Supplementary material

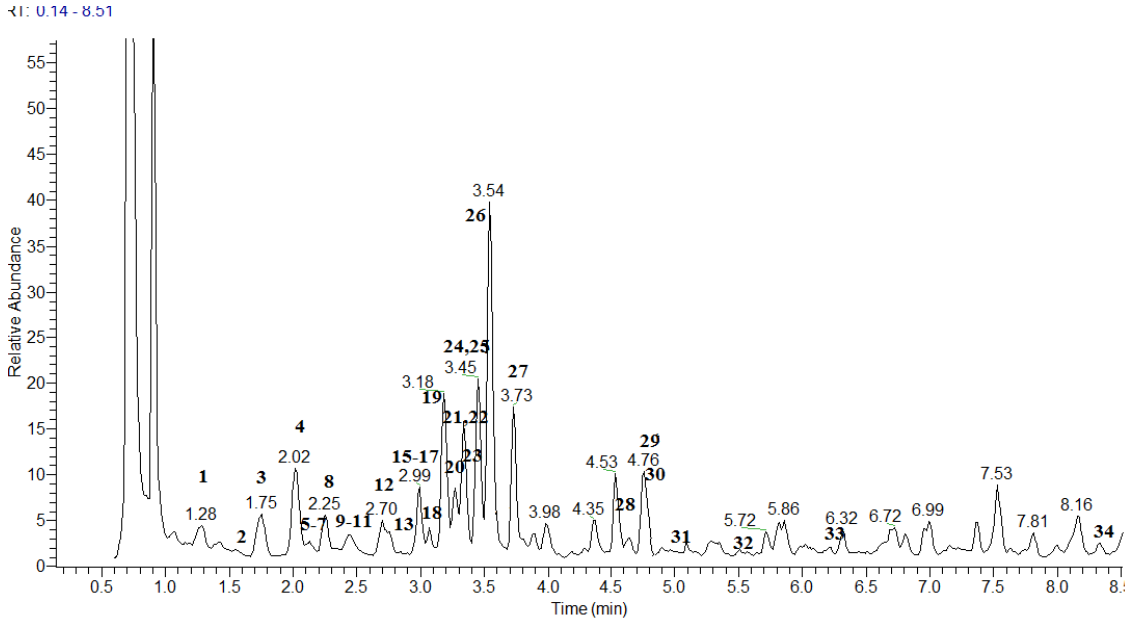


Figure S1. Extracted ion chromatograms of hydroxybenzoic and hydroxycinnamic acids and their derivatives (for numbers and fragmentation patterns, see Table S1).

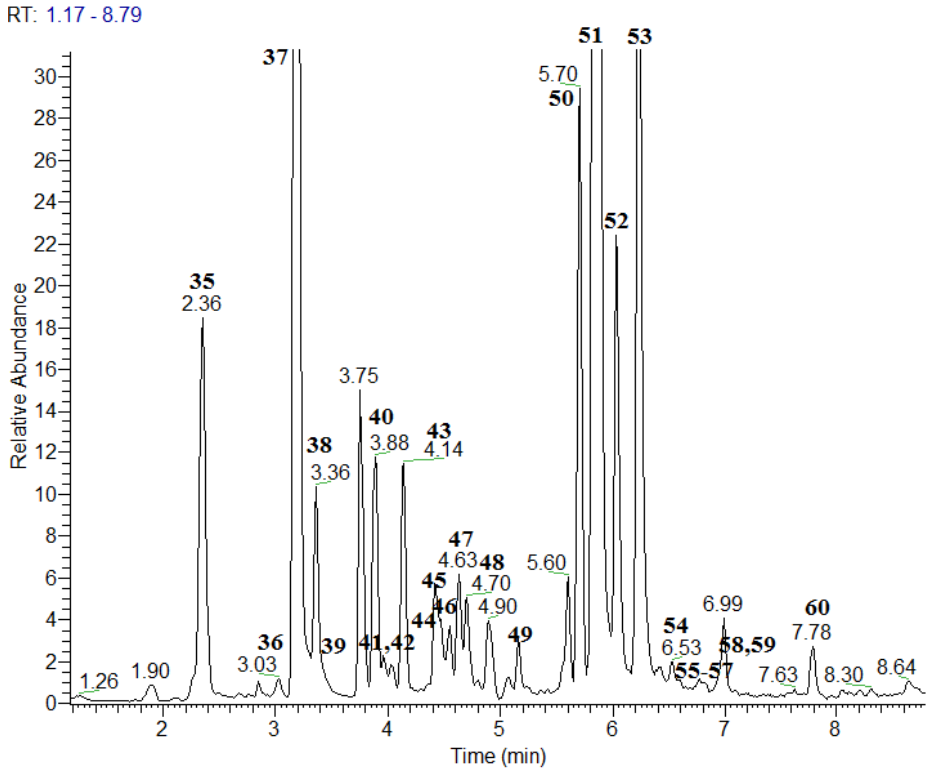


Figure S2. Extracted ion chromatograms of acylquinic acids (for numbers and fragmentation patterns, see Table S1).

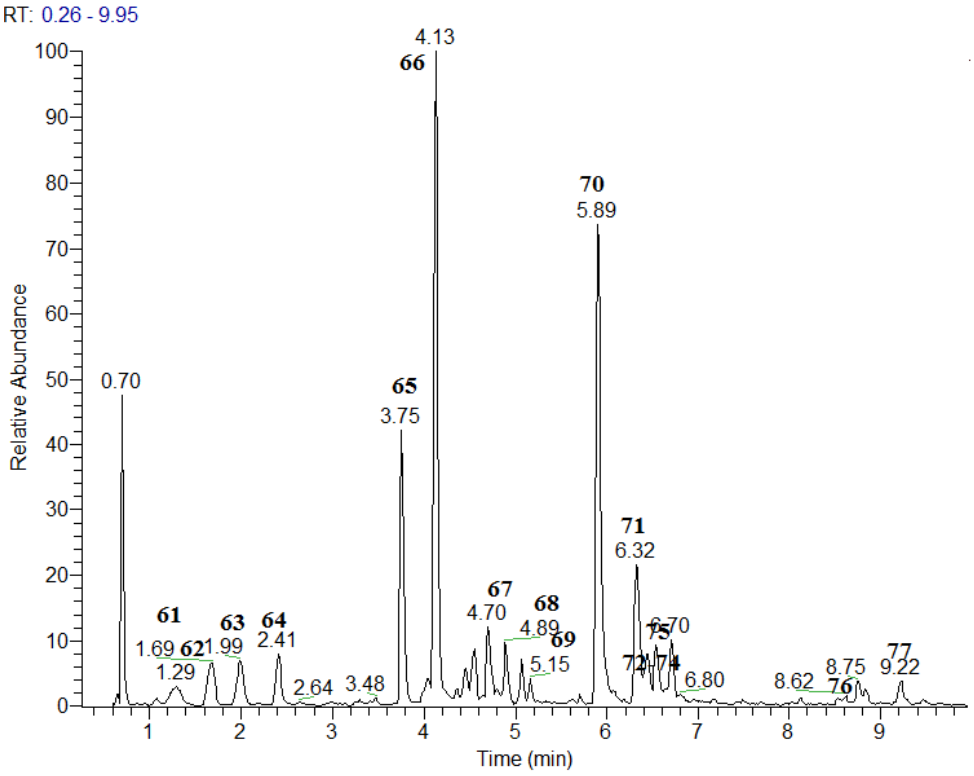


Figure S3. Extracted ion chromatograms of acylhexaric acids (for numbers and fragmentation patterns, see Table S1).

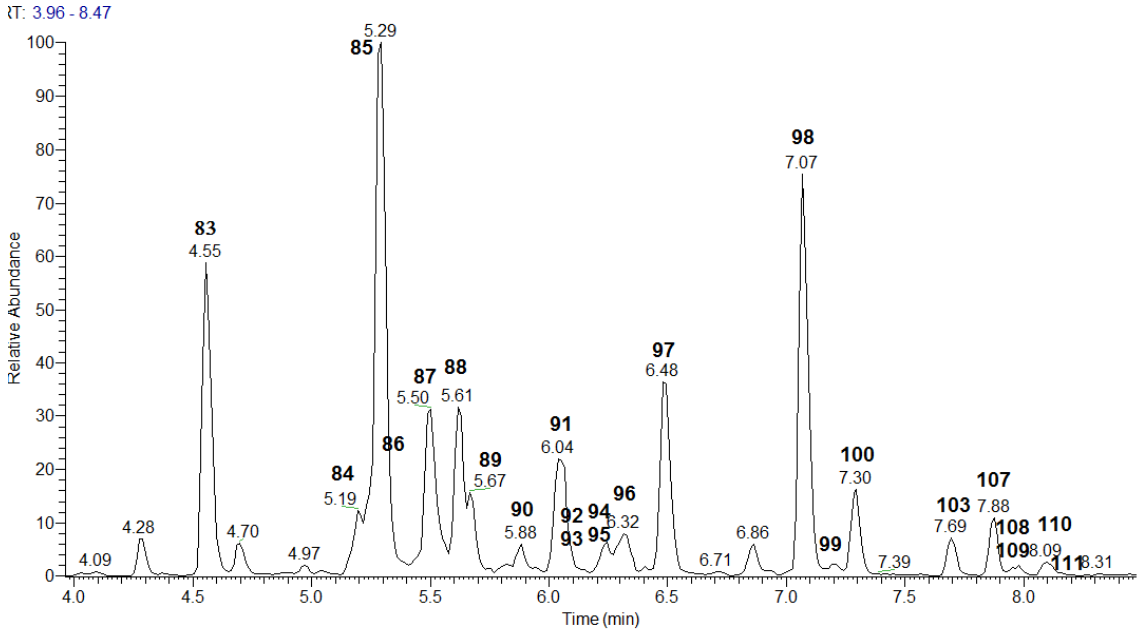


Figure S4. Extracted ion chromatograms of flavonoid glycosides (for numbers and fragmentation patterns, see Table S1).

