

Comparative Metabolomics Study on the Secondary Metabolites of the Red Alga, *Corallina officinalis* and its Associated Endosymbiotic Fungi

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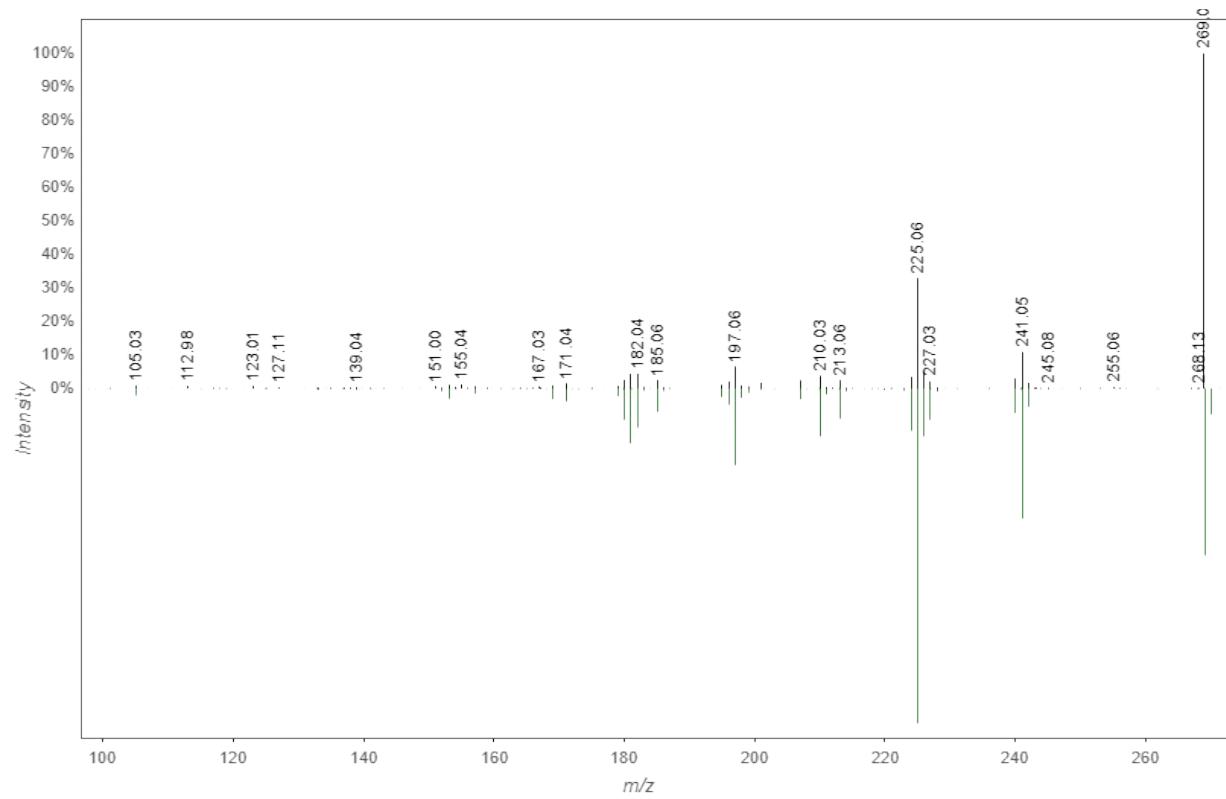


Figure S1. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of Emodin identified from *Aspergillus nidulans* as analyzed by LC/MS in negative ionization mode.

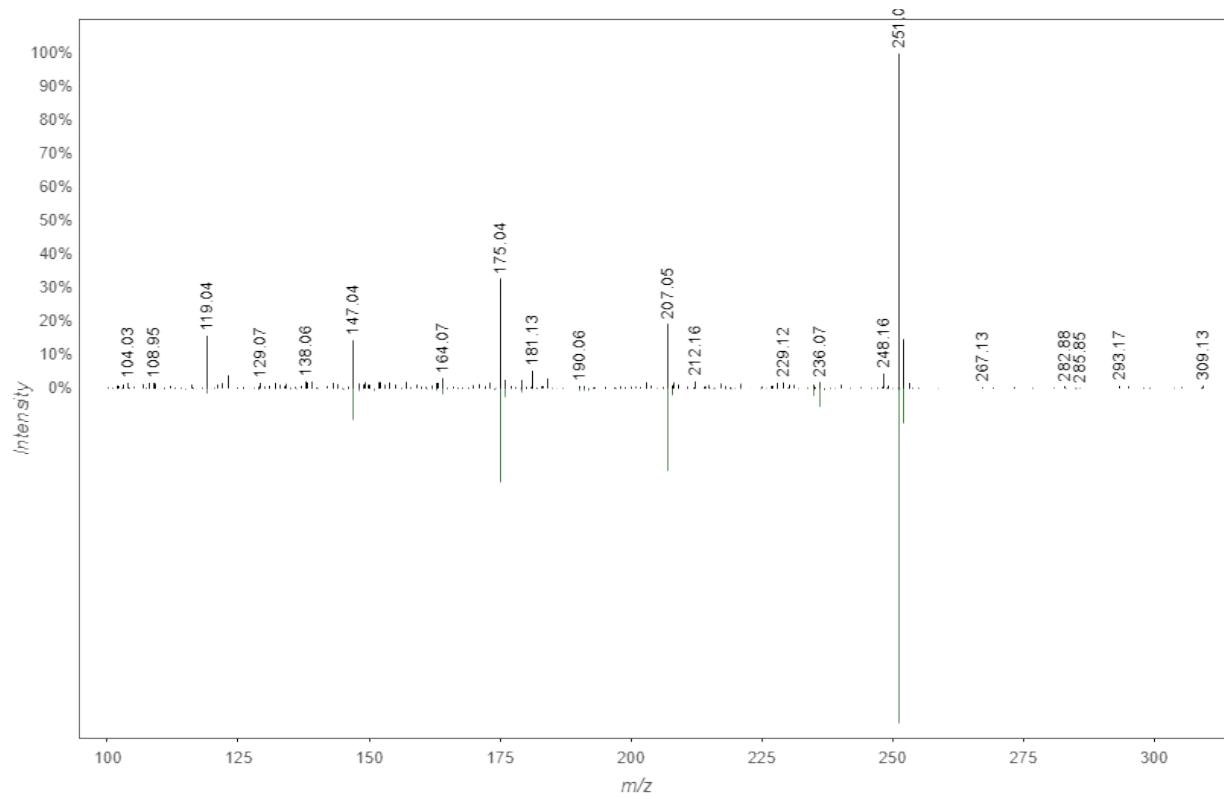


Figure S2. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of Sinapine identified from *Aspergillus flavus* as analyzed by LC/MS in positive ionization mode.

