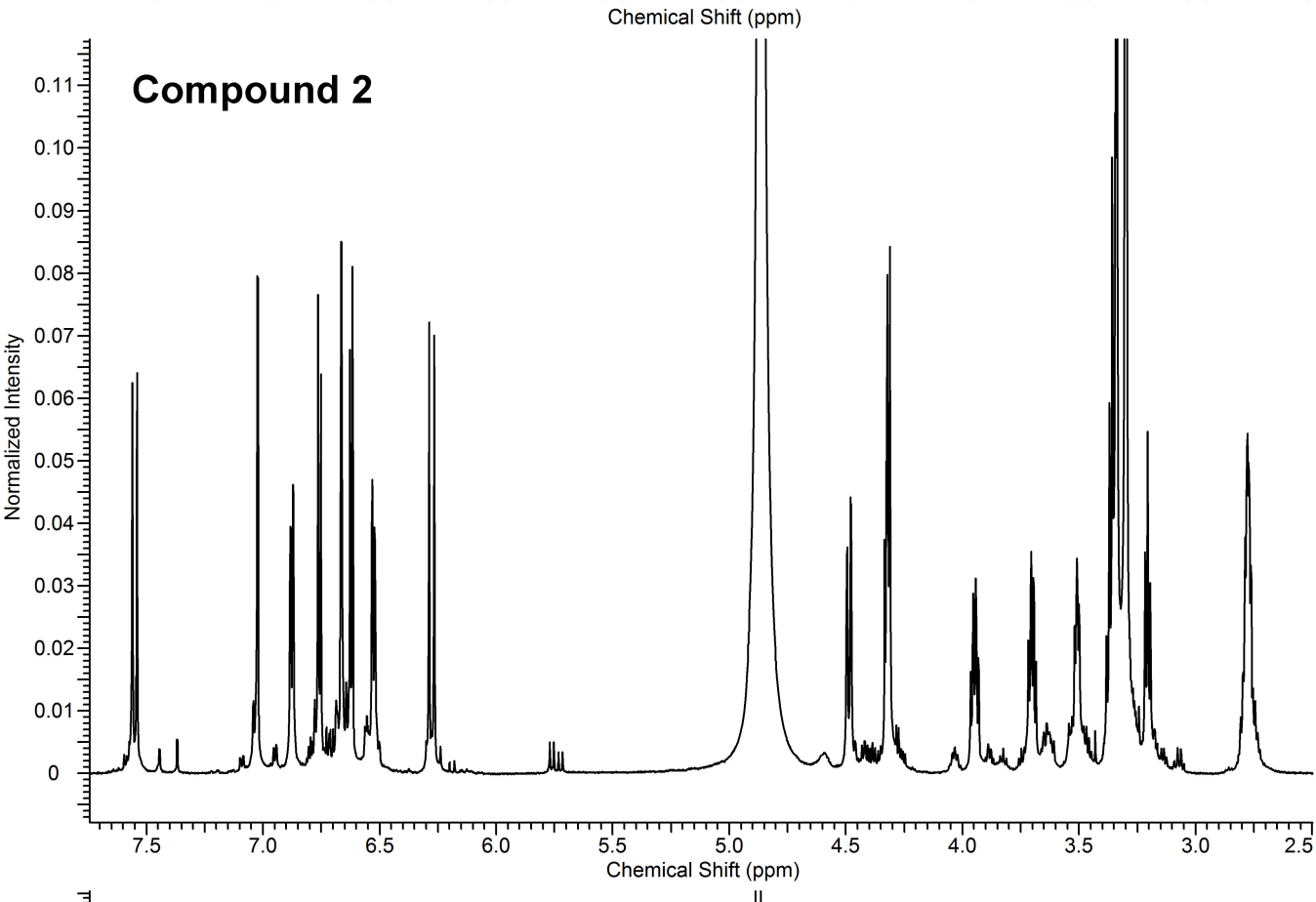
0.10
0.05
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)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0.08
0.07
0.06
0.05
0.04
0.03
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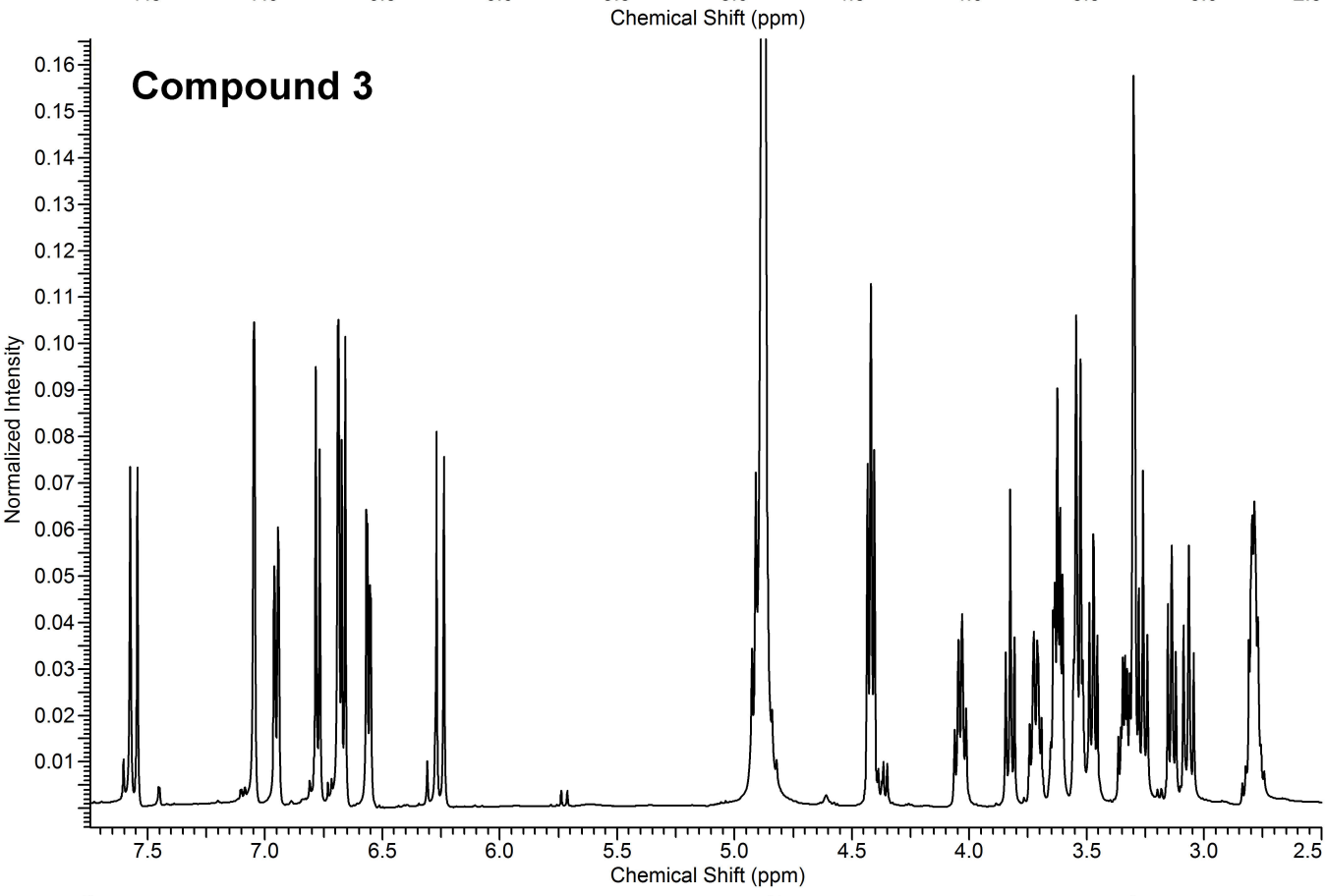
4.0
3.5
3.0
2.5
Chemical Shift (ppm)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0.13
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0.06
0.05
0.04
0.03
0.02
0.01
7.5
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6.0
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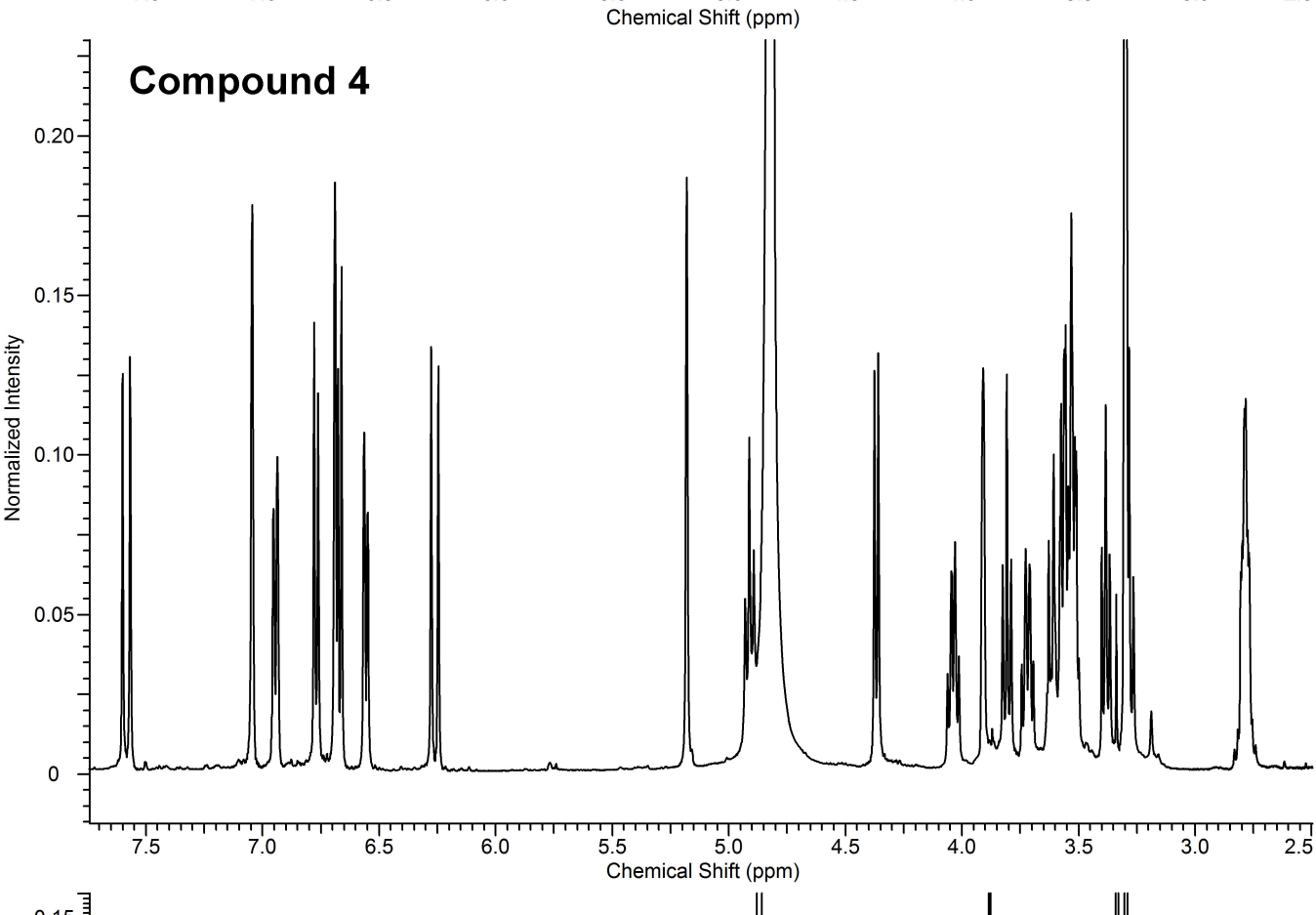
4.0
3.5
3.0
2.5
Chemical Shift (ppm)