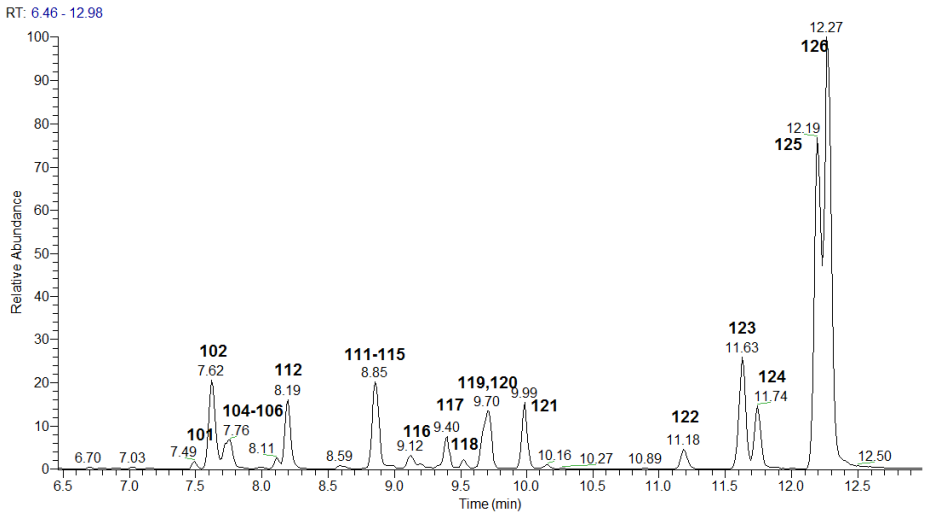


Figure S5. Extracted ion chromatograms of flavonoid aglycones (for numbers and fragmentation patterns, see Table S1).

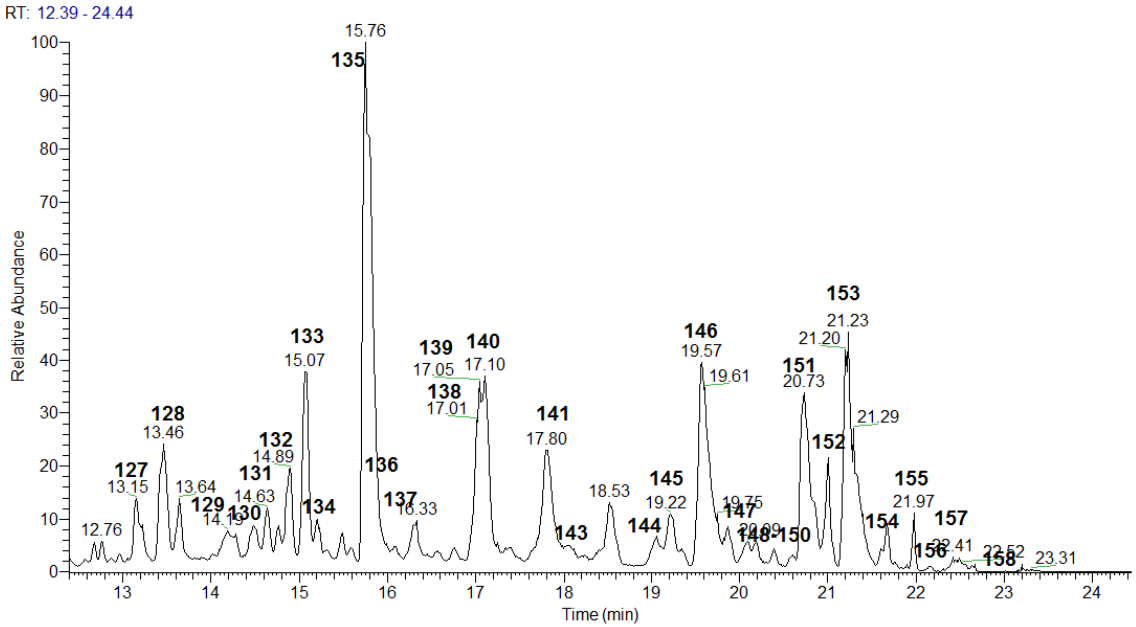


Figure S6. Extracted ion chromatograms of prenylated phloroglucinol α-pyrones (for numbers and fragmentation patterns, see Table S1).

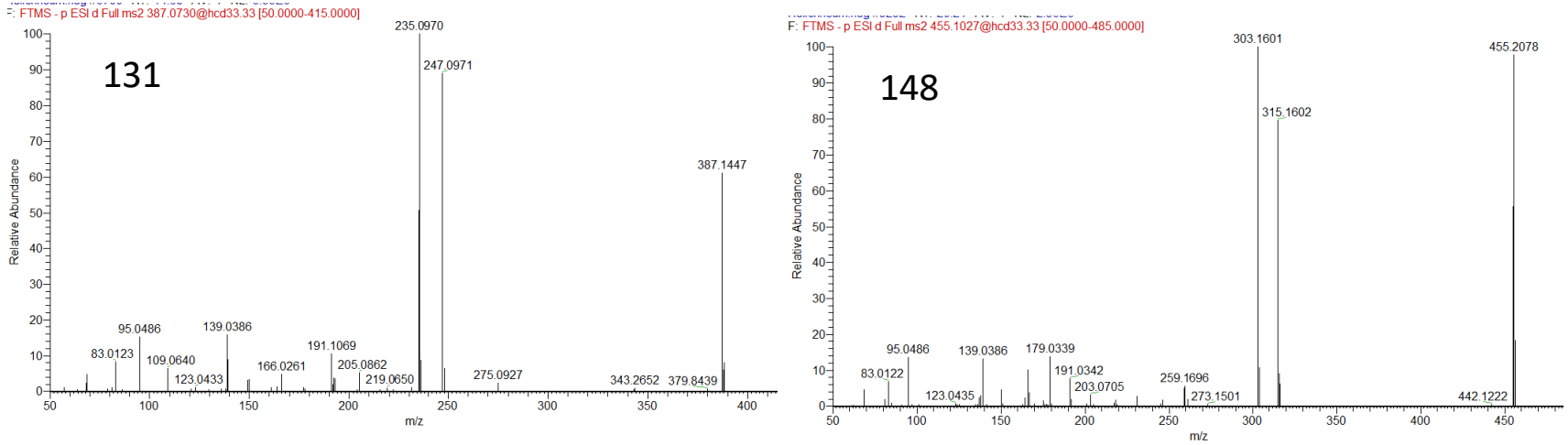
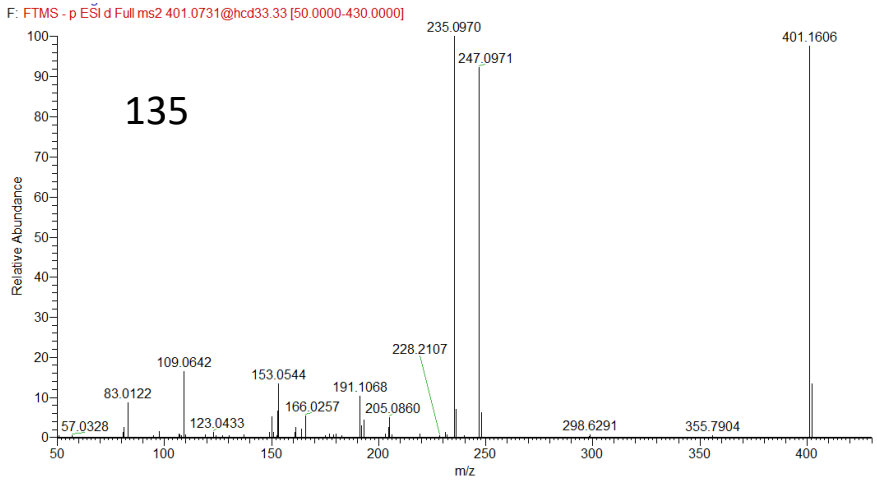