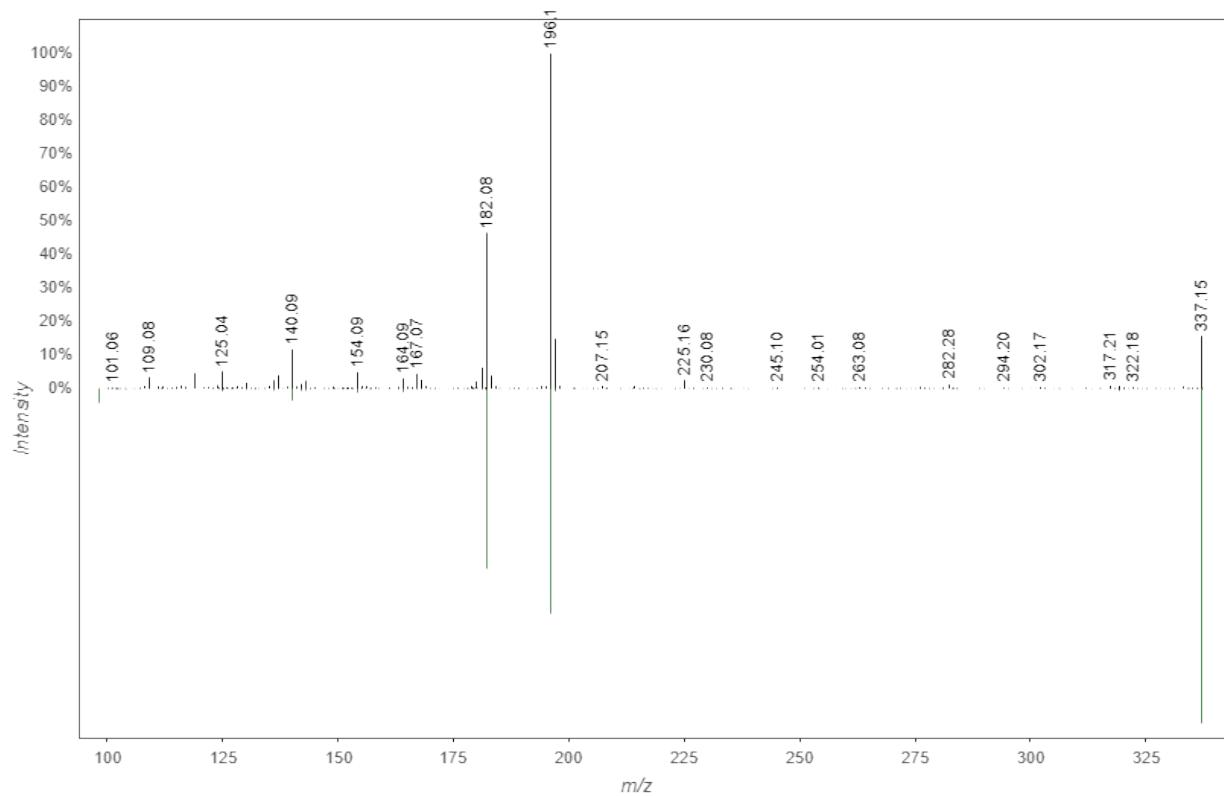


Figure S3. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of Cyclopiazonic acid identified from *Aspergillus flavus* as analyzed by LC/MS in positive ionization mode.

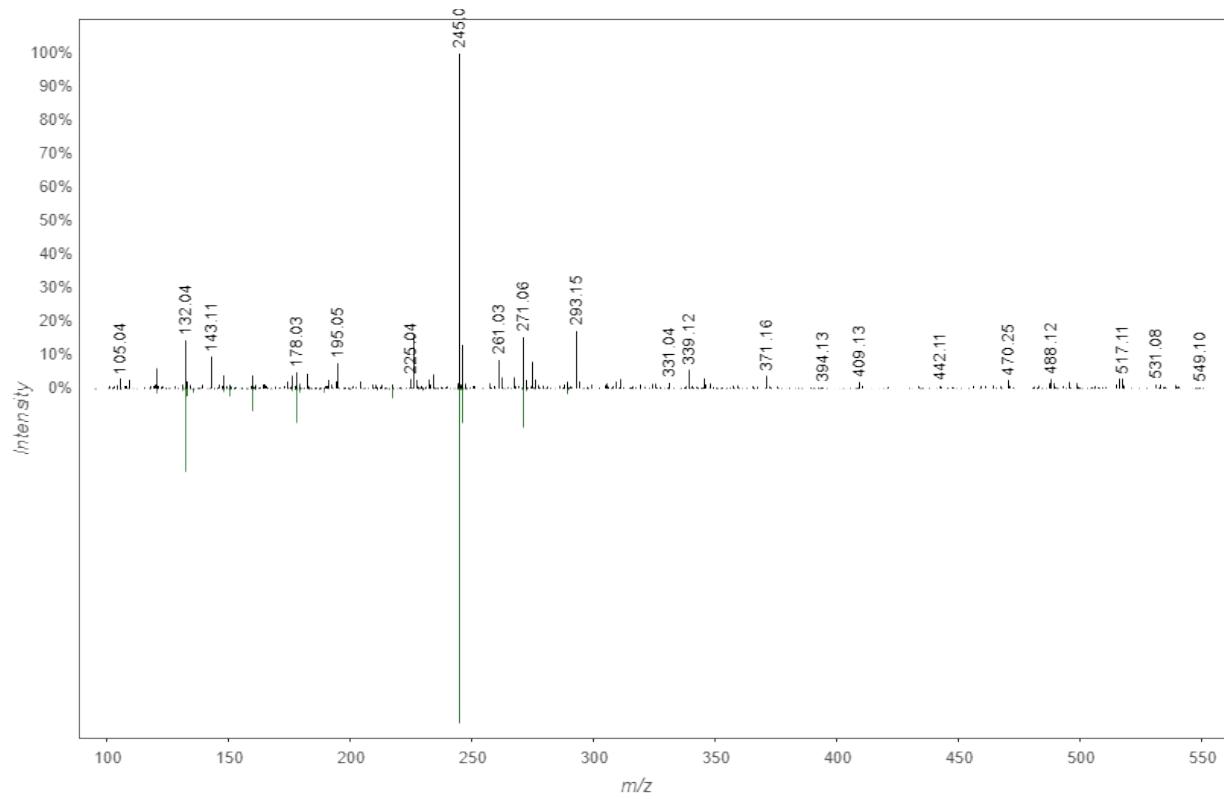


Figure S4. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of Dethiosecoemestrin identified from *Aspergillus nidulans* as analyzed by LC/MS in positive ionization mode.