Compound 4
Normalized Intensity
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0.10
0.05
0
7.5
7.0
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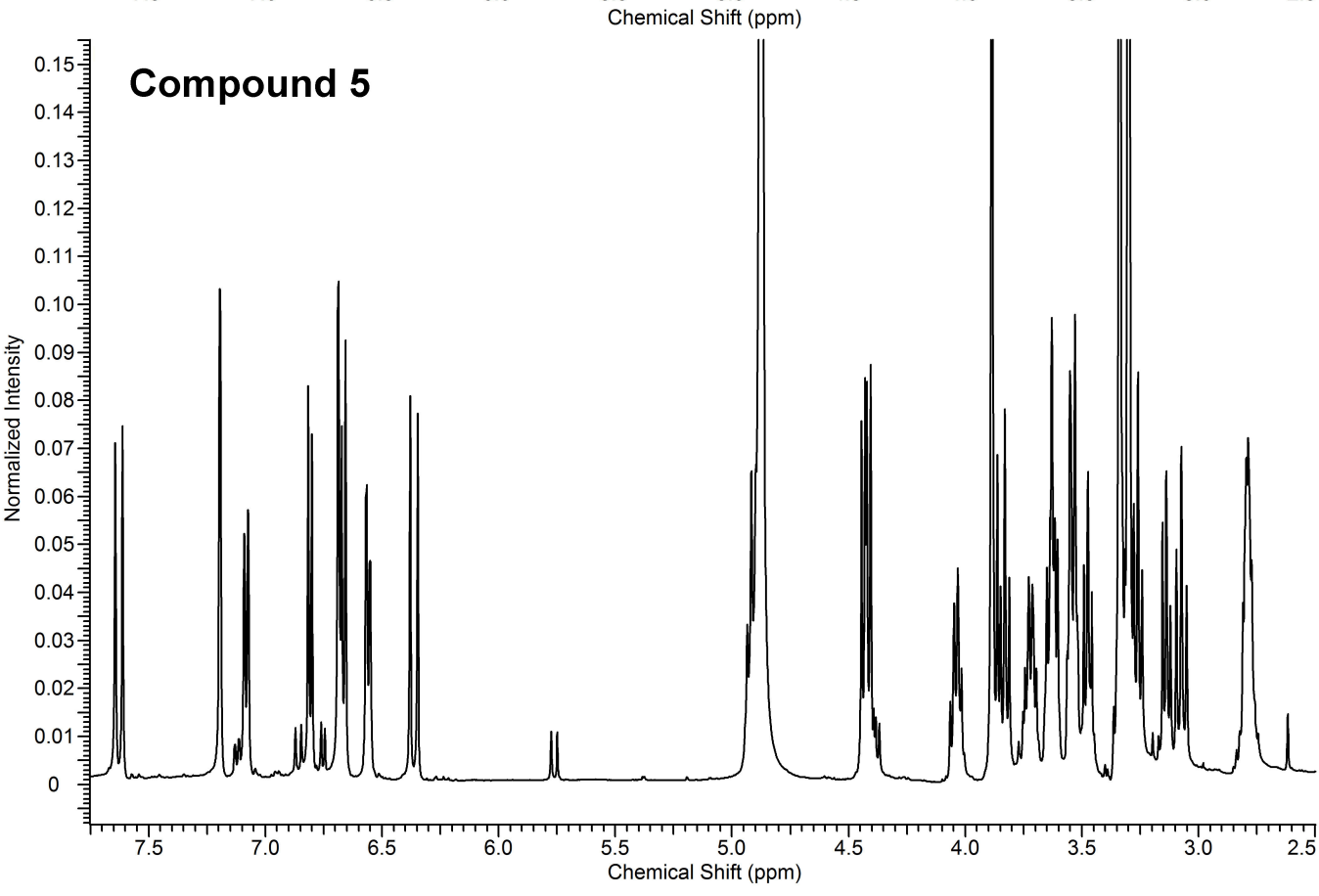
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)


Compound 5
Normalized Intensity
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0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
7.5
7.0
6.5
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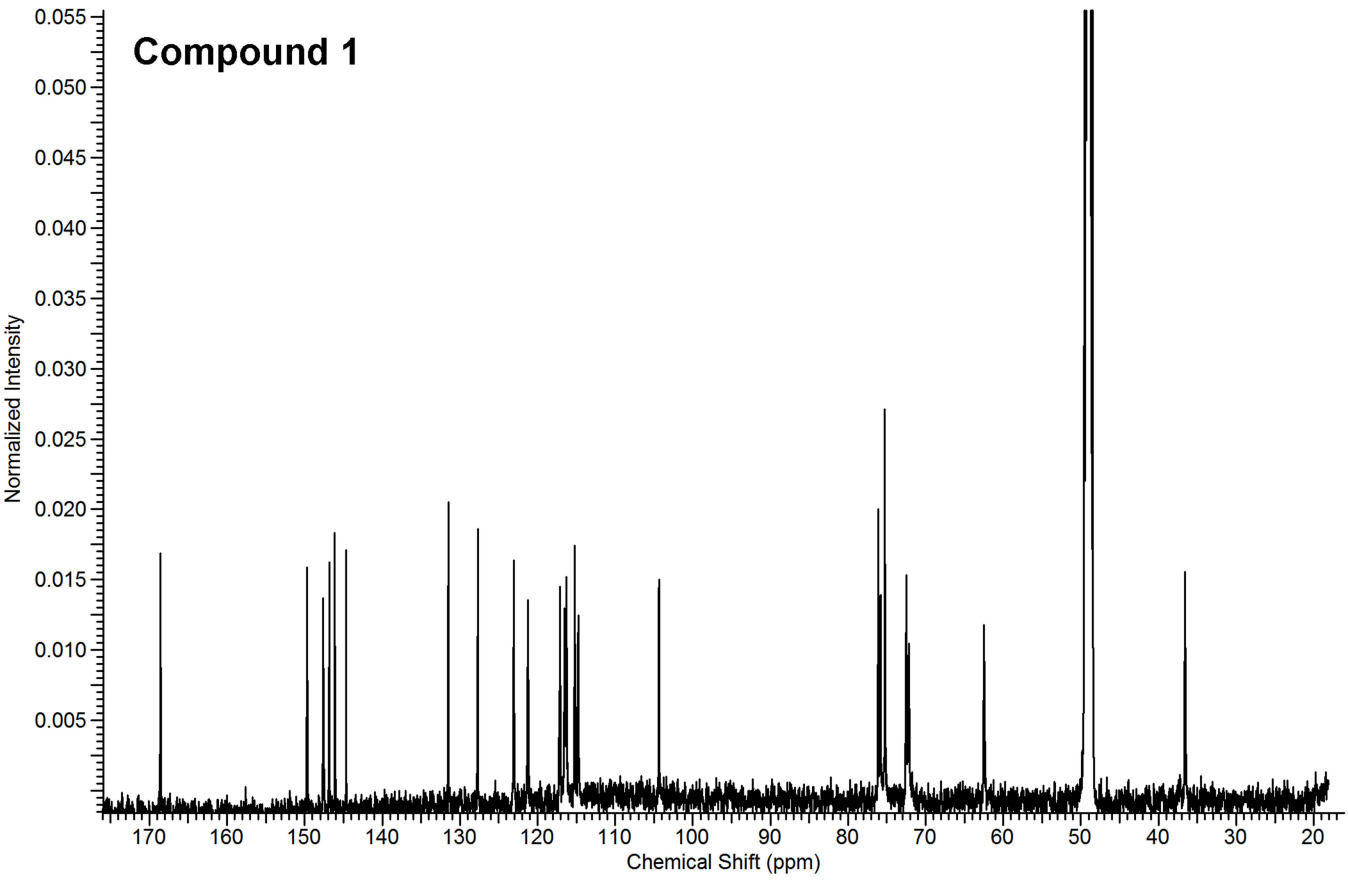
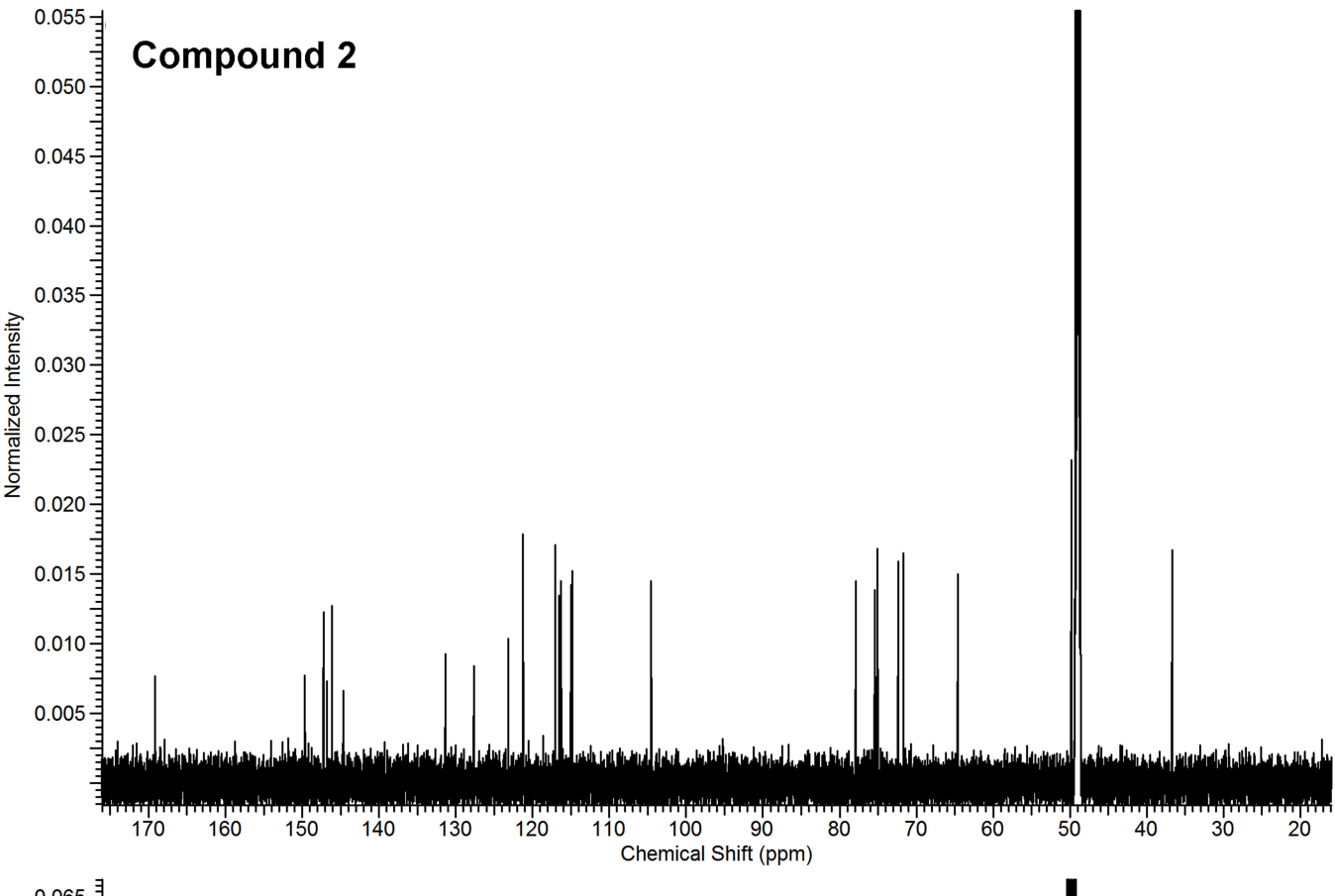
3.5
3.0
2.5
Chemical Shift (ppm)