Figure S7. (-) ESI-MS/MS spectra of methylpyrones (MP) (For compound numbers and fragmentation patterns see Tab. S1).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135
Relative Abundance
m/z
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247.0971
401.1606
228.2107
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153.0544
191.1068
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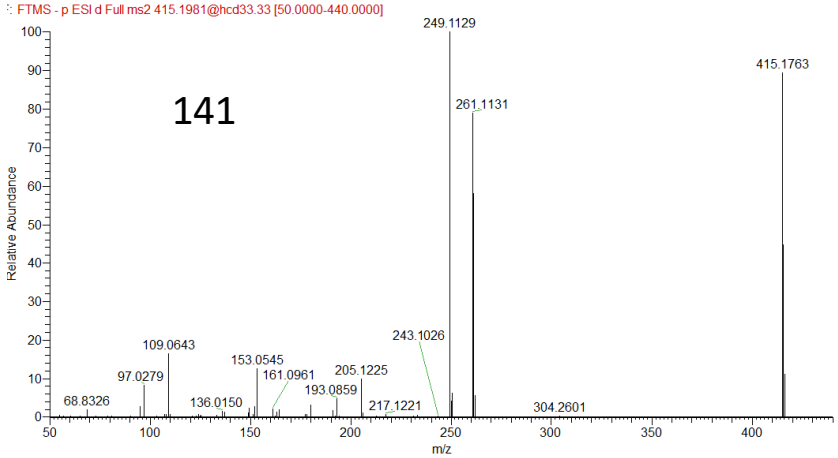
166.0257
205.0860
57.0328
123.0433
298.6291
355.7904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141
Relative Abundance
m/z
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415.1763
261.1131
243.1026
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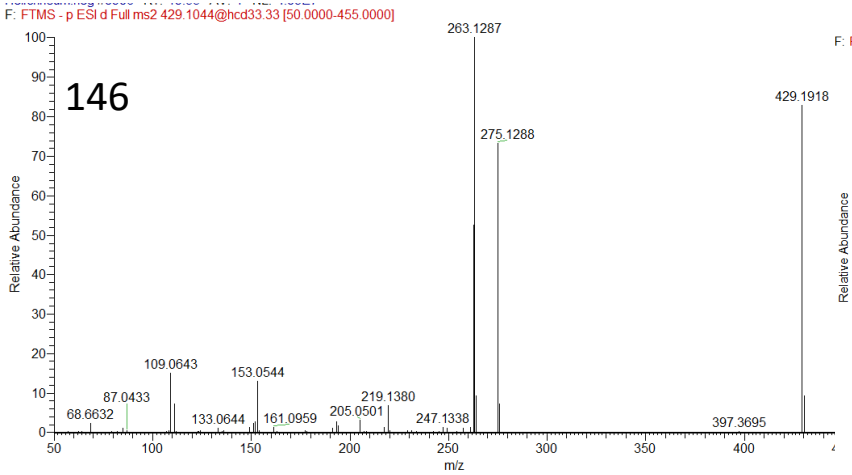
97.0279
161.0961
205.1225
193.0859
68.8326
136.0150
217.1221
304.2601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Relative Abundance
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219.1380
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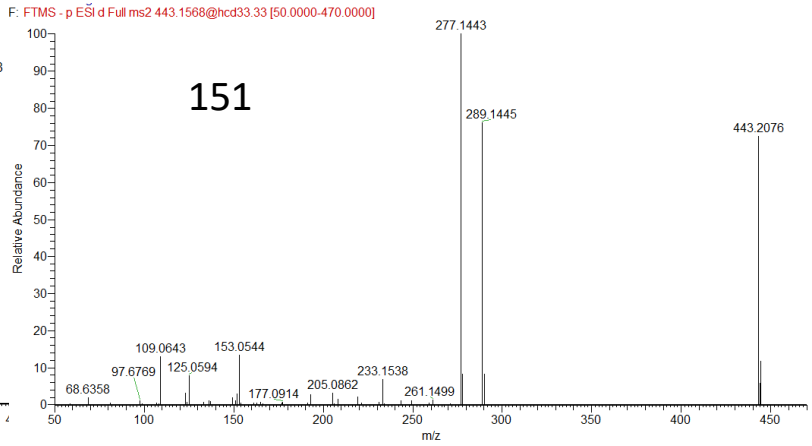
205.0501
133.0644
161.0959
247.1338
397.3695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Relative Abundance
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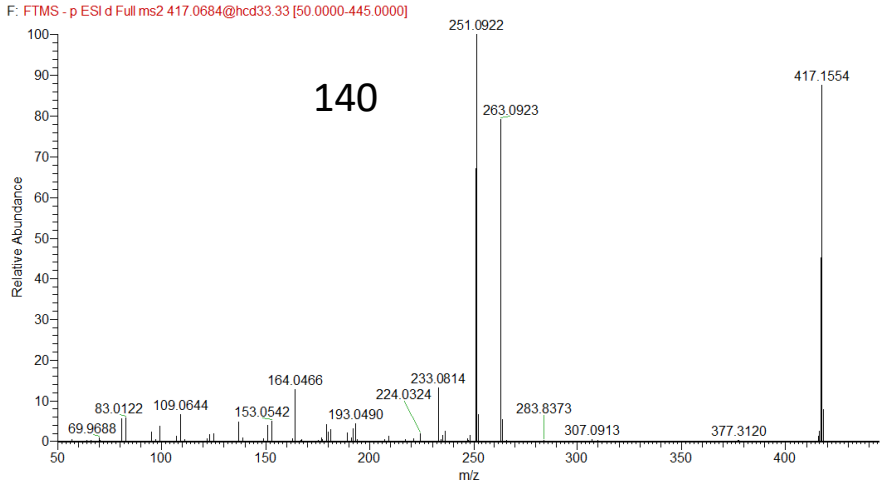
233.1538
68.6358
205.0862
177.0914
261.1499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140
Relative Abundance
m/z
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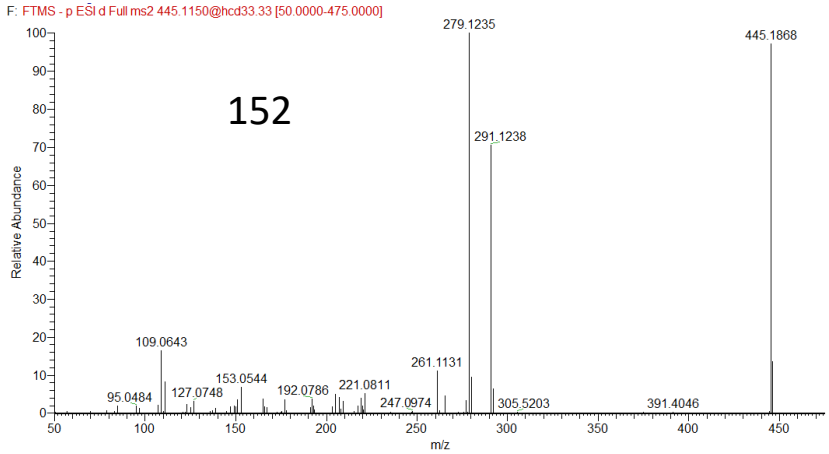
377.3120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152
Relative Abundance
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291.1238
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153.0544
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127.0748
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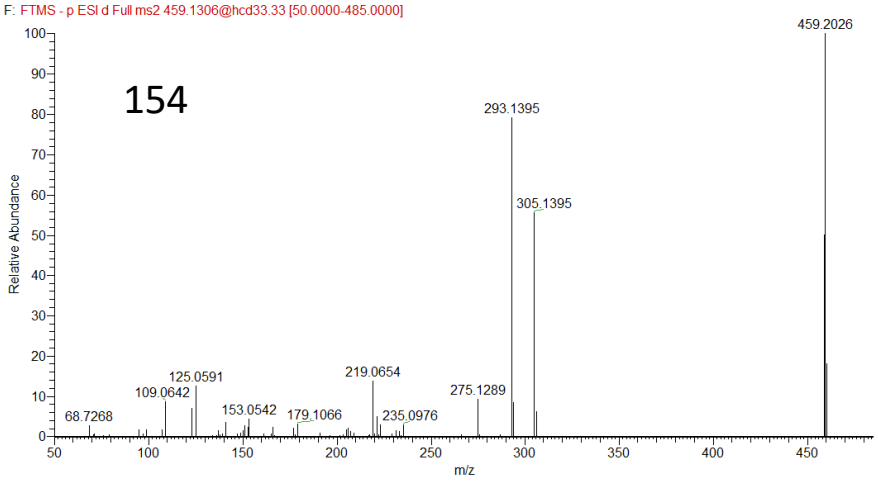
221.0811
247.0974
305.5203
391.4046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154
Relative Abundance
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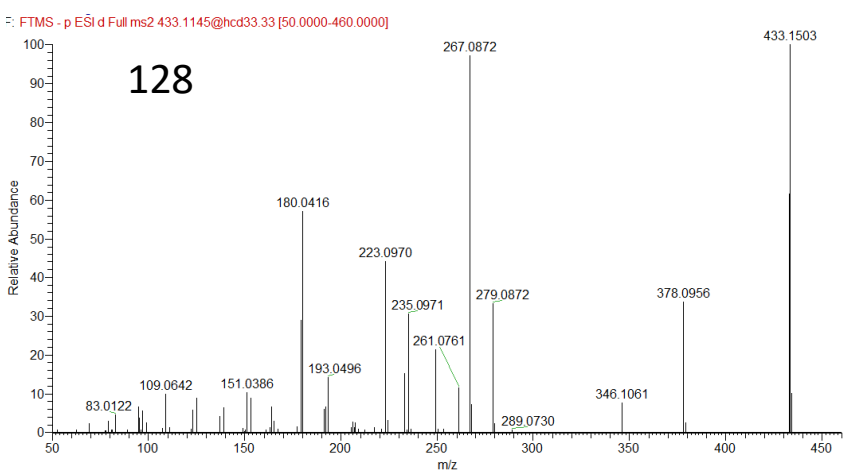
275.1289
153.0542
68.7268
179.1066
235.0976