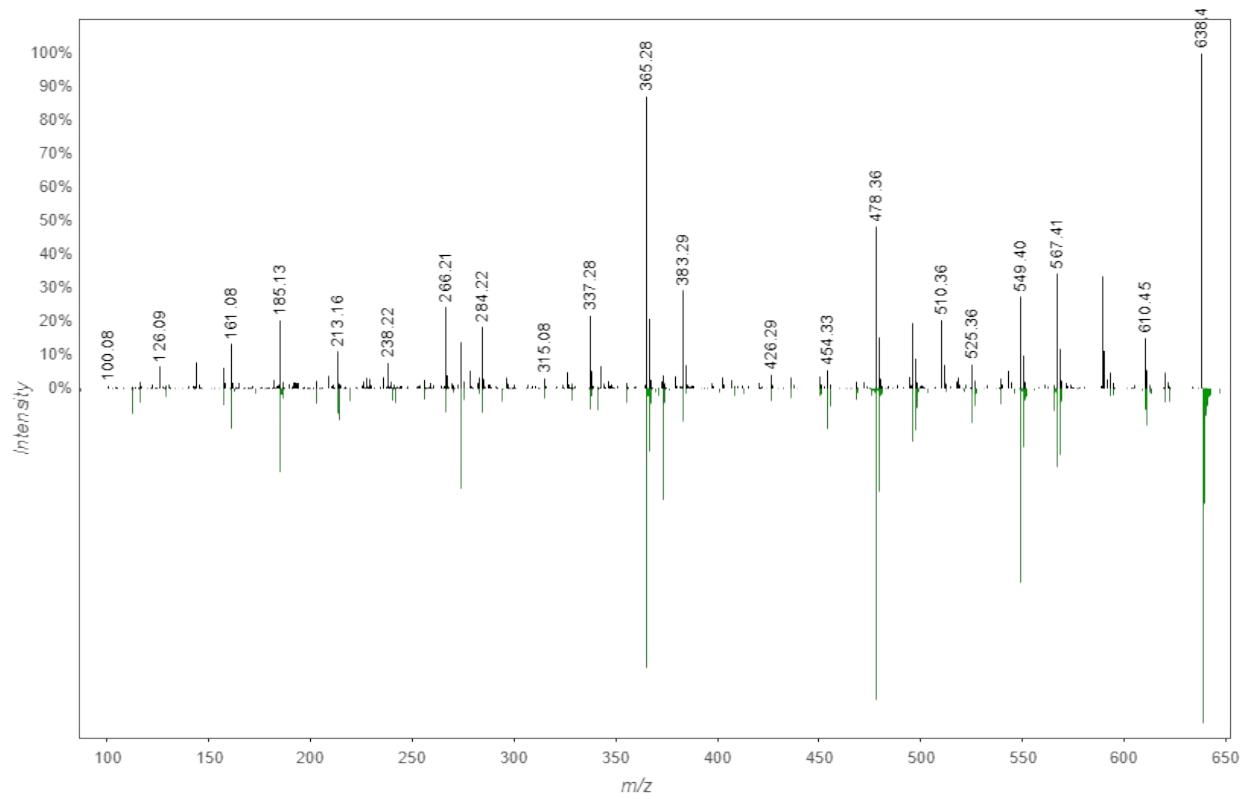


Figure S5. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of Scopularide E identified from *Aspergillus nidulans* as analyzed by LC/MS in positive ionization mode.

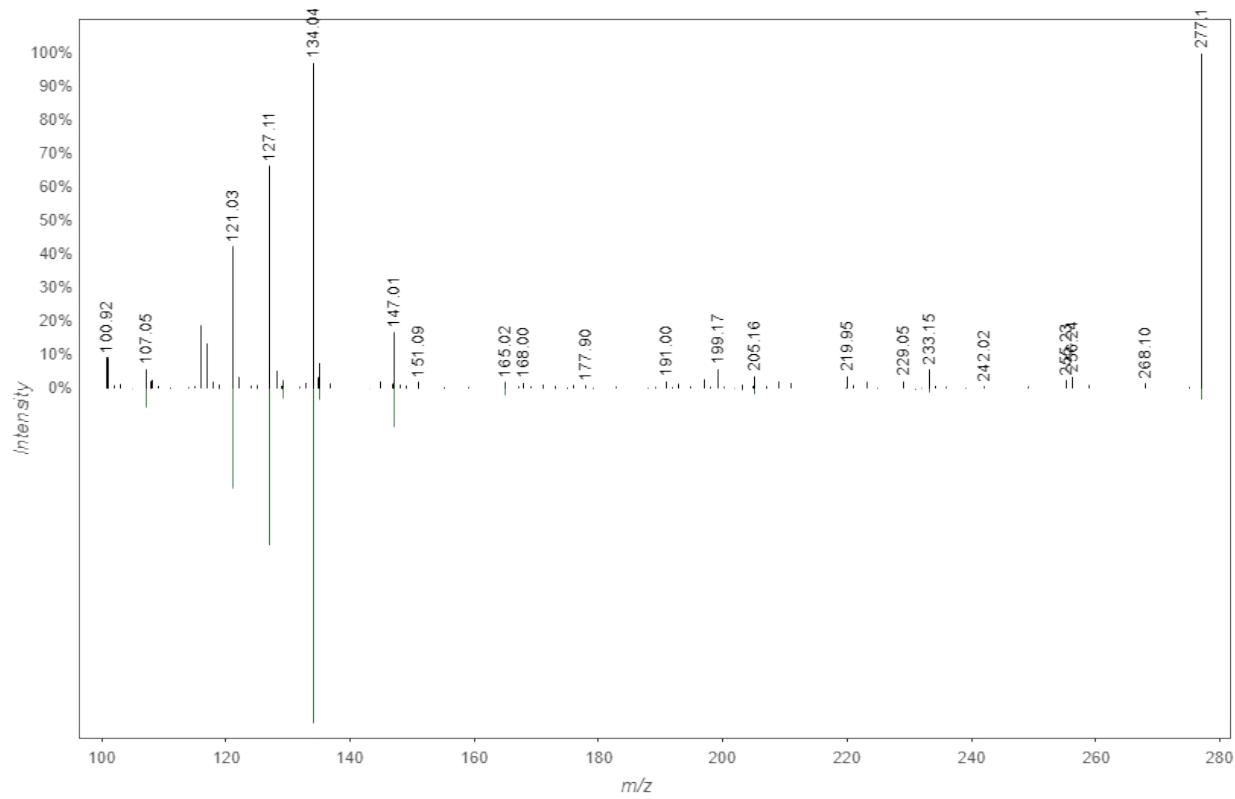


Figure S6. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of 2-((2-Eethylhexyl) oxy) carbonyl) benzoic acid identified from *Aspergillus flavus* as analyzed by LC/MS in negative ionization mode.

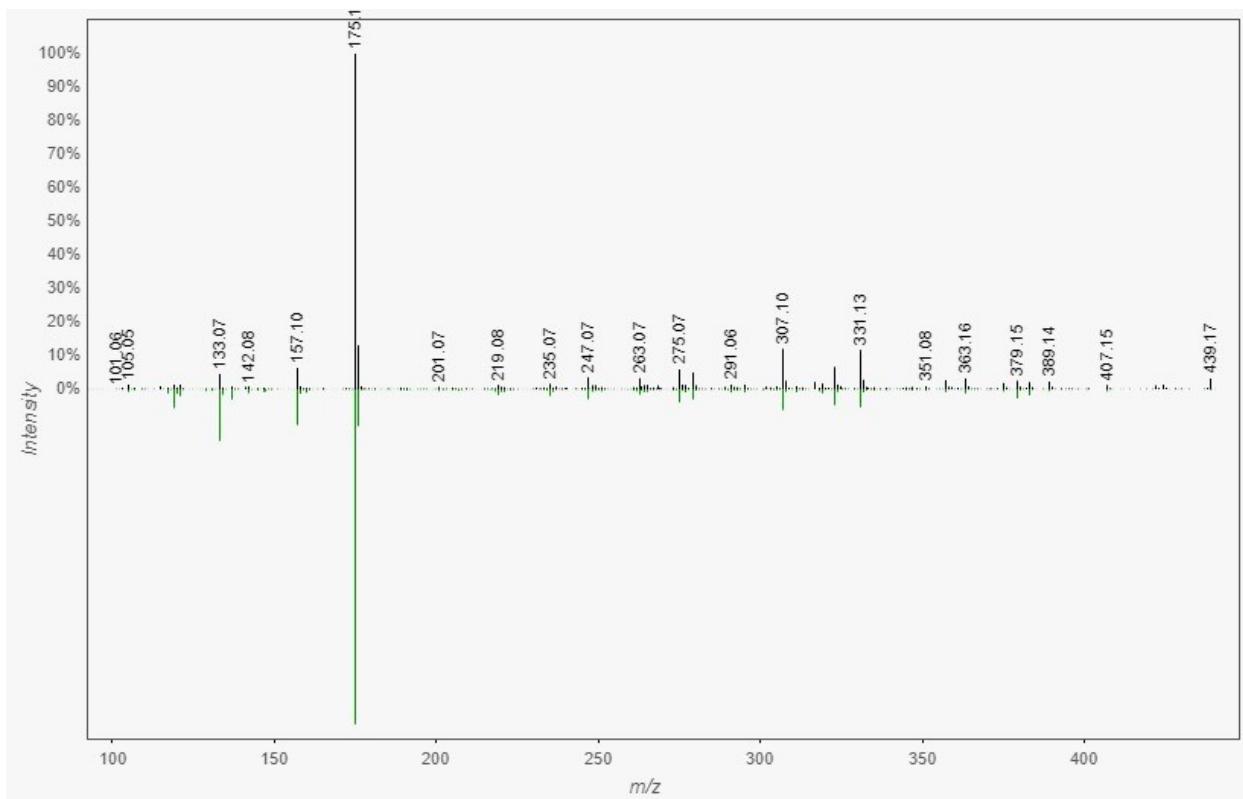


Figure S7. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of Butyrolactone VII identified from *Aspergillus flavipes* as analyzed by LC/MS in positive ionization mode.