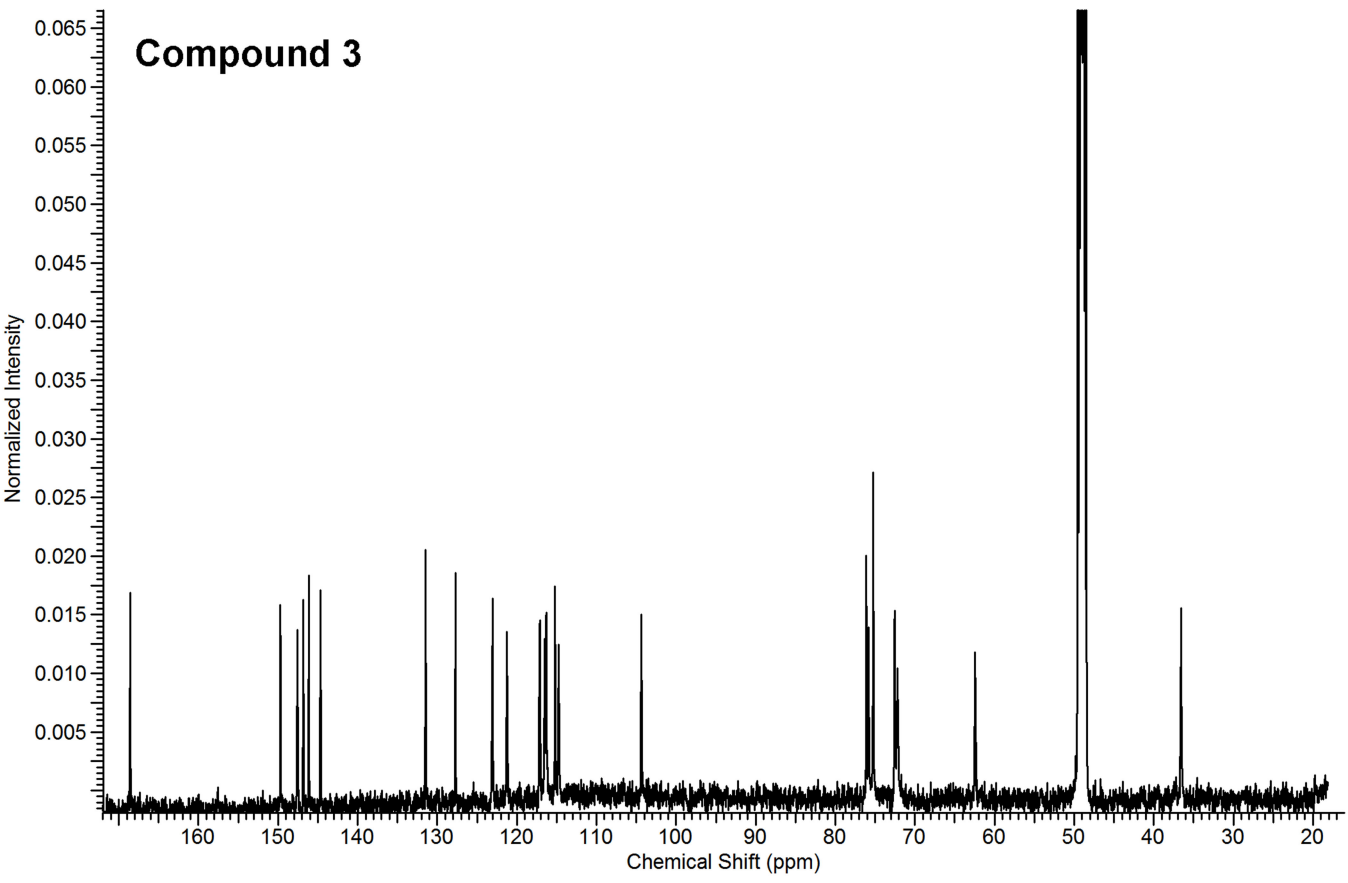
Compound 1



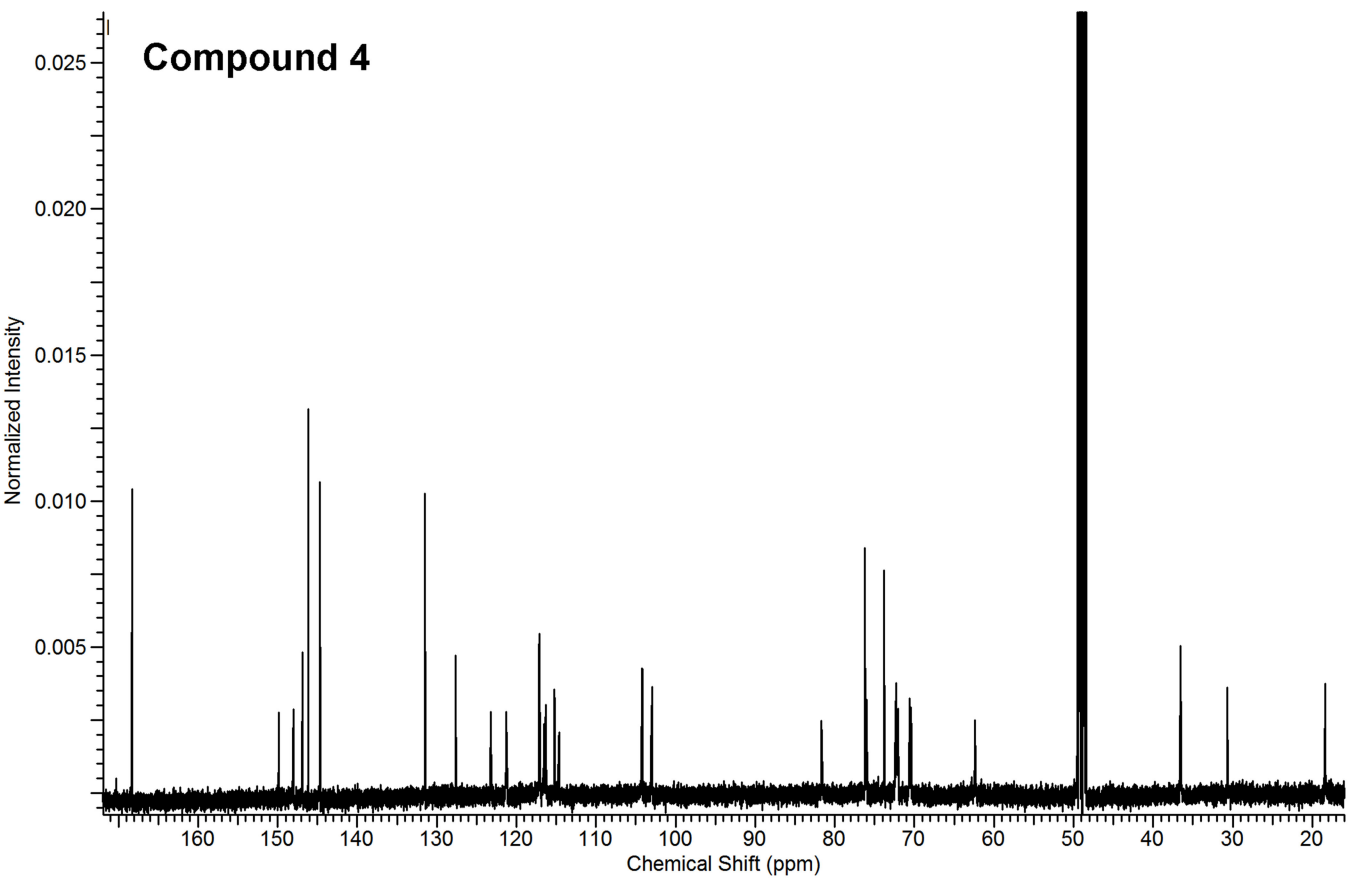
Compound 2



Compound 3



Compound 4

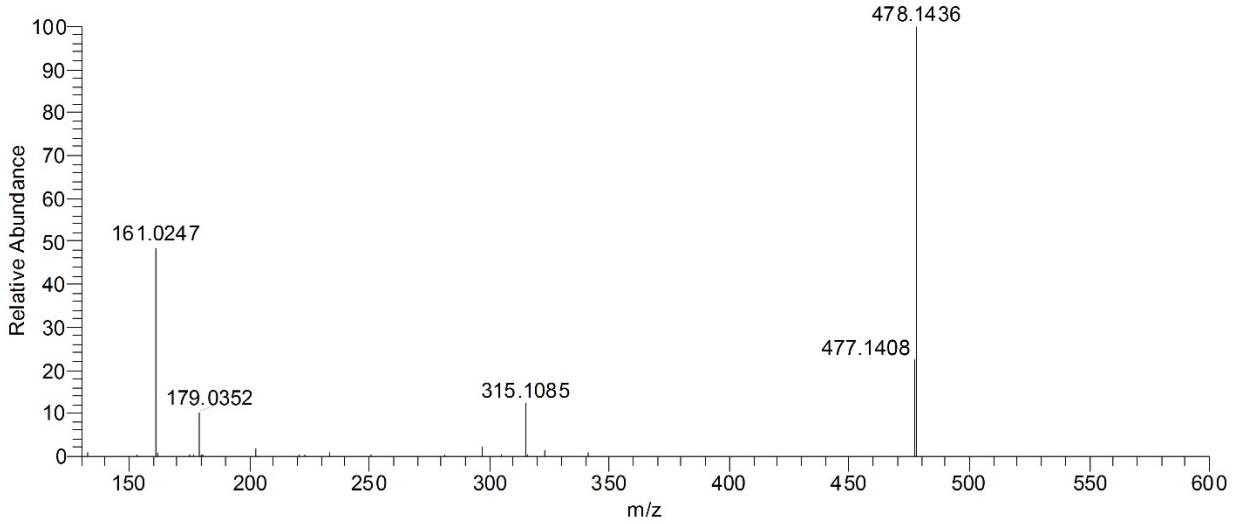


Compound 5

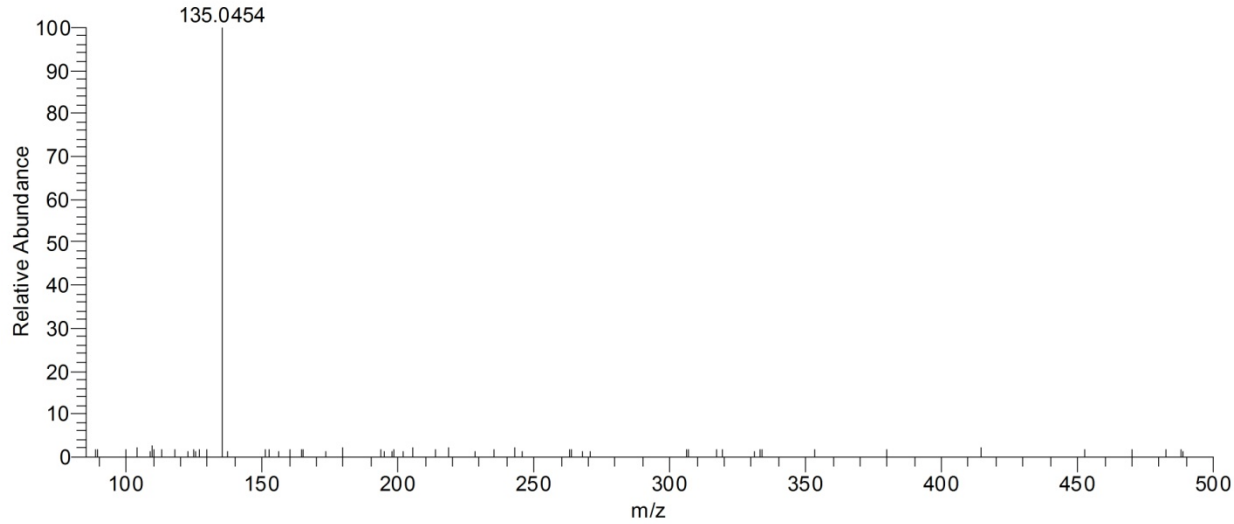
Appendix 1. Keefover-Ring *et al.* Phenylpropanoid glycosides of *Mimulus guttatus* (yellow monkeyflower) - High-resolution tandem mass spectra of five identified (**1**-**5**) and 11 putative phenylpropanoid glycosides from the foliage of *Mimulus guttatus*. See Section 3.4 in Experimental for MS/MS conditions, Figure 1 for fragmentation patterns of compounds **1**-**5**, and Table 2 for a list of main MS^2 and MS^3 (when available) fragments of all compounds

Compound 1 – Calceolarioside A [corresponds to PPG 4 in Holeski et al. (2013)]