FTMS - p ESI d Full ms2 433.1145@hcd33.33 [50.0000-460.0000]
128
Relative Abundance
m/z
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180.0416
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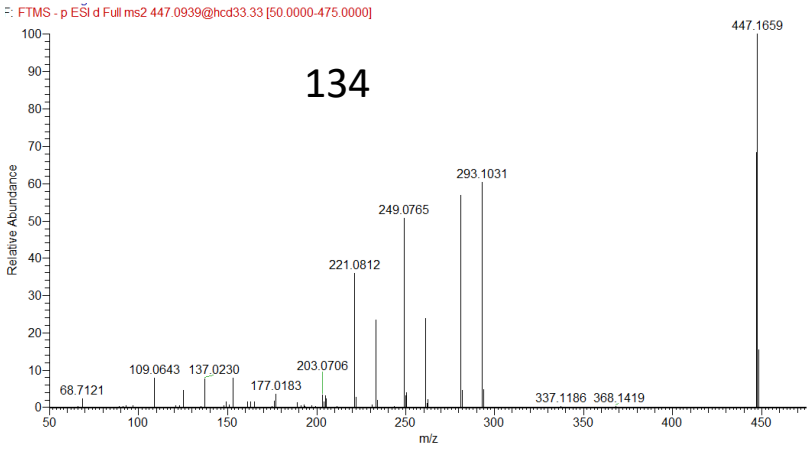
151.0386
83.0122
346.1061
289.0730


FTMS - p ESI d Full ms2 447.0939@hcd33.33 [50.0000-475.0000]
134
Relative Abundance
m/z
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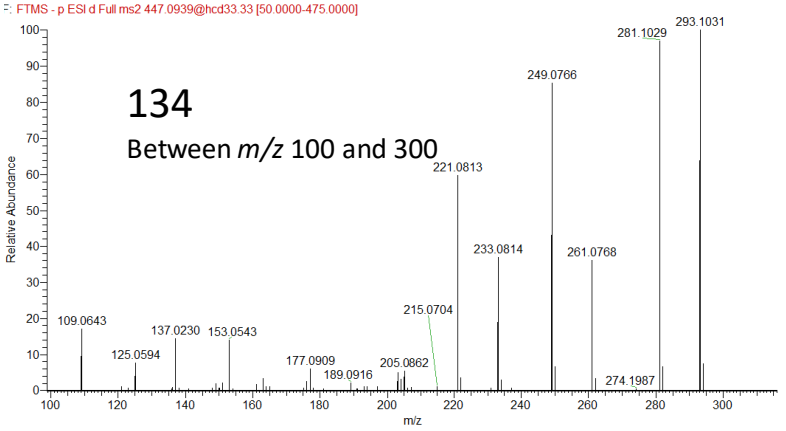
221.0812
109.0643
137.0230
203.0706
177.0183
68.7121
337.1186
368.1419


FTMS - p ESI d Full ms2 447.0939@hcd33.33 [50.0000-475.0000]
134
Between m/z 100 and 300
Relative Abundance
m/z
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281.1029
249.0766
221.0813
233.0814
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215.0704
109.0643
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153.0543
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177.0909
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189.0916
274.1987

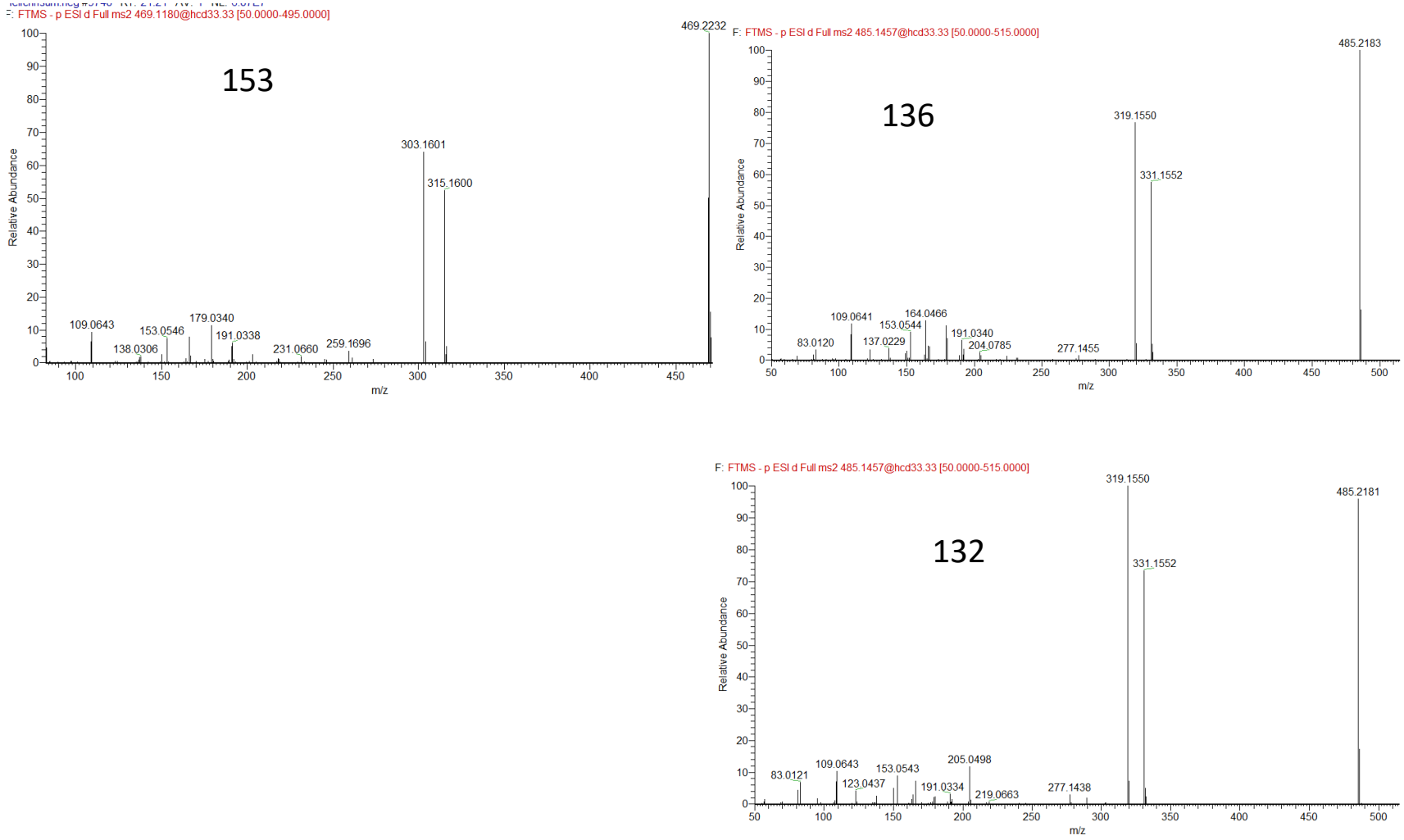


Figure S8. (-) ESI-MS/MS spectra of ethylpyrones (EP) (continue) (For compound numbers and fragmentation patterns see Tab. S1).