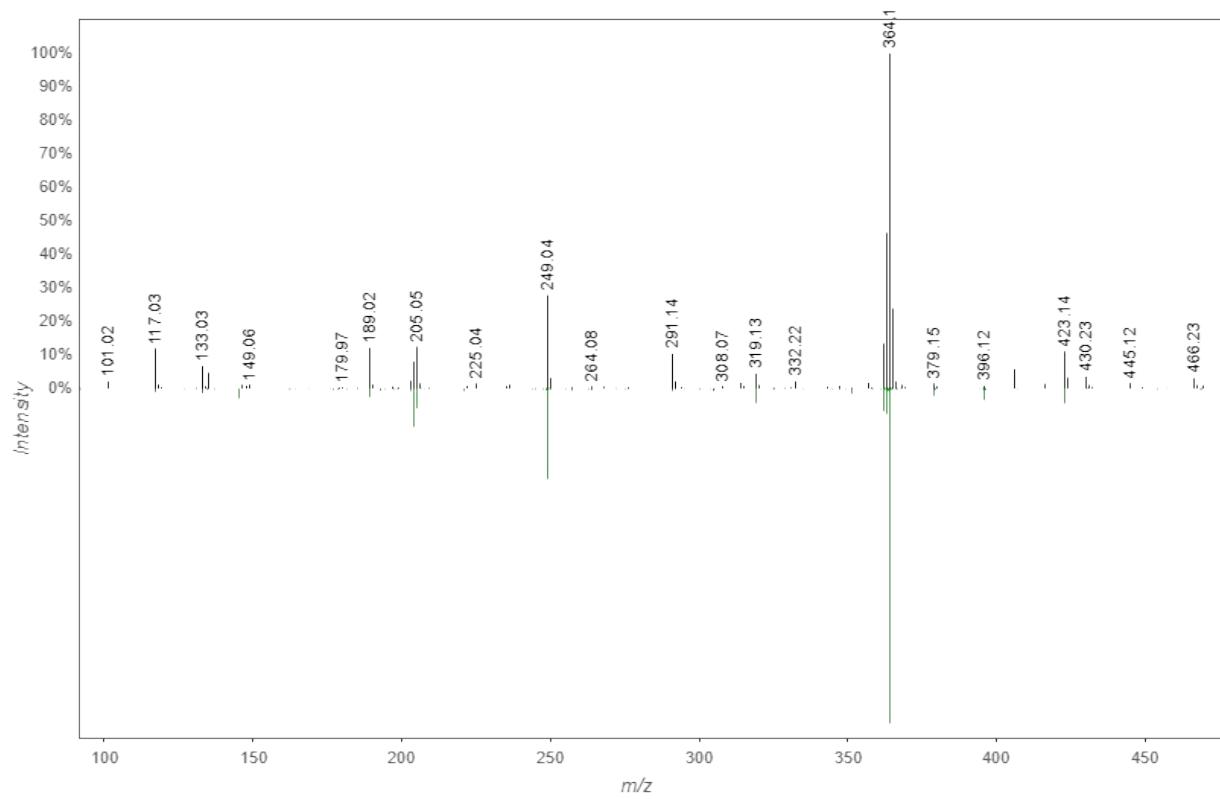


Figure S8. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of Butyrolactone I identified from *Aspergillus flavipes* as analyzed by LC/MS in negative ionization mode.

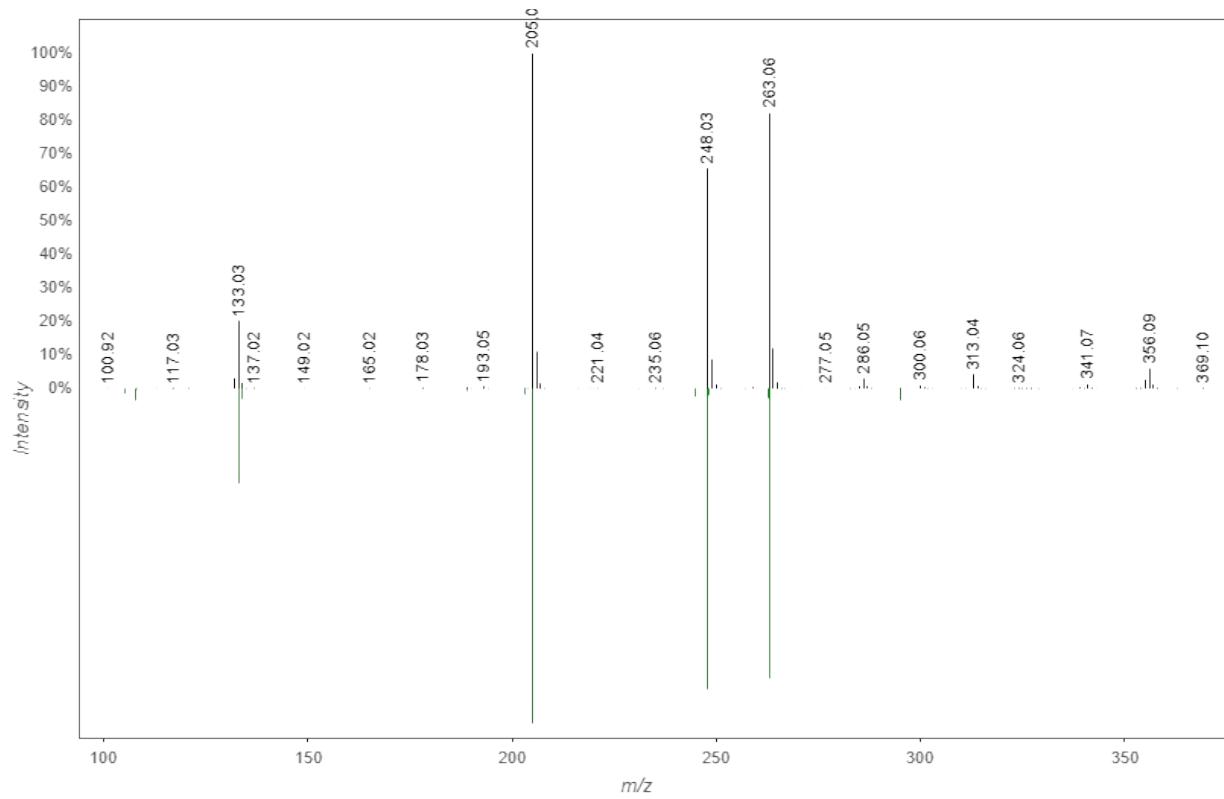


Figure S9. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of 2-O-methylbutyrolactone II identified from *Aspergillus flavipes* as analyzed by LC/MS in negative ionization mode.