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 477.1408

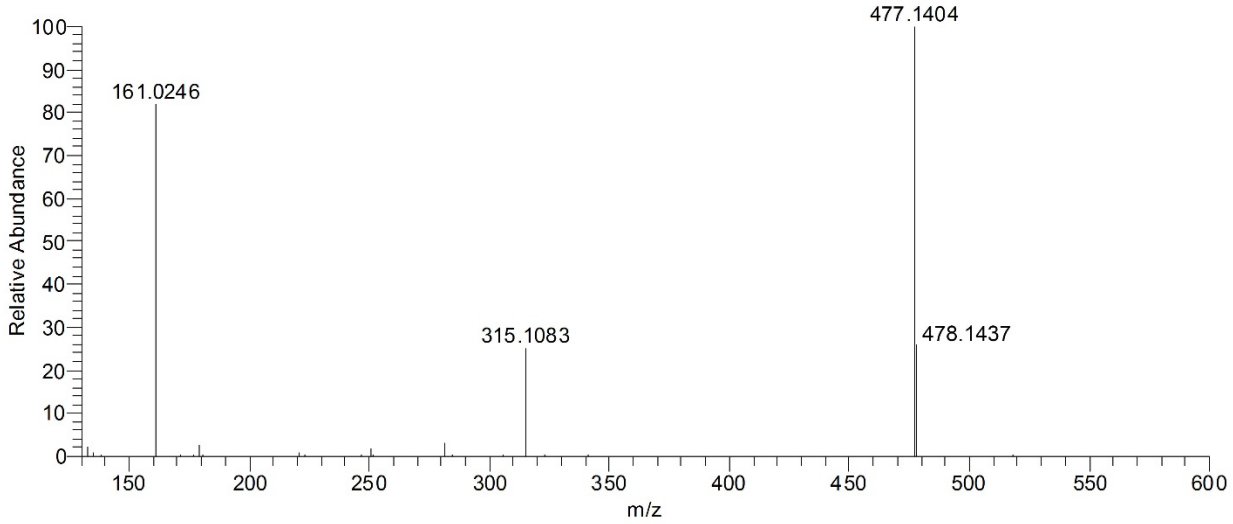


MS^3 spectrum of product ion $[M-H]^-$ *m*/*z* 315.1085

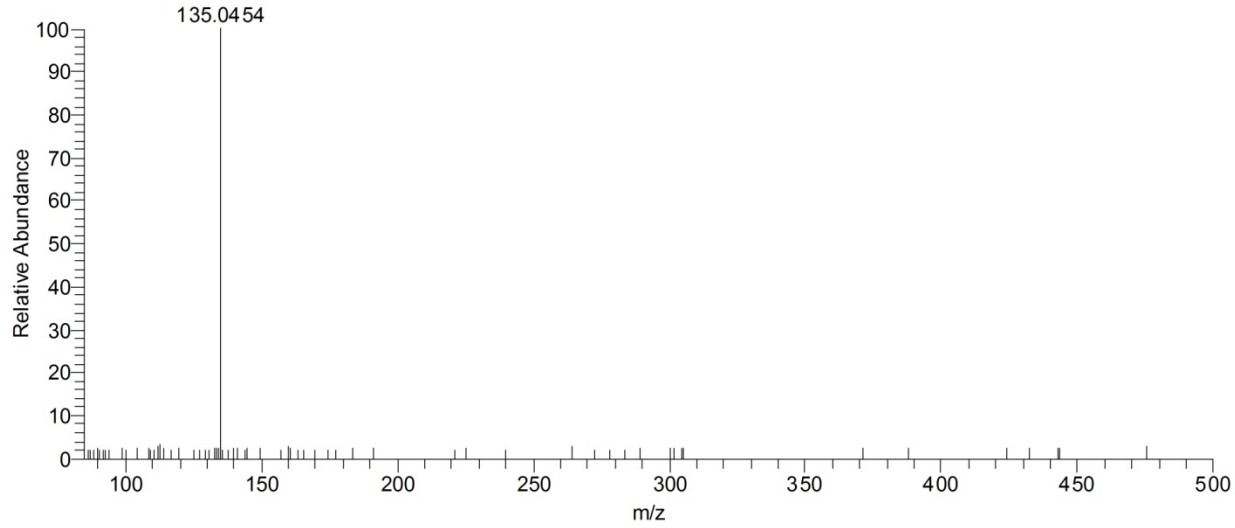


Compound 2 – Calceolarioside B

MS^2 spectrum of precursor ion $[M-H]^-$ *m/z* 477.1404

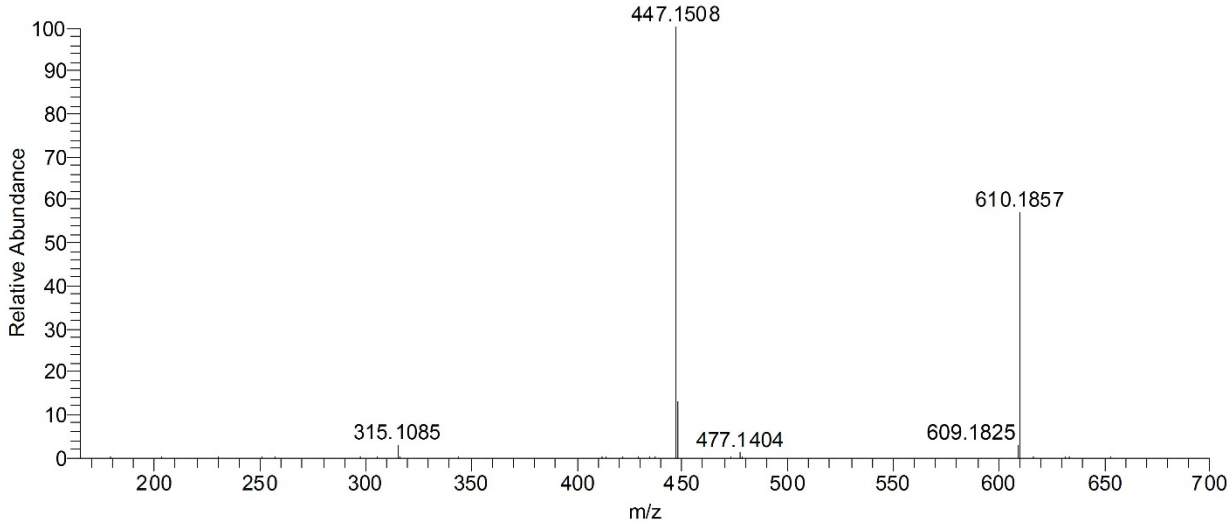


MS^3 spectrum of product ion $[M-H]^-$ *m/z* 315.1083

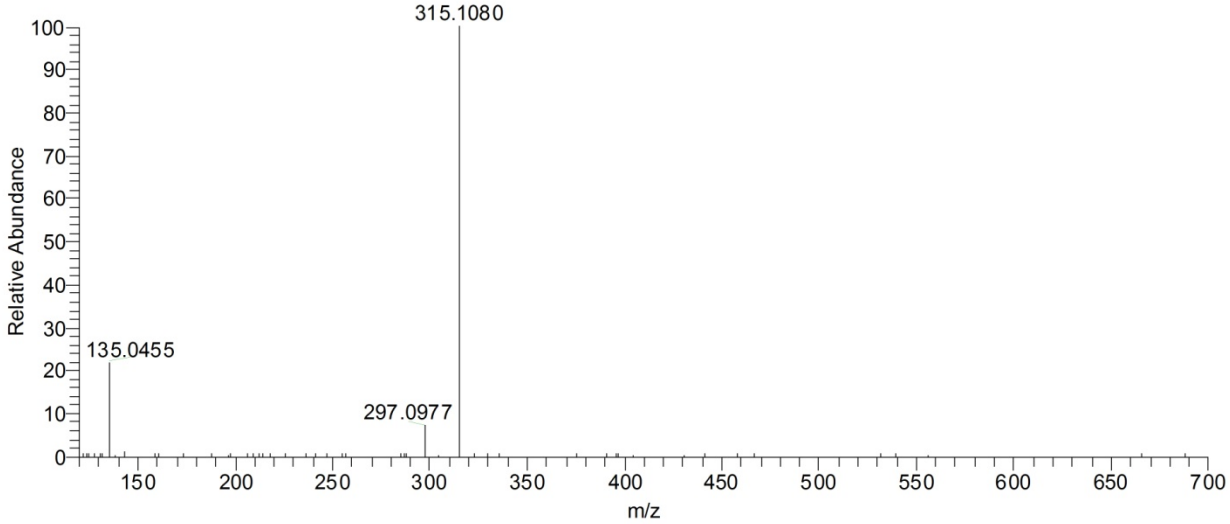


Compound 3 – Conandroside

MS^2 spectrum of precursor ion $[M-H]^-$ *m/z* 609.1825

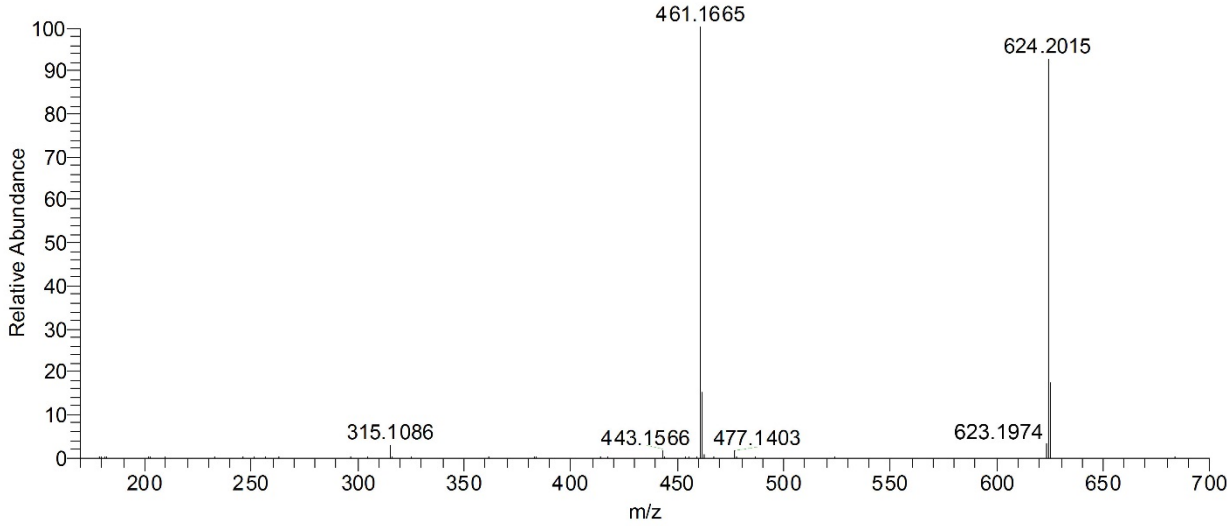


MS^3 spectrum of product ion $[M-H]^-$ *m/z* 447.1508

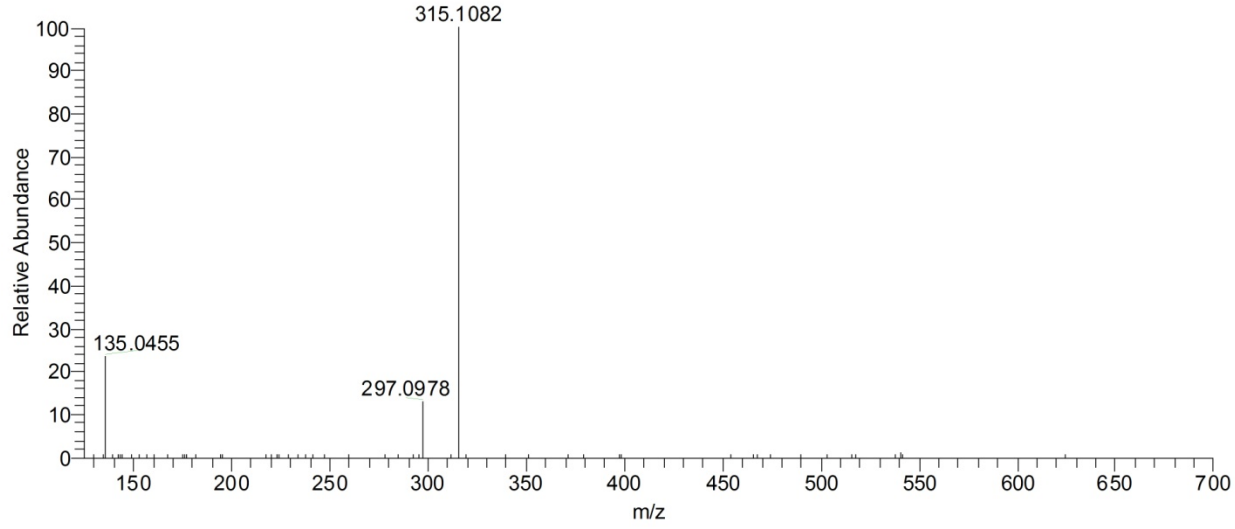


Compound 4 – Verbascoside

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 623.1974

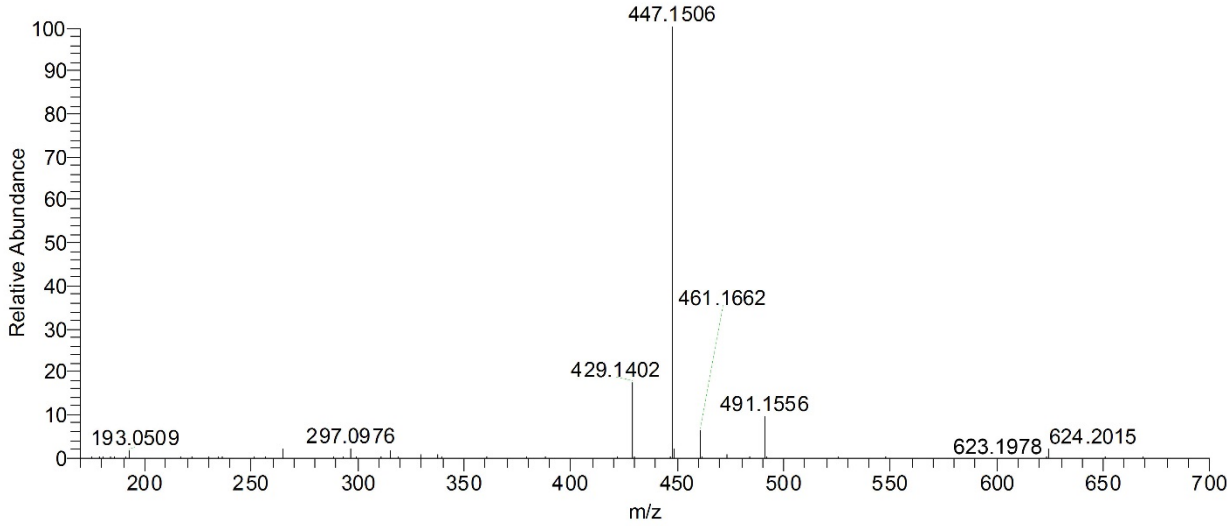


MS^3 spectrum of product ion $[M-H]^-$ *m*/*z* 461.1665

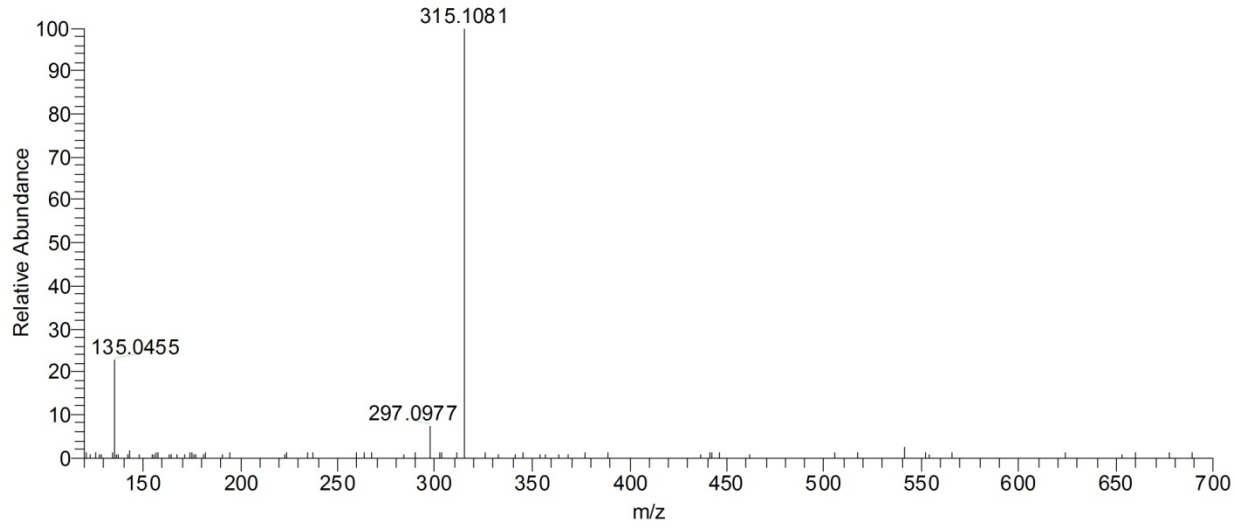


Compound 5 – Mimuloside [corresponds to PPG 5 in Holeski et al. (2013)]