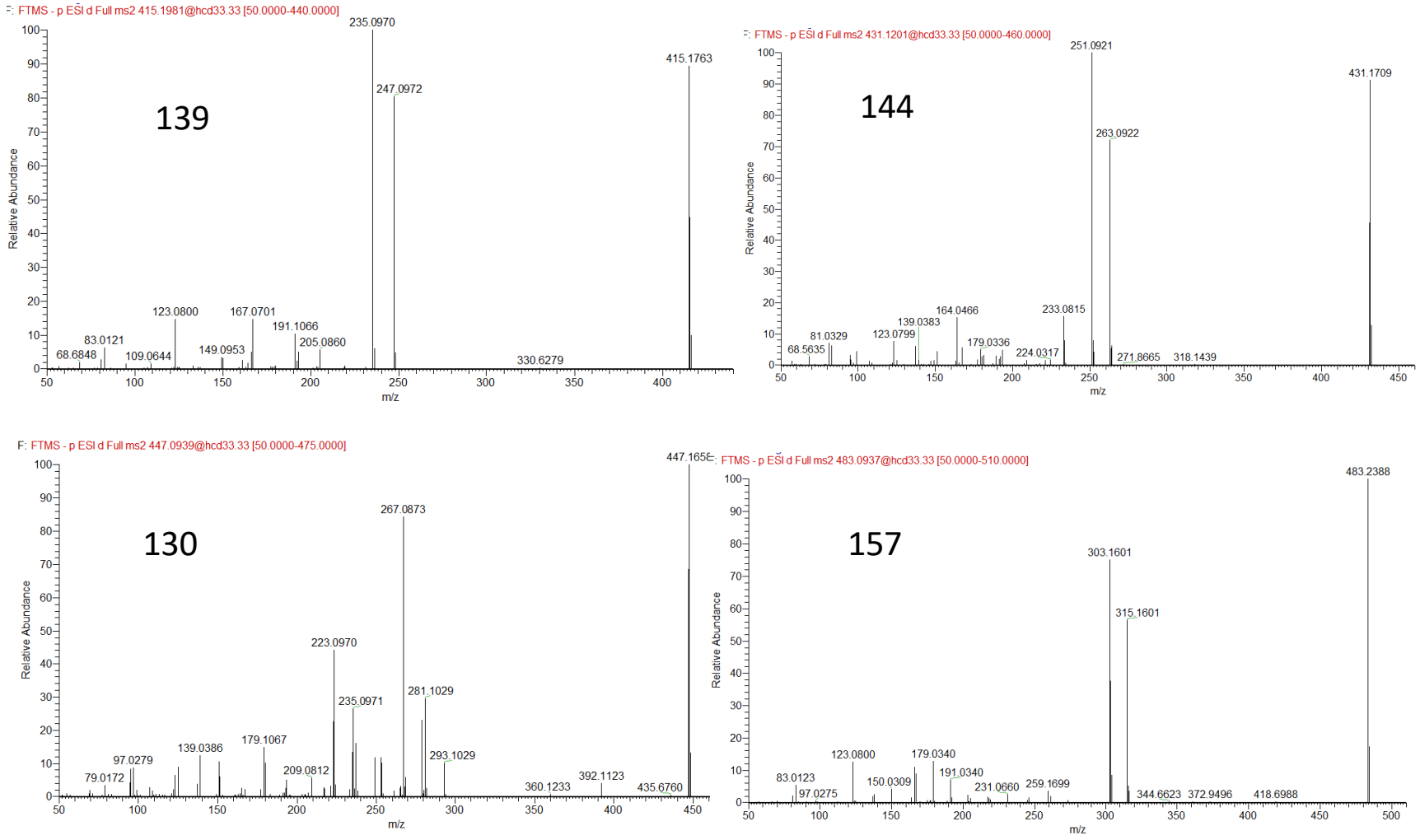


Figure S9. (-) ESI-MS/MS spectra of isopropylpyrones (IPP) (For compound numbers and fragmentation patterns see Tab. S1).

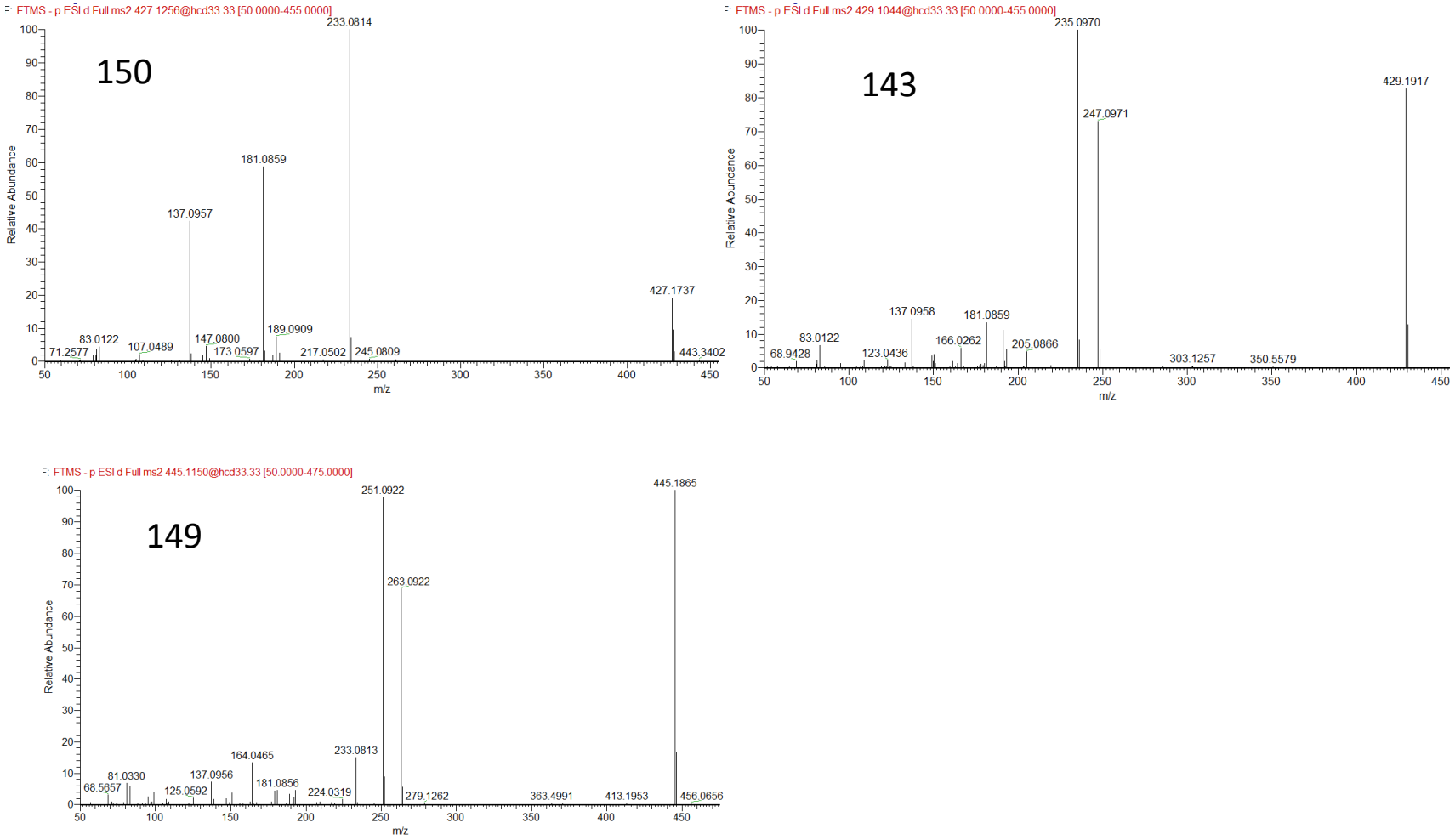


Figure S10. (-) ESI-MS/MS spectra of 1-methyl-propylpyrones (MPP) (For compound numbers and fragmentation patterns see Tab. S1).

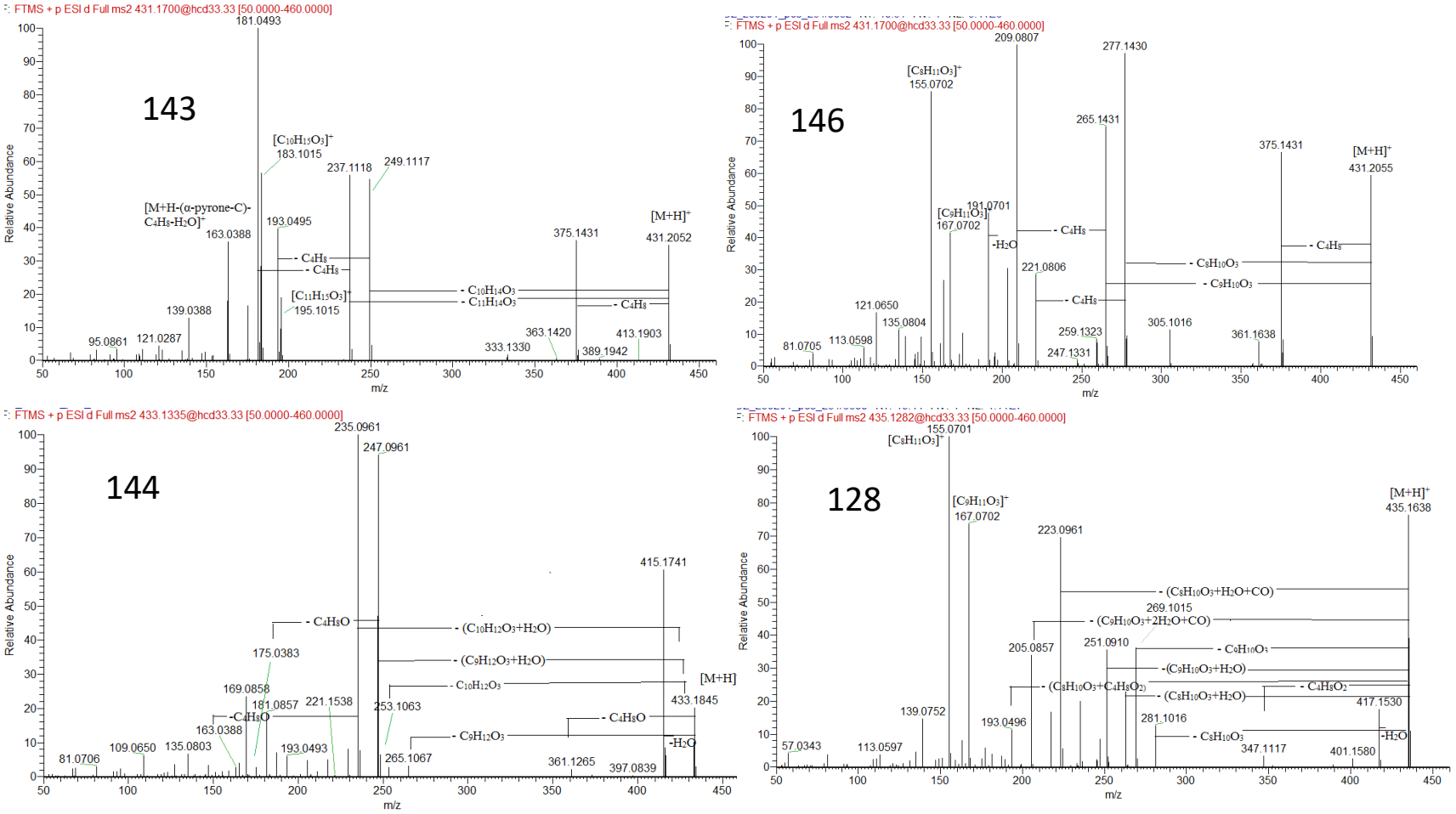


Figure S11. (+) ESI-MS/MS spectra of compounds **143, 144**, **146** and **128.**

Table S1. Secondary metabolites in *Helichrysum italicum* methanol-aqueous extract.