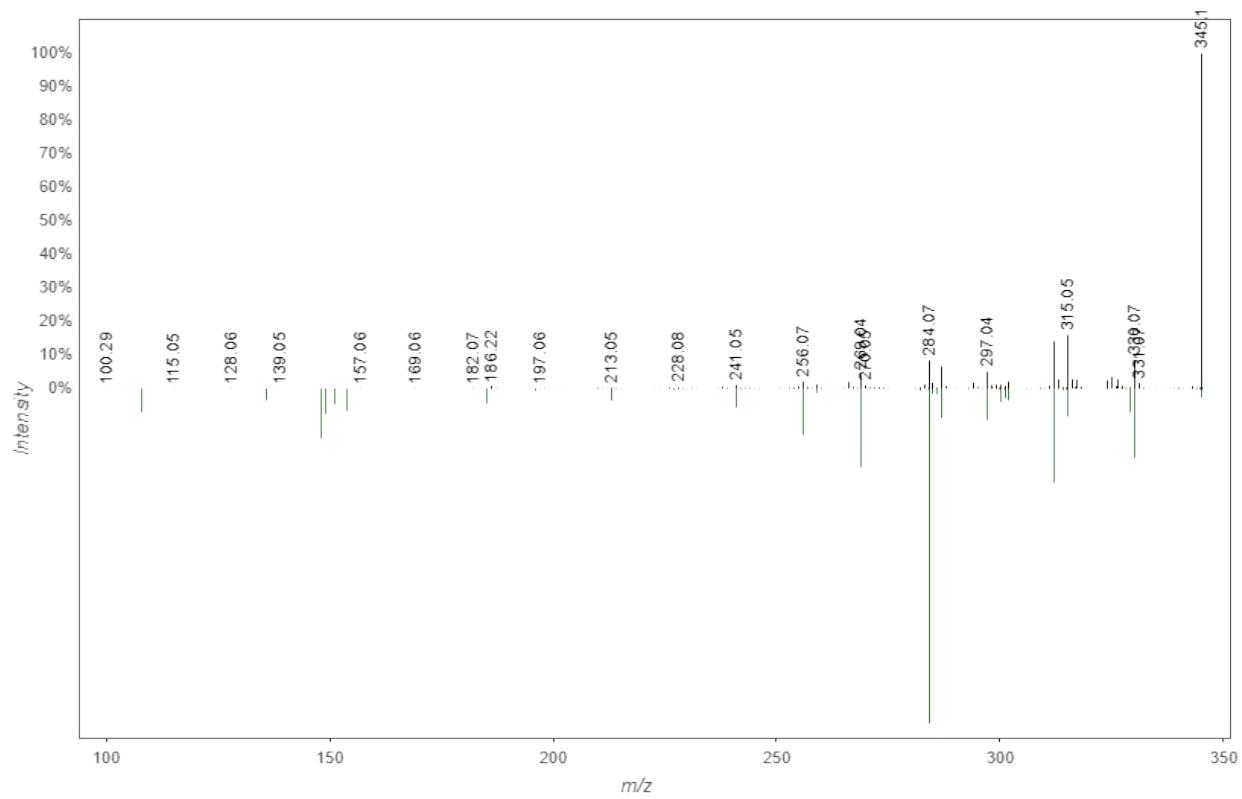


Figure S10. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of 5,2'-Dihydroxy-3,7,8-trimethoxyflavone identified from *Aspergillus flavipes* as analyzed by LC/MS in positive ionization mode.

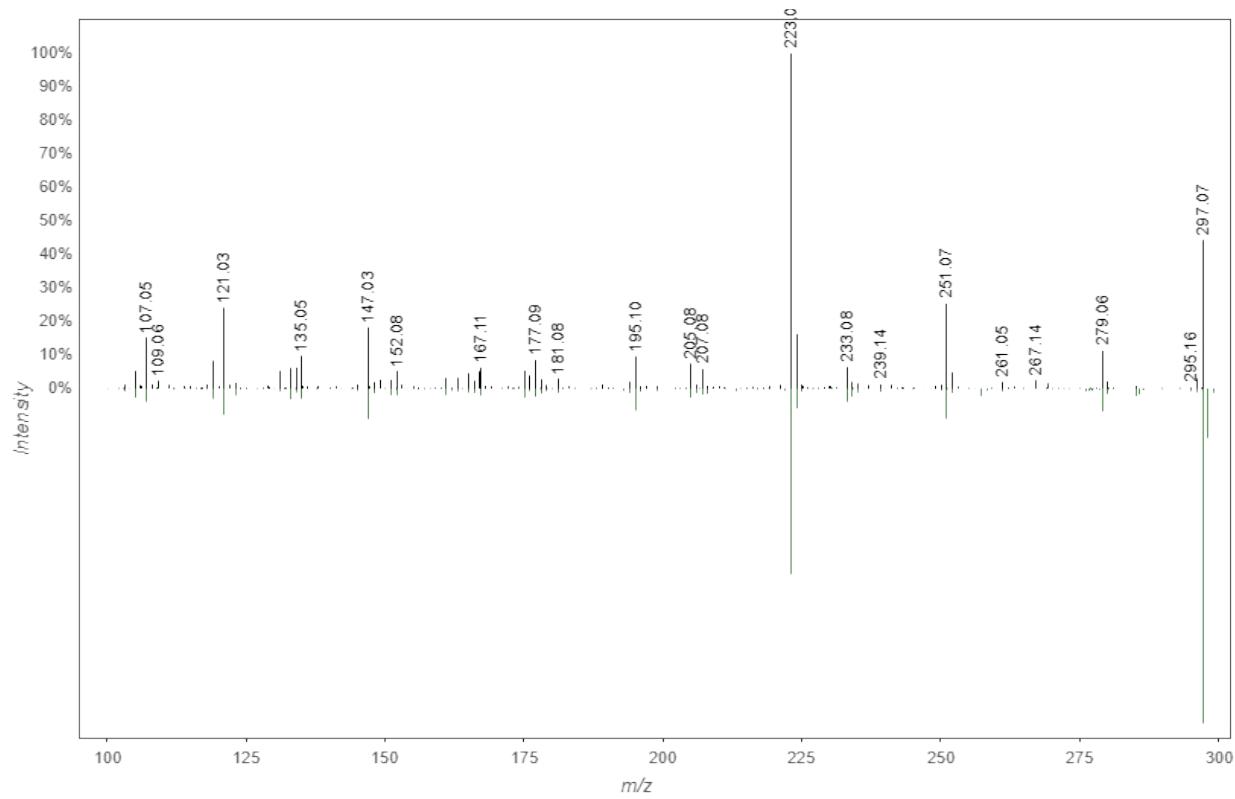


Figure S11. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of Aspergulinone E identified from *Aspergillus flavipes* as analyzed by LC/MS in positive ionization mode.