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 623.1978

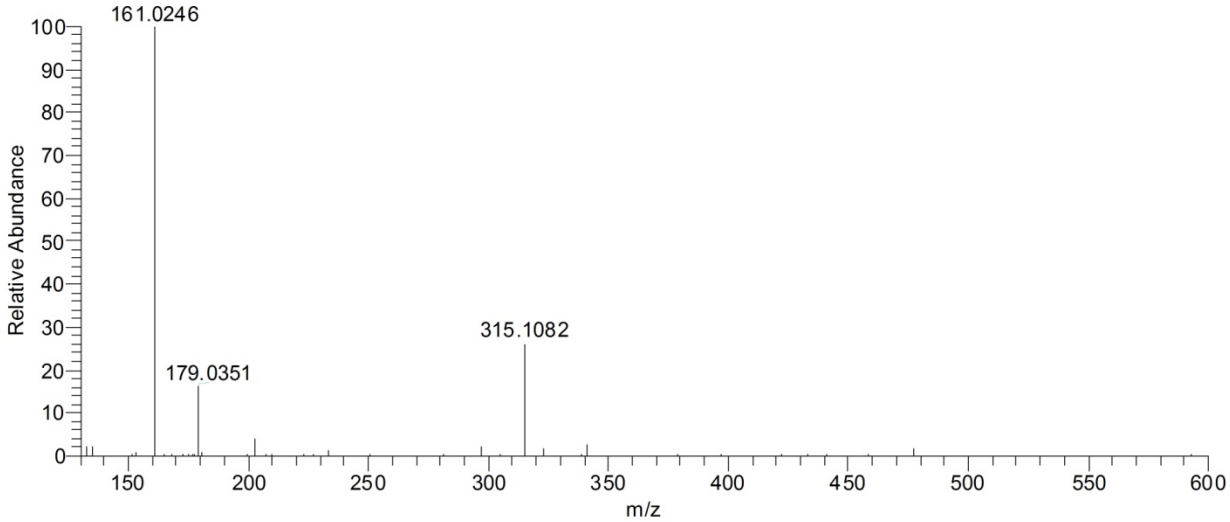


MS^3 spectrum of product ion $[M-H]^-$ *m*/*z* 447.1506

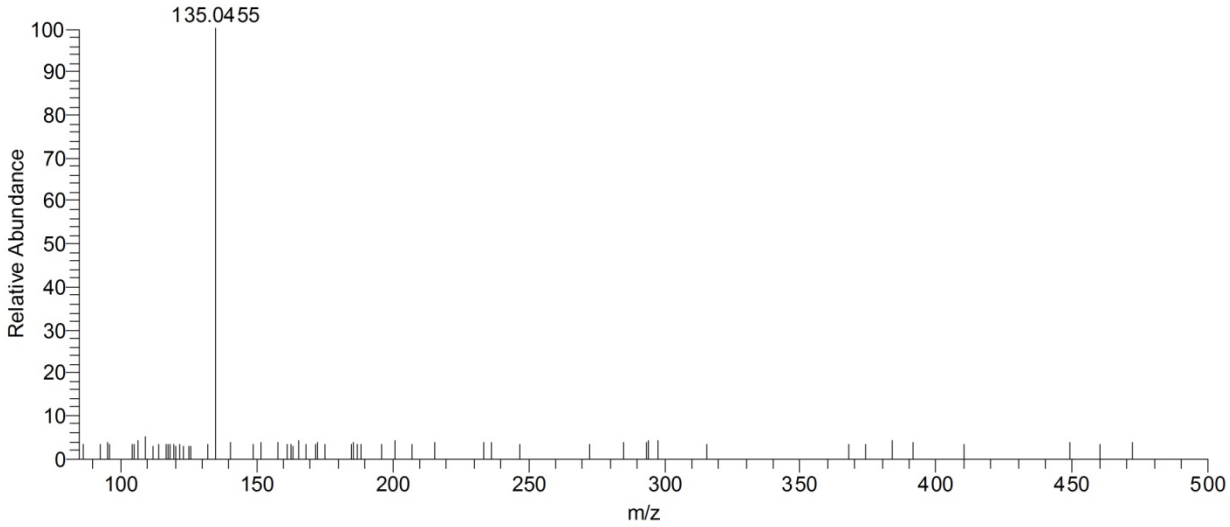


Compound 6

MS^2 spectrum of precursor ion $[M-H]^-$ *m/z* 477.1406

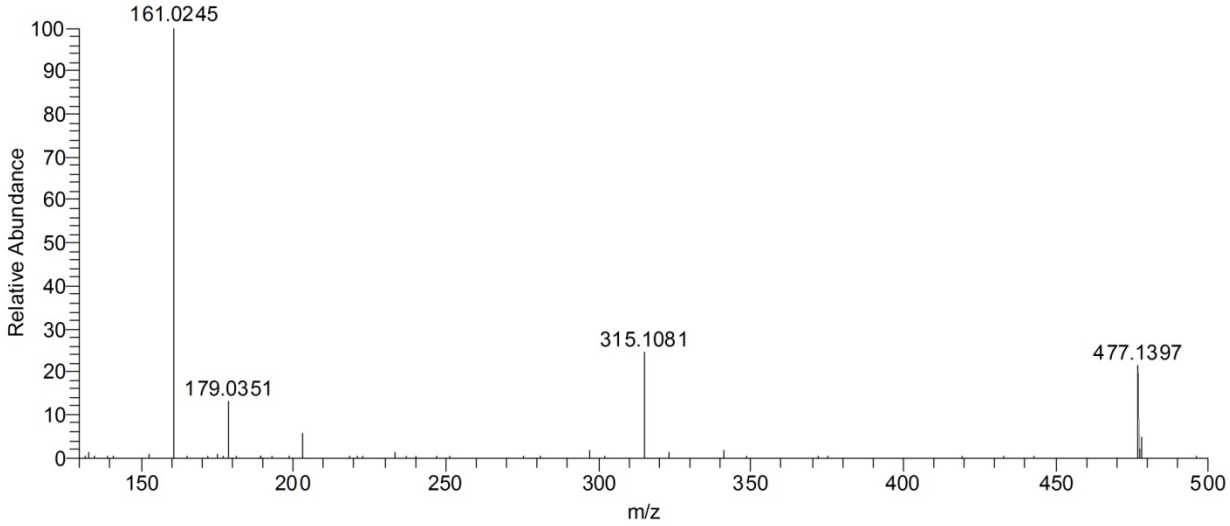


MS^3 spectrum of product ion $[M-H]^-$ *m/z* 315.1082



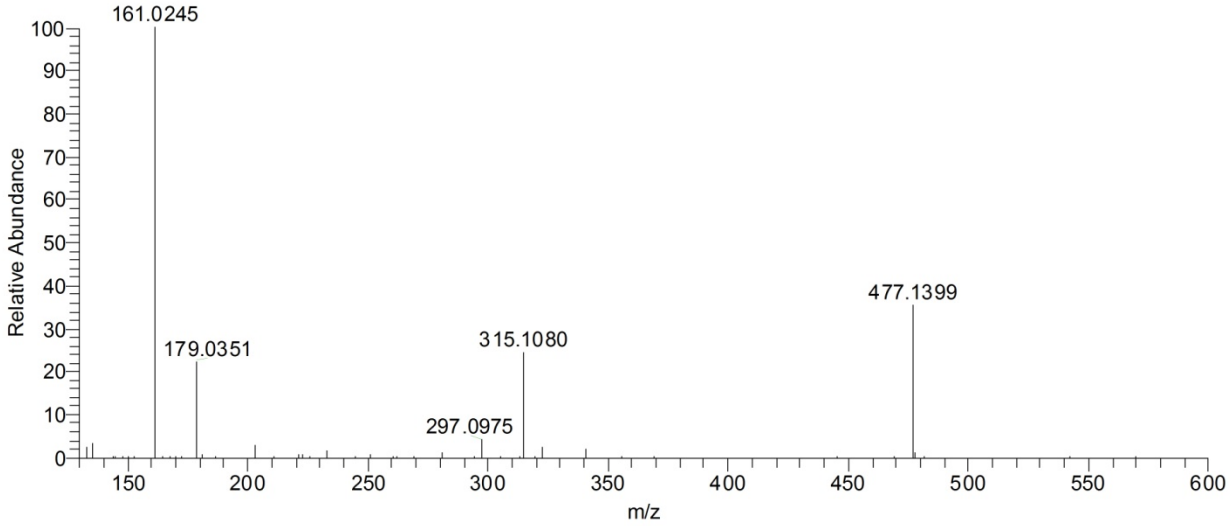
Compound 7

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 477.1397

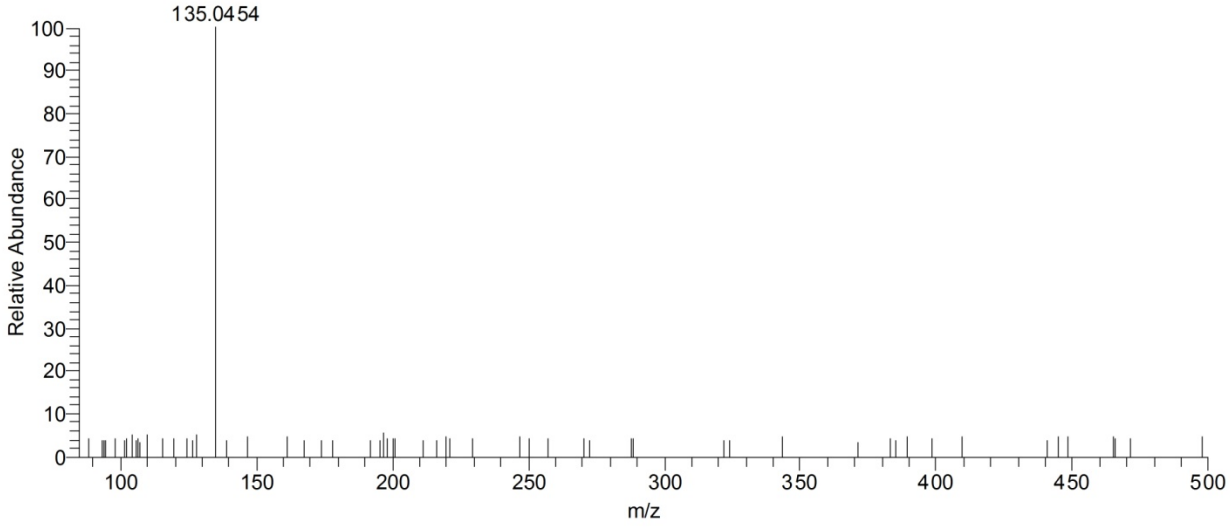


Compound 8

MS^2 spectrum of precursor ion $[M-H]^-$ *m/z* 477.1399

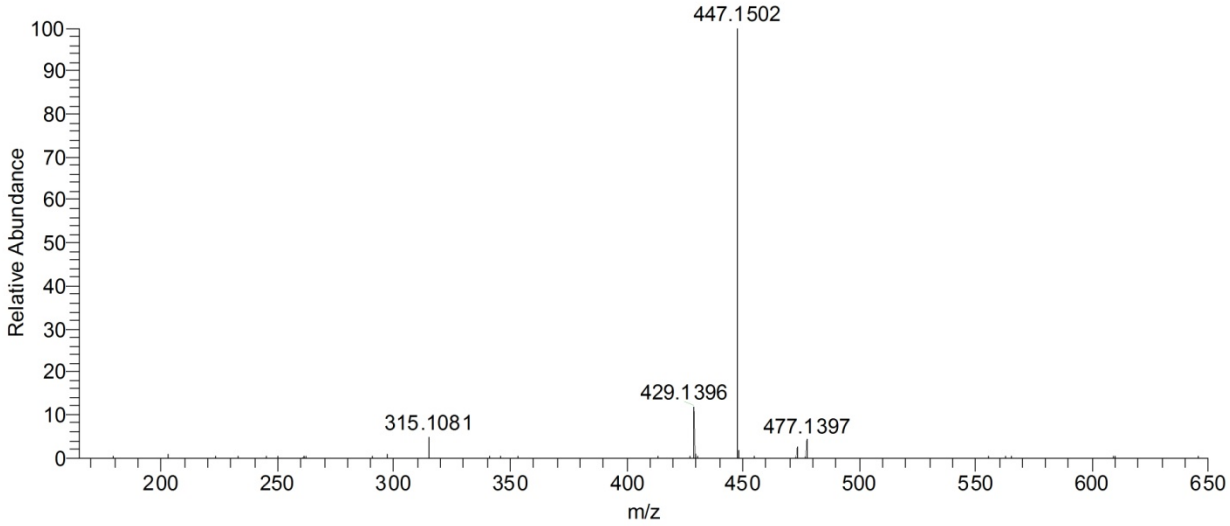


MS^3 spectrum of product ion $[M-H]^-$ *m/z* 315.1080



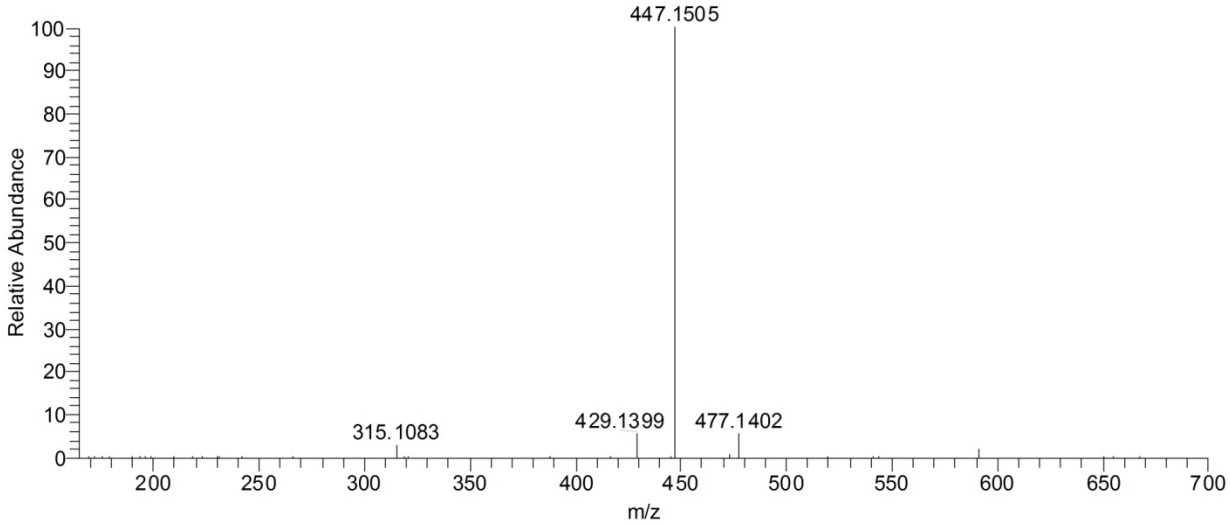
Compound 9

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 609.1824

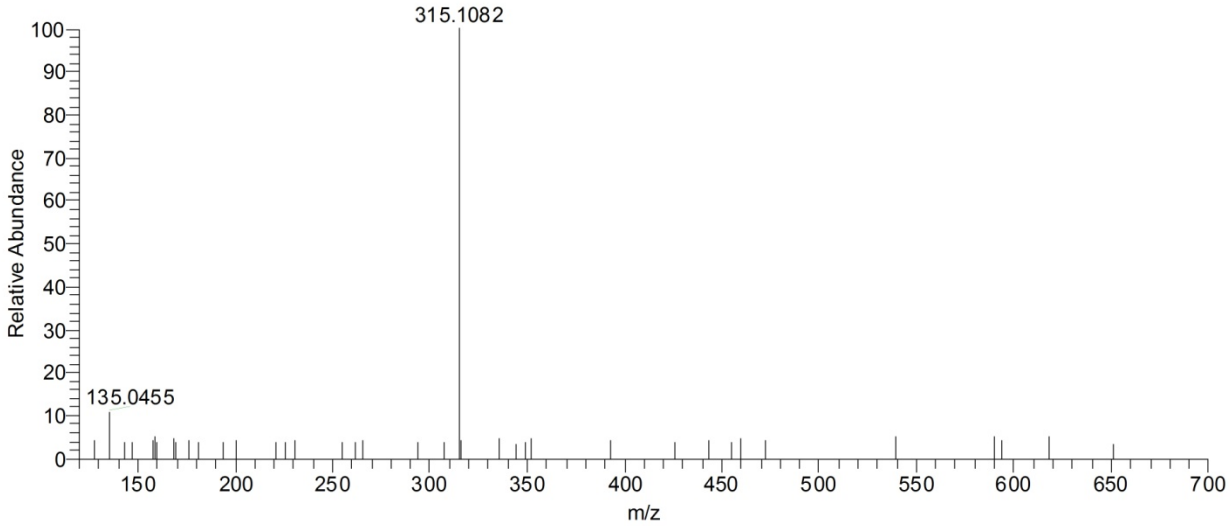


Compound 10 [corresponds to PPG 3 in Holeski et al. (2013)]