№	Identified/tentatively annotated compound	Molecular formula	Exact mass $[M-H]^-$	Fragmentation pattern in (-) ESI-MS/MS	t_R (min)	Δ ppm	Level of confidence	References
				Hydroxybenzoic, hydroxycinnamic and phenylethanoid glycosides				
1.	hydroxybenzoic acid-*O*-hexoside	$C_{13}H_{16}O_8$	299.0778	299.0763 (0.2), 137.0229 (100), 93.0329 (65.8),	1.28	-3.279	2	[1]
2.	protocatechuic acid-*O*-hexoside	$C_{13}H_{16}O_9$	315.0727	315.0723 (100), 153.0181 (28.2), 152.0101 (60.2), 123.0073 (2.7), 109.0286 (11.7), 108.0201 (88.5)	1.68	0.115	2	[1]
3.	vanillic acid-*O*-hexoside	$C_{14}H_{18}O_9$	329.0875	329.0868 (1.8),167.0337 (100), 152.0102 (22.9), 123.0437 (13.8), 108.0201 (35.6)	1.75	-0.198	2	[1]
4.	protocatechuic acid[a]	$C_7H_6O_4$	153.0181	153.0179 (15.2), 109.0279 (100), 91.0173 (0.9), 81.0328 (1.2)	2.02	-1.392	1	[2]
5.	hydroxybenzoyl hexose[b]	$C_{13}H_{16}O_8$	299.0778	299.0772 (91.8), 239.0556 (21.0), 209.0450 (6.2), 179.0330 (46.3), 137.0230 (100), 93.0330 (20.2)	2.04	0.002	2	
6.	protocatechuic acid-*O*-hexoside isomer	$C_{13}H_{16}O_9$	315.0727	315.0723 (48.1), 153.0543 (28.7), 123.0436 (54.7), 109.0279 (35.2)	2.11	1.729	2	
7.	*p*-hydroxyphenylacetic acid *O*-hexoside[b]	$C_{14}H_{18}O_8$	313.0932	313.0932 (100), 151.0387 (24.2), 123.0439 (7.7), 107.0488 (19.2)	2.12	0.988	2	
8.	syringic acid-*O*-hexoside[b]	$C_{15}H_{20}O_{10}$	359.0985	359.0994 (8.4), 197.0446 (100), 182.0209 (19.9), 153.0544 (15.21), 138.0308 (26.4), 123.0072 (39.99)	2.24	0.036	2	
9.	caffeic acid-*O*-hexoside	$C_{15}H_{18}O_9$	341.0871	341.0871 (21.8), 281.0674 (4.5), 251.0553 (2.7), 221.0447 (3.3), 179.0339 (100), 161.0232 (39.0), 135.0437 (59.8)	2.41	-1.980	2	
10.	hydroxybenzoic acid-*O*-hexoside isomer	$C_{13}H_{16}O_8$	299.0778	299.0770 (13.0), 137.0229 (100), 93.0331 (0.1)	2.44	0.800	2	
11.	vanillyl *O*-hexose[b]	$C_{14}H_{18}O_9$	329.0875	329.0878 (100), 269.0669 (6.9), 239.0563 (3.4), 209.0448 (31.0), 167.0337 (53.2), 152.0099 (4.5), 123.0435 (8.0), 108.0200 (2.7)	2.47	0.075	2	
12.	esculetin-*O*-hexoside[b]	$C_{15}H_{15}O_9$	339.0724	339.0720 (2.7), 177.0181 (100), 149.0230 (1.1), 133.0279 (9.0), 105.0330 (3.8), 89.0381 (2.2),	2.70	0.515	2	
13.	syringyl-*O*-hexose[b]	$C_{15}H_{20}O_{10}$	359.0984	359.0983 (100), 269.0674 (1.7), 239.0556 (20.3), 197.0446 (36.7), 182.0209 (3.5), 153.0539 (1.8), 138.0307 (0.7), 123.0074 (2.3)	2.75	-0.278	2	
14.	4-hydroxybenzoic acid[a]	$C_7H_6O_3$	137.0230	137.0229 (100), 119.0124 (2.2), 108.0200 (9.1), 93.0330 (3.0), 65.0379 (1.2)	2.83	-10.928	2	[1, 2]
15.	gentisic acid[a]	$C_7H_6O_4$	153.0181	153.0179 (51.7), 125.0227 (1.2), 123.0072 (23.6), 109.0282 (35.2), 108.0200 (100), 81.0329 (5.7)	2.98	-8.051	1	

16.	*p*-hydroxyphenylacetic acid *O*-hexoside isomer[b]	$C_{14}H_{18}O_8$	313.0929	313.0929 (15.2), 151.0386 (100), 123.0071(0.5), 109.0279 (3.8)	2.99	0.030	2	
17.	hydroxybenzoic acid-*O*-hexoside	$C_{13}H_{16}O_8$	299.0778	299.0770 (13.0), 137.0229 (100), 108.0200 (0.8), 93.0331 (0.1)	2.99	-0.704	2	[1]
18.	caffeic acid *O*-hexoside	$C_{15}H_{18}O_9$	341.0871	341.0875 (8.4), 179.0337 (100), 135.0436 (68.9), 107.0486 (0.8)	3.07	-0.602	2	
19.	quinic acid	$C_7H_{12}O_6$	191.0549	191.0550 (100), 173.0443 (1. 9), 155.0336 (0.2), 127.0385 (4.0), 111.0435 (1.9), 93.0330 (6.0), 85.0279 (17.3)	3.18	-5.817	2	[2]
20.	caffeic acid-*O*-hexoside	$C_{15}H_{18}O_9$	341.0871	341.0875 (8.4), 179.0337 (100), 135.0436 (68.9), 107.0486 (0.8)	3.27	-0.386	2	[1]
21.	coumaric acid-*O*-hexoside	$C_{15}H_{18}O_8$	325.0930	325.0918 (1.3), 163.0387 (100), 1445.0281 (4.1), 119.0487 (87.7)	3.34	-3.355	2	[1, 2]
22.	*p*-coumaric acid[a]	$C_9H_8O_3$	163.0389	163.0387 (6.2), 145.0125 (0.3), 135.0436 (0.4), 119.0486 (100)	3.35	-8.203	1	[2]
23.	vanillic acid *O*-hexoside isomer	$C_{14}H_{18}O_9$	329.0875	329.0873 (2.5), 167.0337 (100), 151.0019 (1.5), 123.0436 (21.8), 107.0120 (0.8)	3.37	0.252	2	[1]
24.	esculetin	$C_9H_6O_4$	177.0193	177.0181 (100), 149.0230 (2.9), 133.0280 (19.9), 105.0329 (11.0), 89.0380 (8.4)	3.46	4.982	2	[1]
25.	*p*-hydroxyphenylacetic acid[a,b]	$C_8H_8O_3$	151.0401	151.0387 (100), 109.0279 (14.4), 124.0150 (4.1)	3.46	-9.252	2	
26.	caffeic acid[a]	$C_9H_8O_4$	179.0339	179.0339 (18.3), 135.0437 (100), 117.0332 (0.5), 107.0487 (1.2)	3.54	-6.044	1	[2]
27.	dehydrochorismic acid[b]	$C_{10}H_8O_6$	223.0248	223.0232 (1.3), 179.0338 (67.0), 153.0180 (23.5), 135.0437 (36.7), 109.0279 (100)	3.73	-7.180	2	
28.	*m*-coumaric acid[a,b]	$C_9H_8O_3$	163.0389	163.0388 (7.6), 119.0487 (100)	4.56	-7.958	1	
29.	syringic acid[a]	$C_9H_{10}O_5$	197.0446	197.0446 (45.5), 179.0339 (1.1), 167.0334 (0.4), 153.0543 (100)	4.76	-4.703	1	[2]
30.	vanillic acid[a,b]	$C_8H_8O_4$	167.0338	167.0337 (100), 152.0102 (24.6), 123.0436 (3.9), 95.0121 (3.3)	4.78	-7.615	1	
31.	*o*-coumaric acid[a,b]	$C_9H_8O_3$	163.0389	163.0388 (8.0), 135.0438 (0.6), 119.0487 (100)	5.01	-7.958	1	
32.	scopoletin	$C_{10}H_8O_4$	191.0350	191.0340 (22.4), 176.0103 (100), 148.0151 (15.4), 120.0200 (1.2), 104.0251 (19.0)	5.06	-5.088	2	[1]
33.	caffeic acid *O*-(hydroxyisovaleryl)-hexoside[b]	$C_{20}H_{26}O_{11}$	441.1402	441.1402 (23.2), 323.0782 (0.8), 179.0338 (100), 135.0437 (68.1), 107.0487 (0.6),	5.58	0.125	2	
34.	salicylic acid[a]	$C_7H_6O_3$	137.0230	137.0230 (33.1), 108.0201 (3.3), 93.0330 (100)	6.27	-10.344	1	[2]