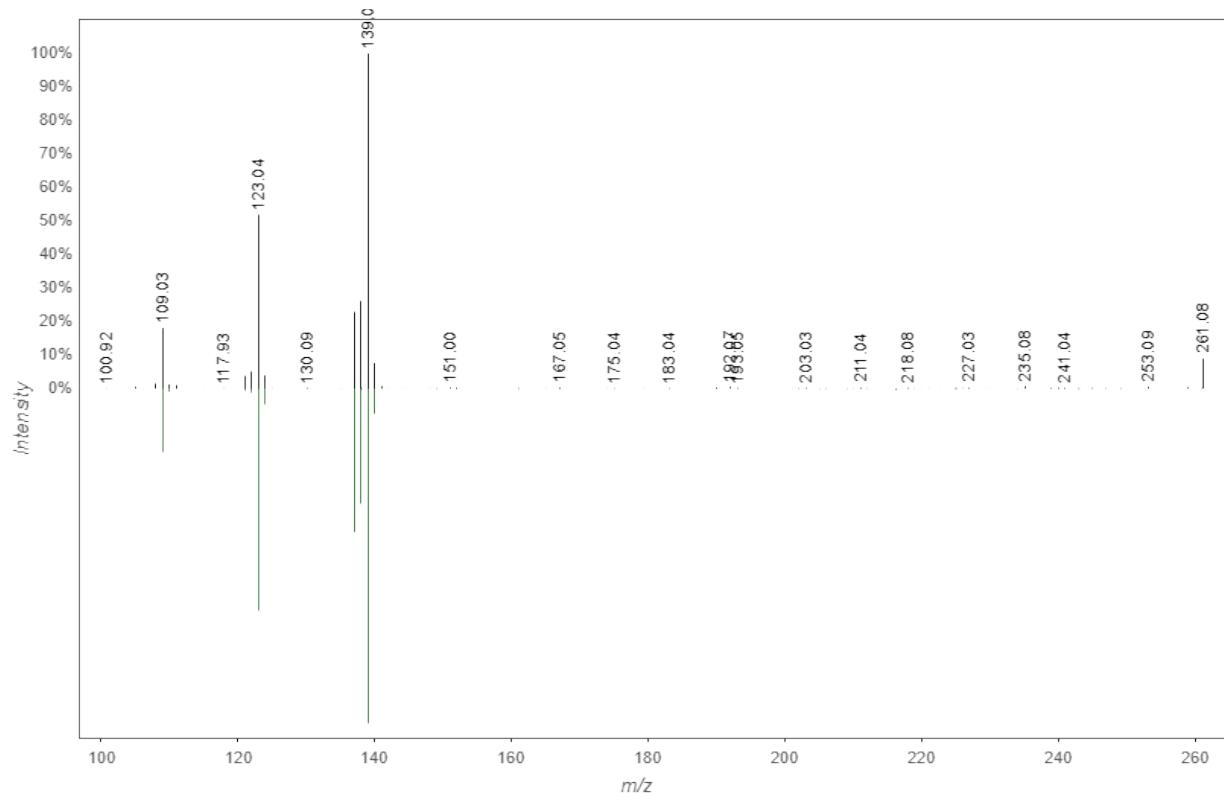


Figure S12. MS/MS spectrum (upper part) mirror matched of with GNPS library (lower part) of violaceol I identified from *Aspergillus nidulans* as analyzed by LC/MS in negative ionization mode.

Table S1. Detailed annotation of metabolites detected in the ethyl acetate extracts of the red alga, *C. officinalis*, and associated Endosymbiotic fungi namely, *A. flavus*, *A. nidulans*, and *A. flavipes* using UPLC-MS/MS Analysis in both positive and negative modes.

Peak no.	tR (min)	Annotated Compound	Adducts	m/z	MS/MS	Elemental Composition	Ref.
1.	4.06	Orsellinic acid	[M-H] ⁻	167.03418	123.0443, 152.0108, 151.0393, 137.0237, 121.0285	C ₈ H ₈ O ₄	¹
2.	4.14	p-hydroxyphenyl acetic acid	[M+H] ⁺	153.0546	131.9639, 113.9639, 105.0702	C ₈ H ₈ O ₃	²
3.	4.17	5-hydroxyaverantin	[M+H] ⁺	389.1238	357.0978, 331.1364, 291.1412, 226.8936, 208.8831, 174.9832, 146.9615, 131.9743, 128.9508, 113.9639	C ₂₀ H ₂₀ O ₈	GNPS
4.	5.09	Terrein	[M-H] ⁻	153.05495	151.0392, 123.0442, 135.0442	C ₈ H ₁₀ O ₃	GNPS
5.	5.13	3-methylorsellinicacid	[M+H] ⁺	183.0652	179.0336, 158.0599, 152.0421, 151.0388, 137.0596, 132.0443, 130.0651, 113.9638, 109.0650, 103.0545	C ₉ H ₁₀ O ₄	³
6.	5.20	Kojic acid methyl ether	[M-H] ⁻ [M+H] ⁺	155.03419 157.04964	153.0357, 151.0394, 146.9379, 135.0444, 132.8671, 123.0443	C ₇ H ₈ O ₄	⁴
7.	5.33	Insulicolide A	[M+H] ⁺	432.1655	417.1415, 349.1830, 279.0736, 261.0630, 248.0914, 239.0816, 209.0441, 195.0285, 181.0493, 138.0310, 113.9638	C ₂₂ H ₂₅ NO ₈	⁵

8.	5.45	Orsellinaldehyde	[M-H] ⁻	151.03934	123.0442, 133.0286, 124.0476, 121.0286	C ₈ H ₈ O ₃	6
			[M+H] ⁺	153.05469			
9.	5.63	Sinapine	[M] ⁺	310.16489	251.0912, 207.0651, 175.0389, 147.0421, 146.9614, 131.9743, 116.9722, 113.9639	C ₁₆ H ₂₄ NO ₅	GNPS
10.	6.18	N-acetyl-L-leucine	[M-H] ⁻	172.09734	112.9848, 130.0866, 135.0306, 109.0650, 121.0287	C ₈ H ₁₅ NO ₃	GNPS
11.	6.43	Penidiamide	[M-H] ⁻	333.1375	119.0493, 129.0007, 149.0432, 199.0432, 211.1450, 229.0904	C ₁₉ H ₁₈ N ₄ O ₂	GNPS
12.	6.60	Asperflavin	[M+H] ⁺	289.1069	285.0753, 257.0807, 236.0914, 223.0598, 179.0337, 151.0389, 131.9742, 121.0285, 113.9639, 107.0494	C ₁₆ H ₁₆ O ₅	7
13.	6.78	Phenylalanine	[M-H] ⁻	164.0710	147.0444, 134.8646, 132.8671, 116.9276, 112.9847	C ₉ H ₁₁ NO ₂	GNPS
14.	6.92	Speradine D	[M+H] ⁺	387.1551	260.0880, 220.0957, 194.0802, 179.0565, 151.0745, 121.0644	C ₂₀ H ₂₂ N ₂ O ₆	8
15.	6.92	Cichorine	[M+H] ⁺	194.0810	179.0565, 165.0538, 151.0745, 123.0675, 121.0644	C ₁₀ H ₁₁ NO ₃	9
16.	7.71	Ferulic acid	[M-H] ⁻	193.0501	178.02520, 176.0450, 149.05910	C ₁₀ H ₁₀ O ₄	10
			[M+H] ⁺	195.0651	180.04380, 177.05580, 147.04610		
17.	7.71	Nidulol	[M+H] ⁺	195.0651	189.0541, 180.0412, 165.0542, 162.0308, 151.0386, 147.0437, 137.0593, 119.0491,	C ₁₀ H ₁₀ O ₄	11