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 609.1818

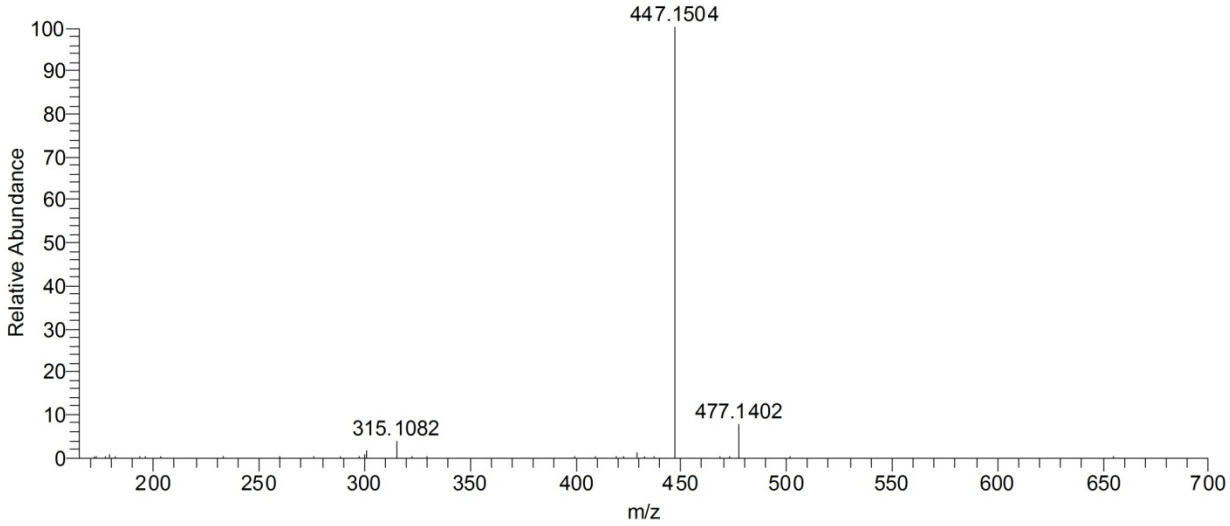


MS^3 spectrum of product ion $[M-H]^-$ *m*/*z* 447.1505

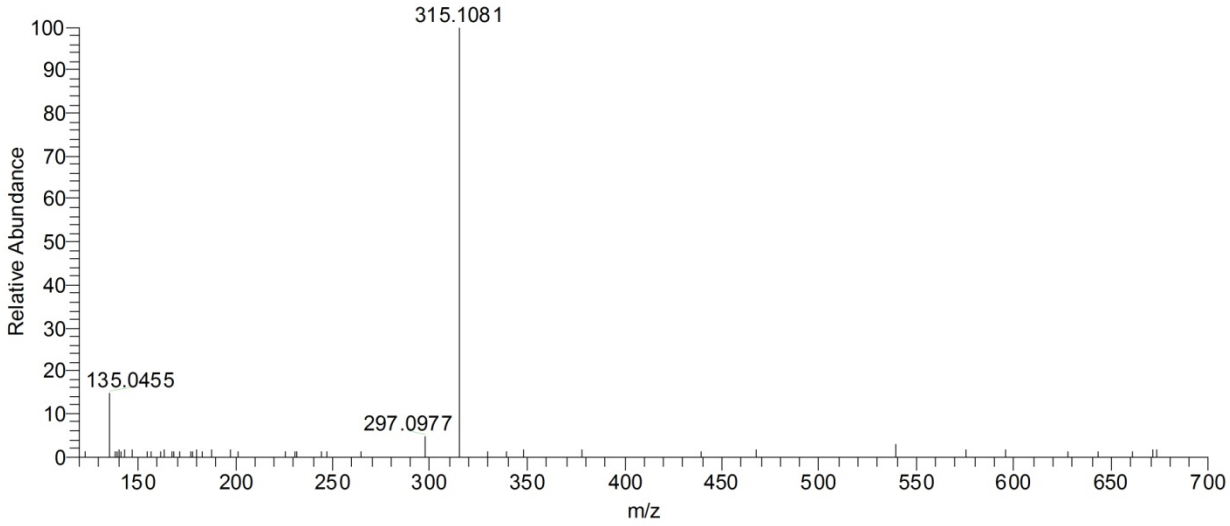


Compound 11

MS^2 spectrum of precursor ion $[M-H]^-$ *m/z* 609.1837

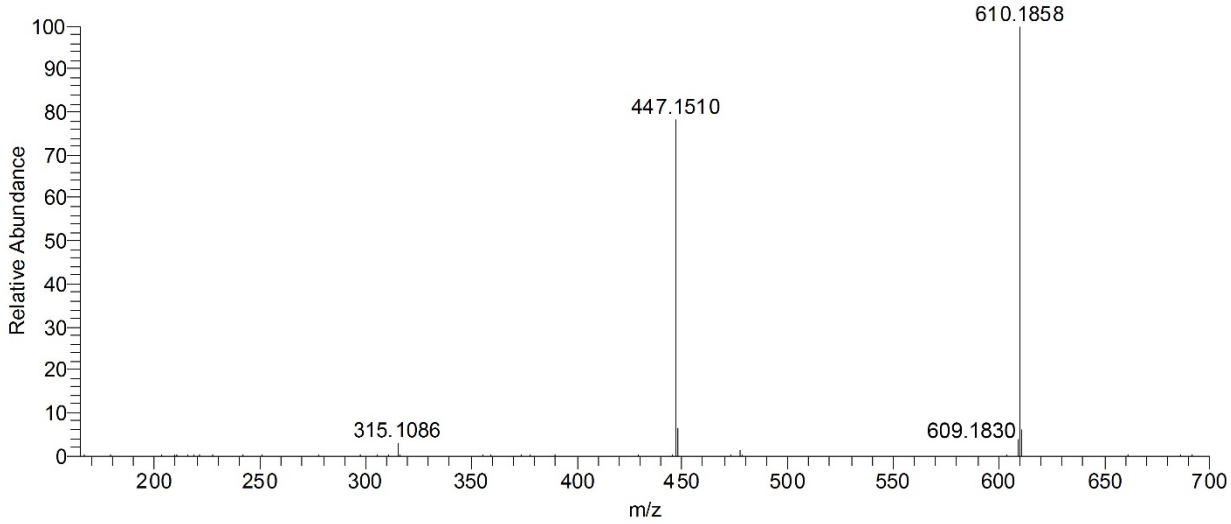


MS^3 spectrum of product ion $[M-H]^-$ *m/z* 447.1504

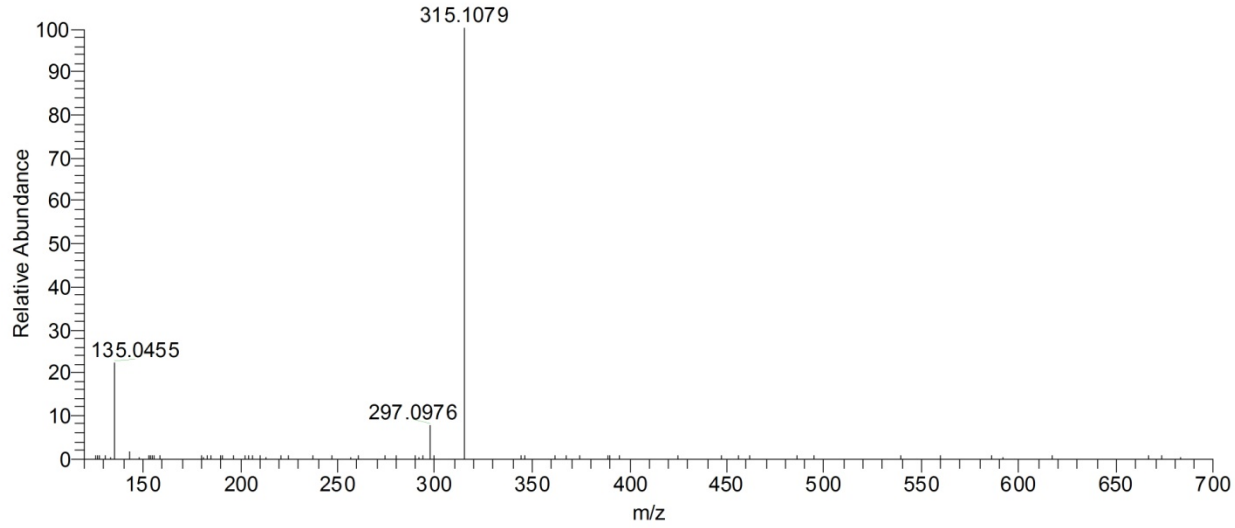


Compound 12

MS^2 spectrum of precursor ion $[M-H]^-$ *m/z* 609.1830

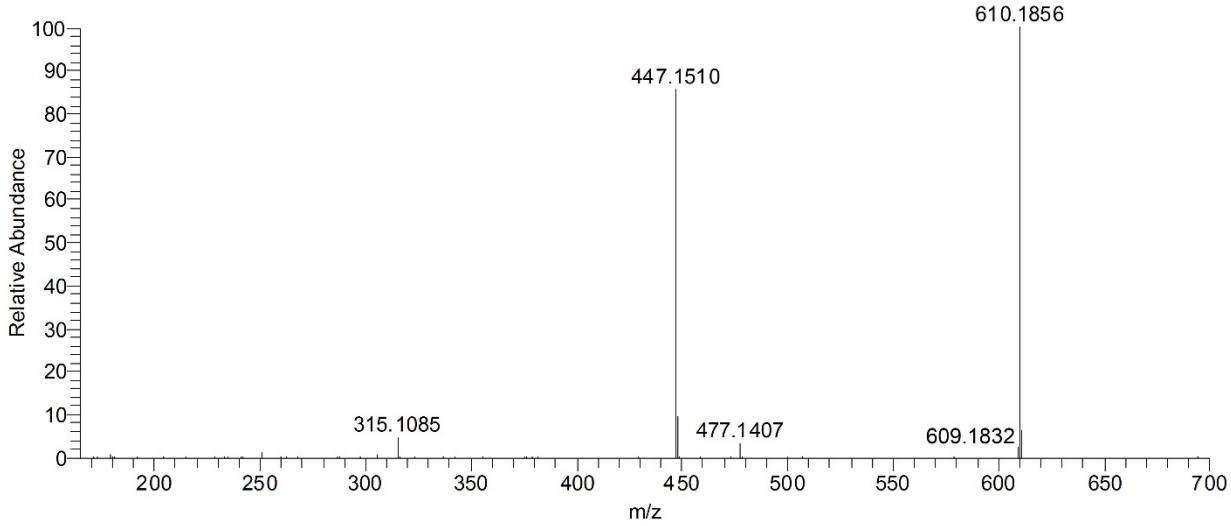


MS^3 spectrum of product ion $[M-H]^-$ *m/z* 447.1510

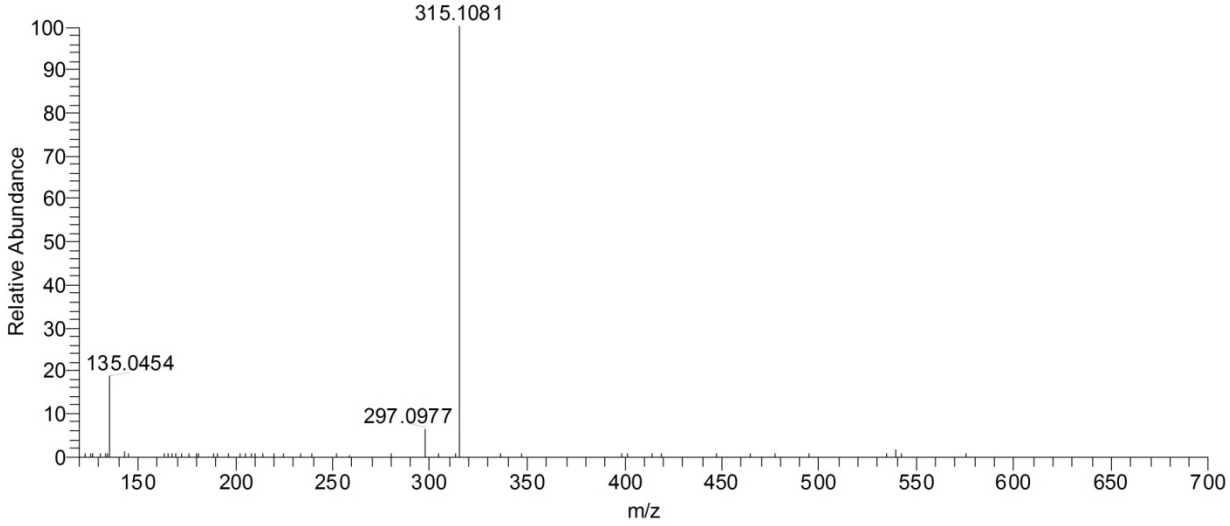


Compound 13

MS^2 spectrum of precursor ion $[M-H]^-$ *m/z* 609.1832

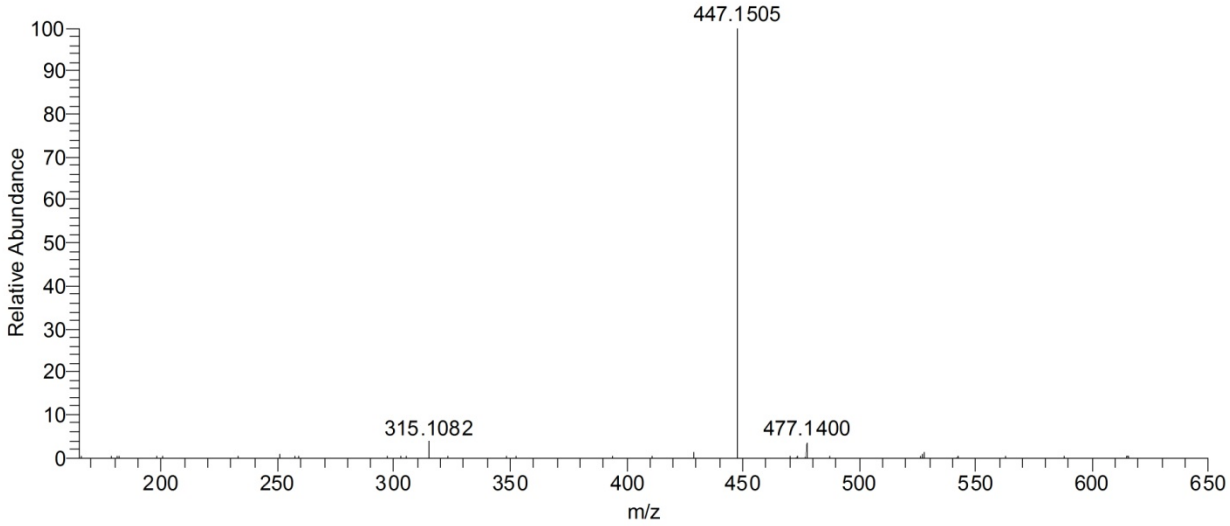


MS^3 spectrum of product ion $[M-H]^-$ *m/z* 447.1510



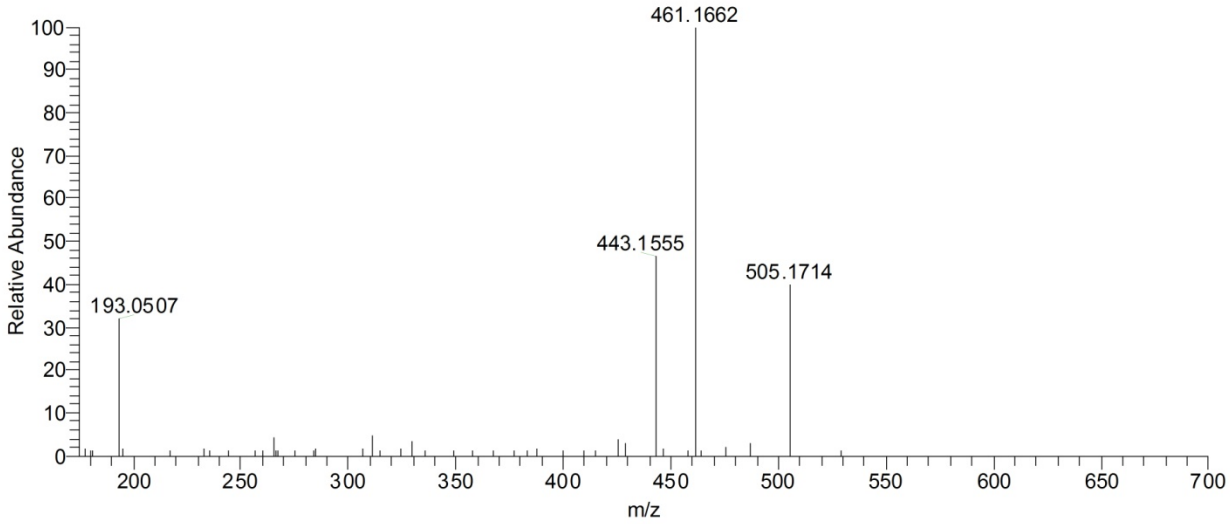
Compound 14

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 609.1829



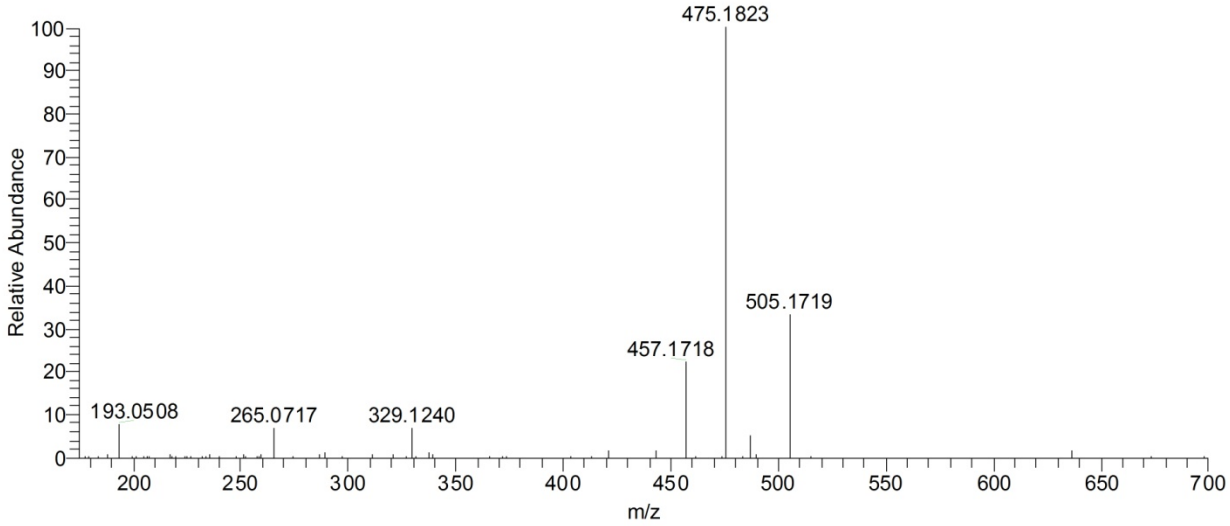
Compound 15 [corresponds to PPG 6 in Holeski et al. (2013)]

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 637.2146



Compound 16 [corresponds to PPG 7 in Holeski et al. (2013)]

MS^2 spectrum of precursor ion $[M-H]^-$ *m*/*z* 651.2297



Appendix 2. Keefover-Ring *et al.* Phenylpropanoid glycosides of *Mimulus guttatus* (yellow monkeyflower)