35.	caffeic acid *O*-(hydroxybensoyl)-hexoside[b]	$C_{22}H_{22}O_{11}$	461.1089	461.1090 (21.7), 323.0780 (4.9), 179.0339 (97.0), 137.0229 (100), 135.0437 (85.5), 93.0330 (38.0)	8.26	0.142	1	
	Mono-, diacyl- and triacylquinic acids							
36.	neochlorogenic (3-caffeoylquinic) acid[a,b]	$C_{16}H_{18}O_9$	353.0867	353.0880 (40.4), 191.0551 (100), 179.0339 (65.2), 173.0442 (3.3), 161.0231 (3.8), 135.0437 (45.3), 111.0433 (2.0), 93.0330 (4.1), 85.0279 (7.5)	2.35	0.495	1	
37.	3-*p*-coumaroylquinic acid	$C_{16}H_{18}O_8$	337.0928	337.0933(14.3), 191.0551 (28.7), 173.0441 (5.5), 163.0387 (100), 135.0435 (1.3), 119.0486 (30.3), 111.0432(1.5), 93.0329 (2.6), 85.0278 (3.0)	3.02	1.096	2	
38.	chlorogenic (5-caffeoylquinic) acid[a]	$C_{16}H_{18}O_9$	353.0874	353.0880 (4.8), 191.0550 (100), 179.0335 (1.0), 161.0231 (1.6), 127.0384 (1.8), 111.0436 (9.7), 93.0329 (2.6), 85.0278 (6.5)	3.18	0.665	1	[1, 2]
39.	4-caffeoylquinic acid	$C_{16}H_{18}O_9$	353.0878	353.0880 (32.0), 191.0551 (60.6), 179.0339 (70.9), 173.0445 (100), 155.0337 (4.8), 135.0437 (51.7), 111.0436 (2.8), 93.0330 (20.6), 85.0278 (9.0)	3.35	-0.100	2	[1]
40.	3-feruloylquinic acid	$C_{17}H_{20}O_9$	367.1034	367.1035 (20.8), 193.0496 (100), 149.0594 (2.8), 134.0358 (53.2), 127.0388 (0.6), 111.0438 (1.0), 93.0329 (1.7)	3.43	..	2	[2]
41.	5-caffeoylquinic acid isomer	$C_{16}H_{18}O_9$	353.0874	353.0880(6.4), 191.0550 (100), 179.0341 (0.9), 173.0446 (0.9), 161.0233 (2.1), 127.0383 (1.7), 93.0330 (2.6), 85.0279 (8.2)	3.88	0.580	2	[1]
42.	5-*p*-coumaroylquinic acid	$C_{16}H_{18}O_8$	337.0928	337.0932 (7.8), 191.0550 (100), 173.0442 (6.6), 163.0389 (5.9), 145.0281 (1.5), 119.0487 (5.2), 93.0328 (18.5), 85.0277 (4.4)	3.96	0.829	2	[1]
43.	3-caffeoyl-5-hydroxy-dihydrocaffeoylquinic acid[b]	$C_{25}H_{26}O_{13}$	533.1288	533.1302 (68.2), 371.0992 (2.7), 353.0874 (17.8), 335.0778 (4.0), 191.0551 (100), 179.0338 (42.9), 173.0444 (14.4), 161.0233 (7.3), 135.0437 (54.8), 111.0435 (2.0), 93.0329 (8.0), 85.0279 (9.3)	4.03	0.236	2	
44.	1, 3- dicaffeoylquinic acid[b]	$C_{25}H_{24}O_{12}$	515.1190	515.1196 (82.0), 353.0879 (38.9), 335.0772 (12.2), 191.0550 (100), 179.0338 (69.5), 161.0230 (7.7), 135.0436 (61.4), 111.0438 (3.5), 93.0328 (5.3)85.0278 (7.2)	4.14	0.137	2	
45.	3-caffeoyl-4- hydroxy-dihydrocaffeoylquinic acid[b]	$C_{25}H_{26}O_{13}$	533.1288	533.1312 (100), 371.0615 (13.7), 353.0875 (6.7), 335.0773 (11.2), 191.0551 (10.4), 179.0339 (21.9), 173.0444 (92.0), 161.0231 (16.1), 135.0437 (71.5), 127.0385 (2.0), 111.0437 (1.5), 93.0330 (19.0)	4.37	2.1	2	
46.	5-feruloylquinic acid	$C_{17}H_{20}O_9$	367.1034	367.1035 (16.7), 193.0497 (5.7), 191.0551 (100), 173.0444 (12.0), 155.0338 (0.4), 134.0359 (10.1), 111.0437 (3.5), 93.0329 (25.2), 85.0278 (5.1)	4.42	-0.096	2	[1]

47.	1-caffeoyl-3-hydroxy-dihydrocaffeoylquinic acid[b]	$C_{25}H_{26}O_{13}$	533.1288	533.1368 (17.8), 371.0991 (26.6), 353.0878 (5.6), 335.0771 (2.9), 191.0551 (26.1), 179.0338 (10.2), 173.0445 (12.5), 161.0235 (3.4), 135.0436 (100), 93.0330 (3.9), 85.0278 (23.7)	4.45	12.710	2	
48.	5-*p*-coumaroylquinic acid isomer	$C_{16}H_{18}O_8$	337.0928	337.0929 (7.4), 191.0550 (100), 173.0444 (1.9), 163.0388 (1.8), 127.0384 (1.5), 111.0435 (1.0), 93.0329 (4.7), 85.0277 (6.7)	4.63	0.028	2	[1]
49.	4-feruloylquinic acid[b]	$C_{17}H_{20}O_9$	367.1034	367.1034 (95.0), 193.0496 (10.9), 191.0562 (1.7), 173.0444 (72.13), 163.0389 (2.2), 134.0359 (22.2), 111.0436 (14.9), 93.0329 (100)	4.69	-0.260	2	
50.	1, 3-dicaffeoylquinic acid-hexoside	$C_{31}H_{34}O_{17}$	677.1723	677.1730 (81.2), 515.1407 (82.0), 353.0876 (17.2), 341.0877 (30.0), 323.0772 (19.9), 191.0551 (82.1), 179.0339 (98.9), 173.0441 (3.8), 161.0230 (29.6), 135.0437 (100), 93.0331 (7.1), 85.0279 (6.9)	5.15	0.956	2	[1]
51.	3,4-dicaffeoylquinic acid[a]	$C_{25}H_{24}O_{12}$	515.1190	515.1196 (100), 353.0877 (12.3), 335.0780 (5.0), 203.0334 (0.4), 191.0551 (24.9), 179.0339 (41.6), 173.0444 (46.7), 161.0232 (13.1), 135.0437 (44.2), 127.0386 (1.9), 111.0436 (3.4), 93.0329 (14.6), 85.0278 (3.1)	5.71	0.254	1	[1, 2]
52.	3,5-dicaffeoylquinic acid[a]	$C_{25}H_{24}O_{12}$	515.1189	515.1197 (19.6), 353.0879 (100), 335.0774 (1.5), 191.0551 (87.0), 179.0339 (38.8), 173.0445 (3.8), 161.0233 (4.7), 135.0437 (1.4), 111.0434 (1.5), 93.0330 (4.1), 85.0279 (7.5)	5.85	0.370	1	[1]
53.	1,3-dicaffeoylquinic acid malonyl[b]	$C_{28}H_{26}O_{15}$	601.1199	601.1207 (37.5), 557.1307 (16.1), 515.1199 (11.1), 439.0883 (26.8), 395.0983 (43.2), 233.0661 (100), 191.0551 (17.5), 179.0338 (14.1), 173.0443 (14.1), 161.0231 (11.1), 155.0334 (3.5), 135.0436 (15.6), 133.0280 (5.3), 127.0385 (1.4), 111.0435 (2.5), 93.0330 (6.3), 85.0278 (1.2), 59.0122 (91.9)	5.95	1.292	2	
54.	1,5-dicaffeoylquinic acid[a]	$C_{25}H_{24}O_{12}$	515.1190	515.1197 (28.5), 353.0878 (83.6), 335.0764 (2.5), 191.0551 (100), 179.0339 (47.4), 173.0445 (7.1), 161.0231 (7.3), 155.0338 (1.4), 135.0437 (56.5), 127.0385 (3.4), 111.0434 (1.9), 93.0330 (5.7), 85.0279 (9.2)	6.03	-0.096	1	[1]
55.	3, 5-dicaffeoylquinic acid malonyl[b]	$C_{28}H_{26}O_{15}$	601.1199	601.1199 (20.6), 557.1304 (13.8), 515.1189 (11.8), 439.0882 (9.9), 395.0982 (80.0), 353.0869 (0.5), 335.0772 (2.5), 233.0661 (100), 191.0551 (6.7), 179.0339 (5.4), 173.0443 (17.3), 161.0233 (8.5), 135.0436 (11.2), 133.0281 (3.4), 111.0435 (2.5), 93.0329 (5.6), 59.0122 (88.4)	6.15	-0.039	2	