						109.0649, 107.0493		
18.	7.97	2-O-methyl-9-dehydroxyeurotinone	[M-H] ⁻	285.0771	135.0444, 147.0444, 214.0873, 179.0345,	C ₁₆ H ₁₄ O ₅		¹²
19.	8.36	Asperfuranone	[M+H] ⁺	287.0914	119.0493			
20.	8.40	4-Hydroxyphenylpyruvic acid	[M-H] ⁻	333.1702	241.1539, 206.1408, 191.1174, 169.0968,	C ₁₉ H ₂₄ O ₅		¹³
					152.0941, 137.0707, 110.0476			
21.	8.66	Homogenentisic acid	[M-H] ⁻	179.0341	108.0207, 121.0286, 135.0305, 115.0391	C ₉ H ₈ O ₄	GNPS	
22.	8.69	Alternariol monomethyl ether	[M-H] ⁻	167.0339	112.9845, 116.9275, 132.8669, 134.8642,	C ₈ H ₈ O ₄		
					136.8623			
23.	8.96	Daidzein	[M-H] ⁻	271.0612	269.0699, 228.0429, 207.0298, 176.0349,	C ₁₅ H ₁₂ O ₅		¹⁴
					148.0398, 137.0237, 122.0366, 107.0368			
24.	9.02	Sterigmatocystin hemiacetal	[M-H] ⁻	253.0509	224.0475, 208.0523, 208.0526, 133.0332,	C ₁₅ H ₁₀ O ₄	GNPS	
					145.0501, 112.9847			
25.	9.20	Erythroglaucin	[M+Na] ⁺	341.0673	325.0690, 269.0794, 237.0523, 179.0330,	C ₁₈ H ₁₄ O ₇		¹⁵
					343.0811	161.0225, 147.0433, 133.0278, 121.0280,		
						105.0333		
26.	9.22	1-hydroxy-6-methyl-8-hydroxymethylxanthone	[M+H] ⁺	301.0705	295.0965, 287.0540, 257.0801, 231.0642,	C ₁₆ H ₁₂ O ₆		¹⁶
					194.0807, 179.0698, 165.0544, 151.0385,			
					123.0439, 109.0284			
					239.0695, 229.0853, 211.0753, 206.0806,	C ₁₅ H ₁₂ O ₄	GNPS	
					201.0904, 193.0491, 169.0643, 165.0543,			

						152.0616, 141.0695, 121.0283, 115.0542,		
						107.0492		
27.	9.32	2,3,6,8,9-pentahydroxy-1- oxo-3-(2-oxopropyl)-1,2,3,4- tetra-hydroanthracene-2- carboxylic acid	[M-H] ⁻	375.0727	376.1639, 364.2257, 354.2414, 344.2206,	C ₁₈ H ₁₆ O ₉	GNPS	
			[M+H] ⁺	377.0865	340.2262, 285.0746, 269.1525, 257.0797, 220.1686, 138.0908, 133.0853, 119.0853, 113.9635			
28.	9.39	Sterigmatocystin	[M-H] ⁻	323.0564	307.0585, 279.0637, 251.0690, 223.0589,	C ₁₈ H ₁₂ O ₆		15, 17, 18
			[M+H] ⁺	325.0707	161.0225, 133.0278, 123.0800, 107.0490			
29.	9.45	Atrochryson carboxylic acid	[M-H] ⁻	317.0665	286.0486, 300.0640, 379.1588, 116.927,	C ₁₆ H ₁₄ O ₇	GNPS	
			[M+H] ⁺	319.0813	253.2539, 183.0116			
30.	9.70	Aspergilloid C	[M-H] ⁻	279.1242	217.1234, 177.0916, 147.0444, 112.9847	C ₁₅ H ₂₀ O ₅		19
31.	9.77	Violaceol i	[M-H] ⁻	261.0773	139.0393, 261.0772, 207.0298, 123.0443, 109.0343	C ₁₄ H ₁₄ O ₅	GNPS	
32.	9.80	Versiquinazoline E	[M+H] ⁺	444.1651	401.1199, 376.1382, 354.1332, 338.1007, 313.1422, 271.0598, 264.1225, 206.0806, 193.0492, 179.0544, 165.0544, 151.0749, 113.9637	C ₂₄ H ₂₁ N ₅ O ₄		20
33.	9.93	Aspulinone E	[M+H] ⁺	297.0759	279.0640, 251.0693, 233.0845, 223.0745, 205.0821, 195.1042, 177.0935, 147.0433, 121.0743, 107.0491	C ₁₇ H ₁₂ O ₅	GNPS	

34.	10.02	Aspergiterpenoid A	[M+H] ⁺	237.1848	207.1488, 191.1176, 177.1018, 165.1020, 163.0863, 137.0708, 120.0808, 113.9638	C ₁₅ H ₂₄ O ₂	²¹
35.	10.08	Epicoccolide B	[M+H] ⁺	359.0761	341.0686, 313.0690, 297.0743, 285.0742, 251.0690, 223.0743, 147.0433, 121.0280	C ₁₈ H ₁₄ O ₈	²²
36.	10.20	5-methoxydihydrosterigmatocystin	[M-H] ⁻ [M+H] ⁺	355.0822 357.0966	339.0843, 325.0682, 269.0791, 223.0744, 181.0487, 147.0432, 131.0277, 121.0279	C ₁₉ H ₁₆ O ₇	¹⁵
37.	10.87	Alternariol	[M-H] ⁻	257.0455	245.0822, 237.0924, 213.0556, 207.0298, 143.0495, 139.0394, 137.0236, 122.0365	C ₁₄ H ₁₀ O ₅	¹⁴
38.	11.33	Curvularin	[M-H] ⁻	291.1236	115.0755, 179.0344, 270.1350, 123.0442	C ₁₆ H ₂₀ O ₅	GNPS
39.	11.96	Aspoquinoline C	[M-H] ⁻	482.2176	468.2398, 426.2294, 418.2608, 300.0643, 263.0564, 208.0977, 179.0344, 142.0344	C ₂₇ H ₃₃ NO ₇	²³
40.	12.12	Cytochalasin Z17	[M+H] ⁺	464.2438	456.2343, 450.2233, 402.2633, 384.2528, 364.1887, 303.0851, 206.1170, 166.0857, 135.0800, 107.0491	C ₂₈ H ₃₃ NO ₅	²⁴
41.	12.35	Dethiosecoemestrin	[M+NH ₄] ⁺	550.1457	488.1190, 319.0624, 293.1484, 271.0591, 245.0549, 226.2156, 179.0695, 178.0321, 132.0440	C ₂₇ H ₂₀ N ₂ O ₁₀	GNPS
42.	12.58	Emestrin	[M+H] ⁺	599.0783	594.3244, 580.3612, 579.3527, 578.3495, 517.1217, 499.1112, 489.1264, 471.1168,	C ₂₇ H ₂₂ N ₂ O ₁₀ S ₂	²⁵

						443.1211, 415.1260, 386.1022, 285.1106, 257.0542, 229.0596, 201.0647, 132.0437, 115.0494		
43.	12.67	Cytochalasin z8	[M+H] ⁺	466.2593	448.2463, 430.2358, 366.2043, 356.1475, 303.0846, 217.0484, 166.0854, 120.0804	C ₂₈ H ₃₅ NO ₅	²⁴	
44.	12.70	Fellutamide A	[M-H] ⁻	570.3521	534.1860, 518.2125, 474.2226, 416.2194,	C ₂₇ H ₄₉ N ₅ O ₈	²⁶	
			[M+H] ⁺	572.3651	356.1471, 290.1520, 240.1367, 217.0481, 120.0802			
45.	12.74	Acyl-hemiacetal sterigmatocystin	[M+H] ⁺	385.0918	343.0800, 325.0694, 310.0459, 297.0748, 248.1270, 167.0332, 113.9635	C ₂₀ H ₁₆ O ₈	¹⁵	
46.	12.80	Butyrolactone I	[M-H] ⁻	423.1449	364.1318, 319.1334, 249.0442, 205.0523, 179.0344, 133.0313	C ₂₄ H ₂₄ O ₇	GNPS	
47.	13.27	Butyrolactone VII	[M+H] ⁺	439.1755	422.2278, 331.1309, 307.0945, 275.0697, 217.0482, 175.1107, 166.0853, 157.1023, 133.0713	C ₂₅ H ₂₆ O ₇	GNPS	
48.	13.27	2-O-methylbutyrolactone II	[M-H] ⁻	369.0977	341.0669, 311.1691, 291.2005, 263.0624, 255.2333, 248.0335, 205.0122, 183.0116, 133.0326	C ₂₀ H ₁₈ O ₇	GNPS	
49.	13.32	Aspergillide E	[M+H] ⁺	466.22	347.0514, 325.0695, 310.0460, 247.1434, 281.0435, 282.0490, 182.0441, 195.0761, 219.1485	C ₂₅ H ₂₉ N ₄ O ₅	²⁷	