2.1. UHPLC-UV-TOF/MS diode array (UV) and total ion chromatograms (TIC) of the (**a**) crude extract used for isolation of compounds **1**-**3** and **5**, (**b**) a verbascoside standard (from *Plantago lanceolata*), and (**c**-**g**) individual *M. guttatus* foliage samples. See Table A1 for *M. guttatus* sample location information and Table 2 for a list of UV retention times corresponding to the numbered peaks

2.2. UV spectra (210-400 nm) of five identified (**1**-**5**) phenylpropanoid glycosides from *Mimulus guttatus* foliage. See Table 2 for UV λ_{max} values

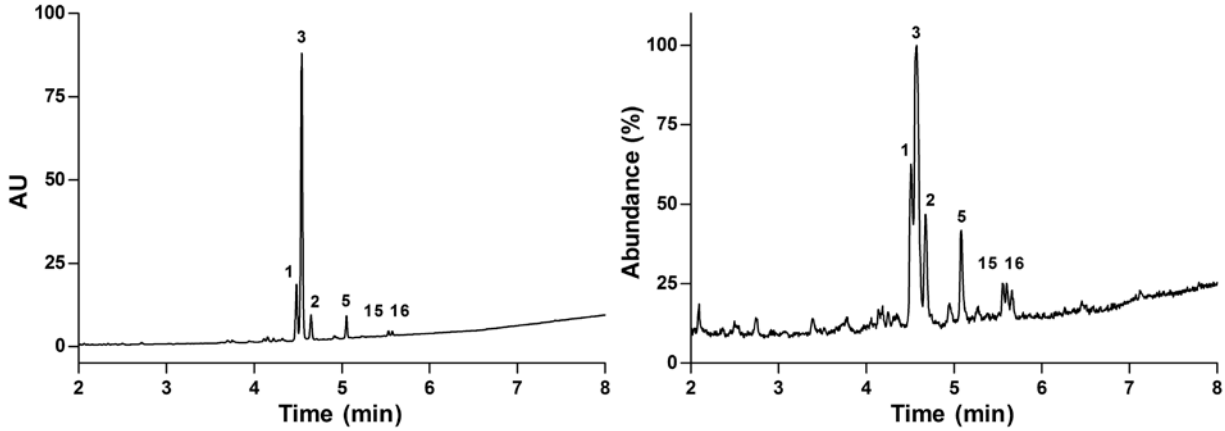
See Section 3.3 in Experimental for UHPLC-UV-TOF/MS conditions

Table A1. *Mimulus guttatus* population locations as numbered in Holeski et al. (2013) for samples analyzed in this study. Population F was not included in Holeski et al. (2013). Representative voucher specimens to be added to the Deaver Herbarium (ASC) at Northern Arizona University

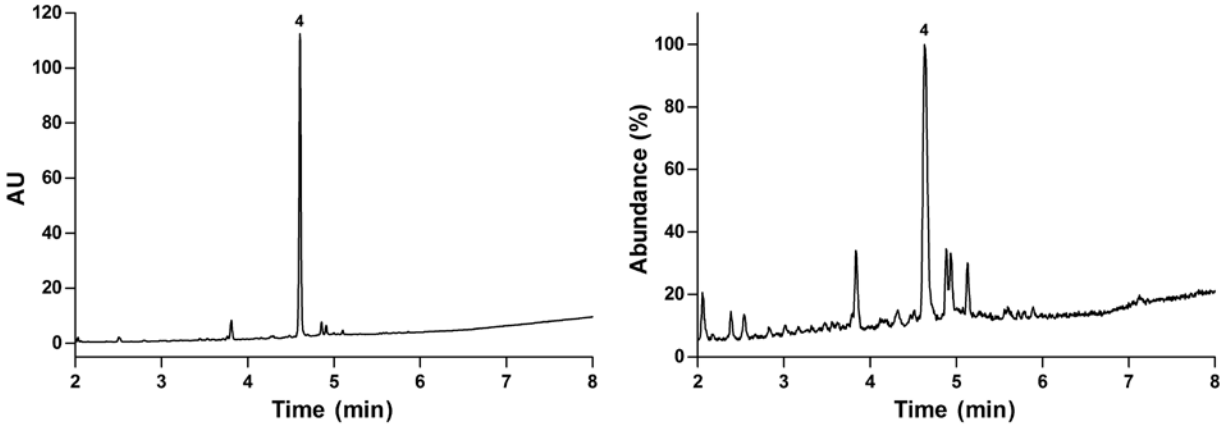
Population	Location	Coordinates (lat., long.)	Elevation (m)
2	Tuolumne county, CA	37.8742, -120.5083	94
3	Monterey county, CA	36.0629, -121.5922	5
10	Mendocino county, CA	39.0360, -123.6905	5
12	Ravalli county, MT	45.9550, -113.8695	2172
F	Lane county, OR	43.9666, -124.1308	2

2.1. UHPLC-UV-TOF/MS diode array (UV) and total ion chromatograms (TIC) of the (**a**) crude extract used for isolation of compounds 1-3 and 5, (**b**) a verbascoside standard (from *Plantago lanceolata*), and (**c**-**g**) individual *M. guttatus* foliage samples. See Table A1 for *M. guttatus* sample location information and Table 2 for a list of UV retention times corresponding to the numbered peaks