50.	13.40	Emericellamide C	[M+H] ⁺	596.4021	568.4059, 554.2728, 547.3453, 525.3638, 454.3265, 341.2424, 325.0686, 291.1694, 266.0648, 244.1647, 226.1541, 179.0697, 159.0912, 130.0648, 123.1166	C ₃₀ H ₅₃ N ₅ O ₇	²⁸
51.	13.45	Fellutamide D	[M-H] ⁻	598.38153	582.3835, 532.2279, 456.2161, 357.1767,	C ₂₉ H ₅₃ N ₅ O ₈	²⁹
			[M+H] ⁺	600.39789	325.0664, 303.0862, 289.0688, 198.2206, 166.0855		
52.	13.49	Emodin	[M-H] ⁻	269.04626	241.0509, 227.0331, 225.0558, 213.0642, 210.0304, 203.0712, 197.0621, 185.0641, 182.0441, 177.0190, 171.0423, 155.0455, 116.9276, 105.0334	C ₁₅ H ₁₀ O ₅	GNPS
53.	13.49	Eurotinone	[M+H] ⁺	289.07068	288.0609, 243.0635, 201.1624, 166.0851	C ₁₅ H ₁₂ O ₆	³⁰
54.	13.49	Monodictyphenone	[M+H] ⁺	289.07068	201.1636, 169.9771, 154.9900, 146.9801, 144.9820, 139.9877, 110.0202, 113.9638	C ₁₅ H ₁₂ O ₆	³¹
55.	13.72	Cyclopiazonic acid	[M+H] ⁺	337.15463	337.1502, 216.0650, 196.1117, 182.0807, 140.0703	C ₂₀ H ₂₀ N ₂ O ₃	³²
56.	13.76	Sydonic acid	[M-H] ⁻	265.14838	263.0565, 248.0328, 205.0139, 179.0344	C ₁₅ H ₂₂ O ₄	³³
57.	13.92	Emericellamide A	[M+H] ⁺	610.41785	582.4222, 561.3615, 539.3798, 468.3429, 441.2694, 355.2584, 330.0964, 325.0697, 301.0336, 250.0703, 216.0650, 184.0729,	C ₃₁ H ₅₅ N ₅ O ₇	²⁸

						179.0729, 130.0649, 123.1167		
58.	13.99	Asperphenamate	[M+H] ⁺	507.22897	456.2124, 303.0862, 289.0686, 256.1317, 238.1213, 117.0695, 105.0333	C ₃₂ H ₃₀ N ₂ O ₄		³⁴
59.	13.99	2-((2-Ethylhexyl)oxy)carbonylbenzoic acid	[M-H] ⁻	277.14456	255.2333, 183.0117, 265.1483, 152.9951, 147.0135, 134.0365, 127.1119, 116.9276, 107.0542	C ₁₆ H ₂₂ O ₄	GNPS	
60.	14.08	2-methyleurotinone	[M-H] ⁻	301.0718	286.0485, 271.0252, 243.0300	C ₁₆ H ₁₄ O ₆		³⁵
			[M+H] ⁺	303.0862				
61.	14.11	Emericellamide E	[M+H] ⁺	624.4332	502.3316, 437.1952, 404.3529, 284.3313, 184.0734, 184.0734, 143.1180, 105.0703	C ₃₂ H ₅₇ N ₅ O ₇		²⁸
62.	14.15	1-hexadecanoylglycerophosphocholine	[M+FA-H] ⁺	540.3314	480.3103, 311.1691, 291.2005, 255.2333,	C ₂₄ H ₅₀ NO ₇ P	GNPS	
63.	14.22	8-Hydroxy-9,12-octadecadienoic acid	[M-H] ⁻	295.2285	262.1454, 183.0117, 116.9276, 195.1387, 277.2177, 281.2491, 279.2334	C ₁₈ H ₃₂ O ₃	GNPS	
64.	14.25	6,8-O-dimethylaverantin	[M-H] ⁻	399.1458	389.0984, 354.0748, 326.0796, 370.1015, 384.1218	C ₂₂ H ₂₄ O ₇	GNPS	
65.	14.25	5,2'-Dihydroxy-3,7,8-trimethoxyflavone	[M+H] ⁺	345.0966	345.1021, 331.0744, 330.0708, 325.0655, 315.0655, 315.0475, 312.0605, 297.0437, 287.0527, 284.0657, 270.0424, 256.0721	C ₁₈ H ₁₆ O ₇	GNPS	
66.	14.26	Hormonemate F	[M-H] ⁻	607.3275	473.2845, 334.1821, 311.1695, 281.2492,	C ₂₉ H ₅₂ O ₁₃	GNPS	

					262.1456, 255.2334, 221.1547, 183.0118, 152.9952, 116.9276		
67.	14.35	Flavoglaucin	[M+H] ⁺	305.2105	313.2734, 277.1797, 184.0732, 137.0596, 122.0965, 111.0443, 104.1073	C ₁₉ H ₂₈ O ₃	¹⁶
68.	14.37	Scopularide E	[M+H] ⁺	638.4491	610.4521, 589.3916, 567.4099, 549.3994, 525.3612, 478.3625, 454.3312, 383.2890, 365.2784, 352.1892, 337.2801, 266.2103, 216.0646, 213.1602, 185.1334, 161.0821	C ₃₃ H ₅₉ N ₅ O ₇	GNPS
69.	14.56	Aversin	[M-H] ⁻ [M+H] ⁺	367.0818 369.0964	345.0954, 303.0850, 289.0687, 184.0725	C ₂₀ H ₁₆ O ₇	¹⁸
70.	14.5	7-hydroxy-8,14-dimethyl-9-hexadecanoic acid	[M-H] ⁻	297.2439	281.2491, 255.2334, 183.0117, 152.9952, 116.9276	C ₁₈ H ₃₄ O ₃	³⁶
71.	14.69	Isoechinulins C	[M+H] ⁺	406.2121	383.2023, 352.1899, 324.3251, 284.3303, 236.1485, 216.0650, 199.0622, 184.0728, 133.0856	C ₂₄ H ₂₇ N ₃ O ₃	³⁷
72.	14.91	Wentinoid A	[M+H] ⁺	349.2370	340.3927, 291.2309, 247.2048, 216.0649, 199.0621, 184.0728, 177.1117, 165.0903, 133.0856, 121.0646, 109.1012	C ₂₁ H ₃₂ O ₄	³⁸

73.	15.62	Glycerol linoleate	[M+H] ⁺	355.2815	277.1795, 239.1481, 184.0730, 177.1120, 133.0857, 121.9661, 105.0700	C ₂₁ H ₃₈ O ₄	4
74.	15.65	Arugosin G	[M-H] ⁻	491.2434	286.0486, 300.0640, 379.1588, 116.927, 253.2539, 183.0116	C ₃₀ H ₃₆ O ₆	39
75.	15.6	Linoleic acid	[M+H] ⁺	281.2474	280.2625, 276.2678, 231.1376, 184.0729, 171.1374, 144.0804, 133.0856, 123.9642, 121.9660, 113.9636, 109.1012	C ₁₈ H ₃₂ O ₂	4
76.	16.22	Versiquinazoline (J)	[M-H] ⁻	382.1772	381.1746, 225.2334, 134.8938, 116.9275, 115.9198, 100.9249	C ₂₁ H ₂₅ N ₃ O ₄	20

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