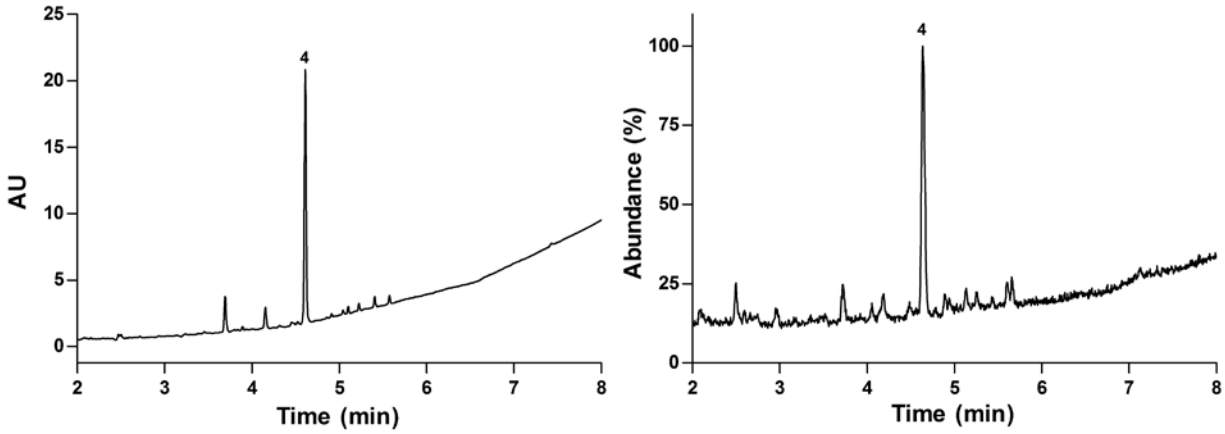
a. UV (left) and TIC (right) chromatograms of crude extract used to isolate **1**-**3** and **5.**



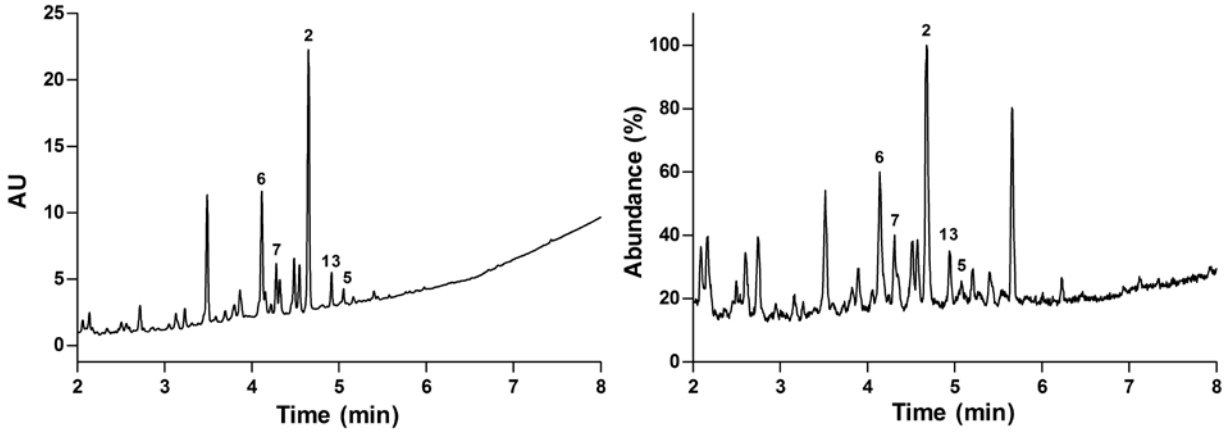
b. UV (left) and TIC (right) chromatograms of verbascoside standard



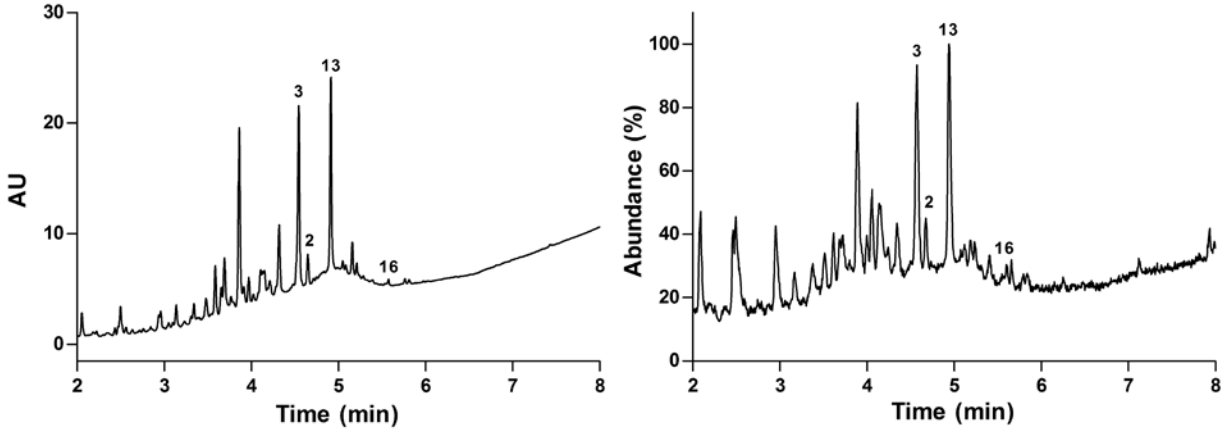
c. UV (left) and TIC (right) chromatograms of sample 27 from population 2



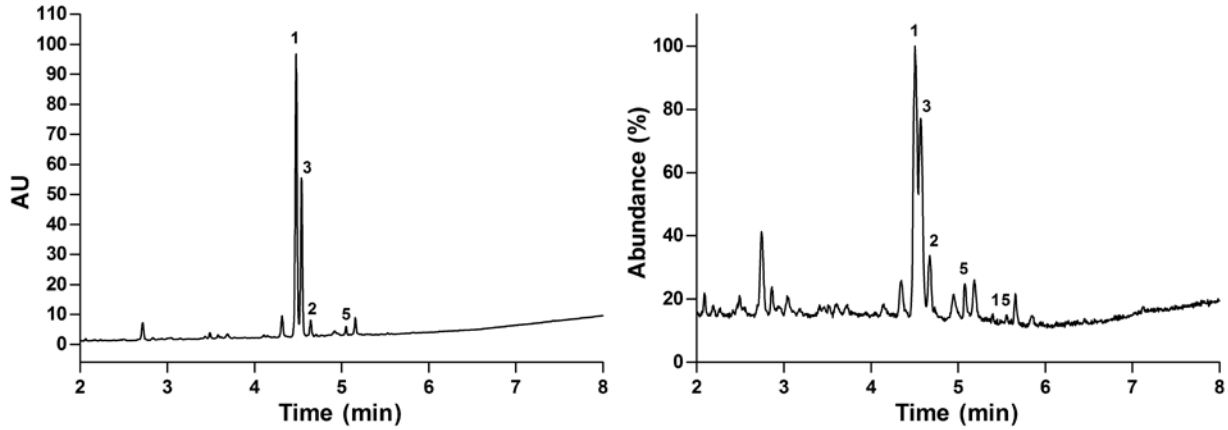
d. UV (left) and TIC (right) chromatograms of sample 55 from population 3



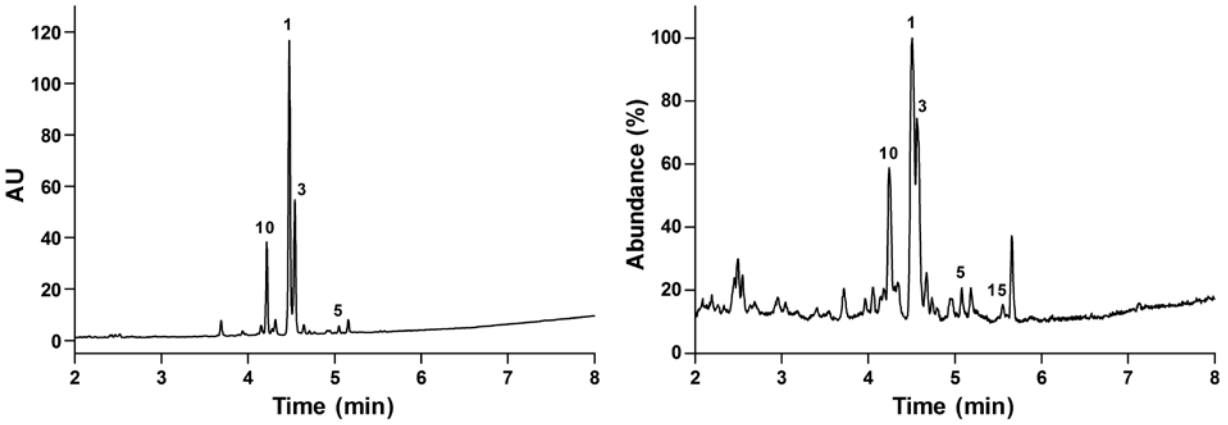
e. UV (left) and TIC (right) chromatograms of sample 180 from population F



f. UV (left) and TIC (right) chromatograms of sample 255 from population 10

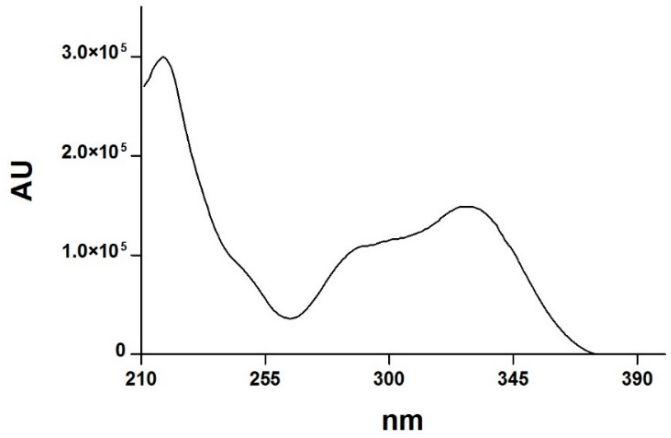


g. UV (left) and TIC (right) chromatograms of sample 312 from population 12

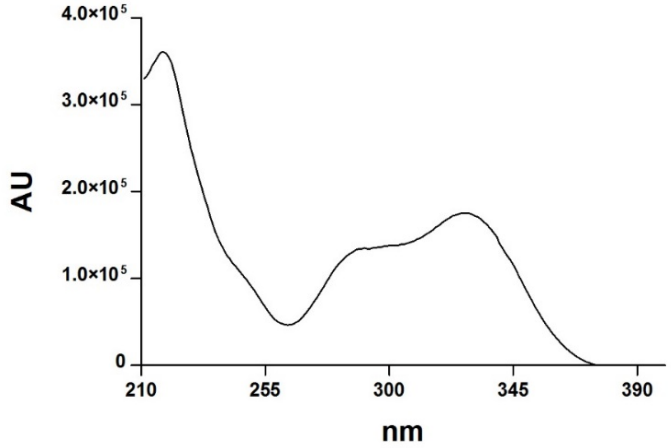


Appendix 2.2. UV spectra (210-400 nm) of five identified (**1**-**5**) phenylpropanoid glycosides from the foliage of *Mimulus guttatus*. See Table 2 for λ_{max} values

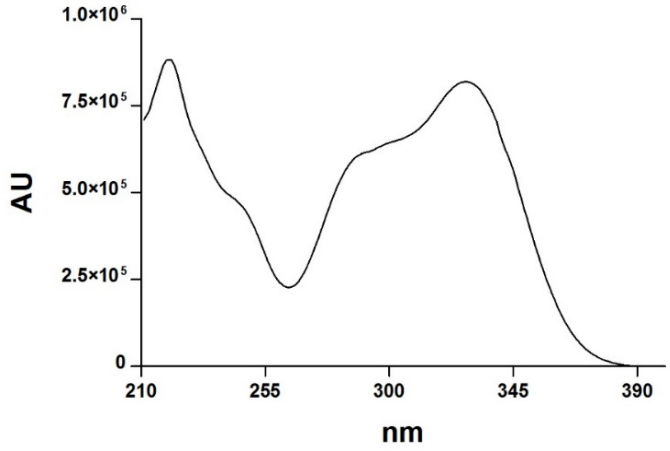
Calceolarioside A (**1**)



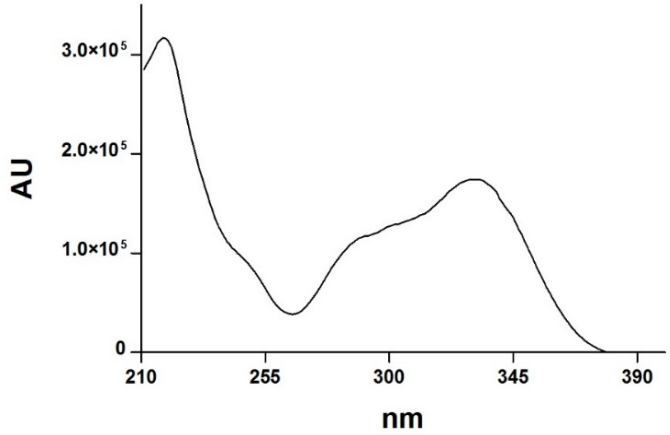
Calceolarioside B (**2**)



Conandroside (**3**)



Verbascoside (**4**)



Mimuloside (**5**)