56.	4,5-dicaffeoylquinic acid	$C_{25}H_{24}O_{12}$	515.1190	515.1196 (100), 353.0878 (64.2), 335.0765 (0.6), 229.0565 (0.6), 203.0345 (3.0), 191.0551 (34.0), 179.0338 (70.0), 173.0443 (85.5), 155.0336 (4.7), 135.0436 (51.0), 127.0383 (0.7), 111.0436 (3.0), 93.0329 (18.7), 85.0280 (3.2)	6.24	0.254	2	[1]
57.	3, 4-dicaffeoylquinic acid malonyl[b]	$C_{28}H_{26}O_{15}$	601.1199	601.1202 (20.6), 557.1302 (11.0), 515.1196 (4.5), 439.0883 (15.8), 395.0984 (46.1), 353.0877 (0.8), 233.0661 (100), 191.0551 (11.6), 179.0339 (7.4), 173.0443 (81.1), 161.0231 (6.4), 155.0336 (4.7), 135.0438 (13.7), 133.0280 (4.3), 111.0438 (4.6), 93.0328 (17.6), 59.0122 (27.4)	6.32	0.577	2	
58.	4, 5-dicaffeoylquinic acid malonyl[b]	$C_{28}H_{26}O_{15}$	601.1199	601.1203 (8.4), 557.1302 (10.0), 515.1190 (10.9), 439.0883 (25.5), 395.0981 (100), 353.0878 (16.1), 335.0777 (16.1), 233.0661 (81.7), 191.0551 (44.8), 179.0338 (25.9), 173.0443 (74.7), 161.0232 (11.2), 155.0337 (5.1), 135.0437 (39.1), 111.0435 (4.2), 93.0329 (16.9), 85.0279 (3.9), 59.0122 (29.0)	6.51	0.677	2	
59.	3-*p*-coumaroyl-5-caffeoylquinic acid[b]	$C_{25}H_{24}O_{11}$	499.1251	499.1259 (28.4), 353.0869 (1.8), 337.0929 (81.4), 335.0773 (2.0), 191.0552 (21.9), 179.0341 (1.2), 173.0443 (8.6), 163.0387 (100), 135.0436 (3.5), 119.0487 (35.6), 93.0330 (4.4), 85.0276 (1.5)	6.53	2.535	2	
60.	3-feruloyl-5-caffeoylquinic acid	$C_{26}H_{26}O_{12}$	529.1356	529.1347 (12.6), 367.1034 (100), 353.0889 (1.4), 335.0789 (0.7), 193.0496 (92.8), 191.0551 (28.3), 179.0342 (2.2), 173.0443 (11.8), 161.0233 (3.9), 155.0336 (2.4), 134.0358 (62.5), 111.0433 (2.2), 93.0329 (0.7), 85.0278 (1.8)	6.83	-0.849	2	[1]
61.	3-caffeoyl-5-feruloylquinic acid[b]	$C_{26}H_{26}O_{12}$	529.1356	529.1356 (47.0), 367.1034 (59.1), 353.0879 (44.1), 335.0770 (1.8), 193.0497 (42.5), 191.0551 (100), 179.0339 (34.3), 173.0444 (16.9), 161.0232 (8.0), 155.0334 (2.4), 135.0438 (36.1), 134.0358 (36.1), 111.0437 (3.4), 93.0329 (16.5), 85.0278 (7.2)	6.90	0.776	2	
62.	4-*p*-coumaroyl-5-caffeoylquinic acid[b]	$C_{25}H_{24}O_{11}$	499.1252	499.1225 (26.5), 353.0879 (1.2), 337.0930 (63.0), 191.0549 (6.5), 173.0443 (100), 163.0388 (19.1), 135.0436 (4.4), 133.0278 (1.4), 127.0385 (1.4), 121.0279 (45.9), 119.0486 (11.2), 111.0435 (3.3), 93.0329 (24.5), 85.0279 (1.9)	6.94	-4.117	2	
63.	4-feruloyl-5-caffeoylquinic acid	$C_{26}H_{26}O_{12}$	529.1356	529.1351 (18.5), 367.1034 (67.2), 353.0881 (0.6), 335.0780 (0.4), 193.0497 (17.8), 173.0443 (100),	7.09	-0.037	2	[1]

64.	4-caffeoyl-5-feruloylquinic acid[b]	$C_{26}H_{26}O_{12}$	529.1356	155.0337 (4.2), 137.0231 (4.4), 134.0359 (16.3), 127.0386 (0.7), 111.0437 (2.6), 93.0330 (23.8) 529.1354 (7.2), 367.1032 (21.7), 353.0879 (55.4), 335.0784 (1.9), 203.0345 (1.8), 191.0551 (72.8), 179.0338 (66.8), 173.0443 (100), 161.0231 (11.0), 135.0437 (60.9), 111.0435 (5.0), 93.0329 (34.5), 85.0278 (7.6), 134.0359 (8.8)	7.18	0.474	2	
65.	3,4,5-tricaffeoylquinic acid[a]	$C_{34}H_{30}O_{15}$	677.1528	677.1523 (100), 515.1199 (50.2), 353.0880 (44.9), 335.0772 (14.7), 299.0559 (0.6), 255.0667 (0.8), 203.0342 (0.9), 191.0552 (41.4), 179.0339 (71.4), 173.0444 (87.5), 161.0232 (22.2), 135.0437 (74.3), 111.0437 (5.6), 93.0330 (20.3), 85.0279 (3.8)	7.78	1.605	1	
				Caffeoylhexaric acids				
66.	caffeoylhexaric acid[b] 1	$C_{15}H_{16}O_{11}$	371.0620	371.0625 (36.1), 209.0295 (100), 179.0338 (3.2), 173.0086 (0.7), 161.0228 (2.2), 147.0286 (4.3), 135.0437 (0.8), 129.0178 (4.0), 111.0076 (2.4), 93.0329 (9.7), 85.0278 (48.7)	1.29	1.470	2	
67.	caffeoylhexaric acid[b] 2	$C_{15}H_{16}O_{11}$	371.0620	371.0612 (3.1), 209.0295 (100), 191.0188 (21.5), 179.0337 (2.2), 173.0079 (1.6), 147.0286 (4.9), 135.0437 (3.9), 129.0182 (3.1), 111.0074 (2.3), 85.0278 (43.8)	1.69	-1.979	2	
68.	caffeoylhexaric acid[b] 3	$C_{15}H_{16}O_{11}$	371.0620	371.0605 (3.0), 209.0294 (100), 173.0079 (1.6), 147.0286 (3.7), 135.0436 (2.0), 129.0178 (3.9), 111.0066 (2.0), 85.0274 (42.0)	1.99	-4.028	2	
69.	caffeoylhexaric acid[b] 4	$C_{15}H_{16}O_{11}$	371.0620	371.0594 (2.5), 209.0294 (100), 191.0187 (21.0), 147.0282 (3.2), 135.0437 (1.5), 129.0176 (2.1), 111.0071 (2.2), 85.0278 (36.2)	2.41	-6.956	2	
70.	dicaffeoylhexaric acid 1	$C_{24}H_{22}O_{14}$	533.0937	533.0938 (13.0), 371.0620 (95.9), 353.0513 (2.3), 209.0295 (100), 191.0188 (26.2), 179.0333 (3.3), 161.0236 (0.6), 173.0081 (0.7), 147.0289 (4.2), 135.0439 (5.2), 129.0177 (5.3), 111.0072 (2.9), 85.0279 (51.5)	3.75	0.134	2	[1]
71.	dicaffeoylhexaric acid[b] 2	$C_{24}H_{22}O_{14}$	533.0937	533.0893 (13.4), 371.0618 (85.3), 209.0294 (100), 191.0186 (23.6), 179.0341 (6.3), 173.0081 (0.8), 147.0285 (3.0), 135.0436 (11.3), 129.0178 (6.6), 111.0072 (4.1), 85.0278 (48.4)	4.13	-8.213	2	
72.	dicaffeoylhexaric acid[b] 3	$C_{24}H_{22}O_{14}$	533.0937	533.0862 (15.4), 371.0610 (89.8), 353.0517 (4.5), 335.0406 (0.5), 209.0295 (100), 191.0188 (28.8), 179.0340 (4.9), 161.0232 (0.9), 147.0283 (4.0), 135.0437 (14.6), 129.0179 (6.9), 111.0074 (2.8), 93.329 (4.2), 85.0278 (48.2)	4.71	-14.066	2	

73.	dicaffeoylhexaric acid[b] 4	$C_{24}H_{22}O_{14}$	533.0937	533.0859 (15.4), 371.0615 (76.1), 353.0512 (3.3), 209.0294 (100), 191.0188 (25.7), 179.0341 (3.8), 173.0446 (4.6), 161.0234 (1.2), 147.0285 (3.2), 135.0437 (12.3), 129.0178 (6.6), 129.0178 (4.5), 111.0072 (2.7), 93.0329 (1.3), 85.0278 (49.3)	4.89	-14.516	2	
74.	dicaffeoylhexaric acid[b] 5	$C_{24}H_{22}O_{14}$	533.0937	533.0892 (16.1), 371.0619 (91.0), 353.0510 (0.3), 209.0295 (100), 191.0188 (31.9), 179.0339 (3.7), 161.0229 (2.7), 147.0285 (5.0), 135.0438 (8.7), 129.0178 (5.7), 111.0070 (3.1), 85.0278 (55.0)	5.15	-8.457	2	
75.	tricaffeoylhexaric acid 1	$C_{33}H_{28}O_{17}$	695.1254	695.1259 (24.2), 533.0938 (31.6), 371.0619 (19.4), 353.0510 (1.7), 209.0294 (100), 191.0148 (14.8), 179.0339 (3.8), 161.0233 (0.8), 147.0285 (3.5), 135.0437 (6.3), 129.0178 (6.1), 111.0072 (2.6), 85.0278 (37.9)	5.89	0.788	2	[1]
76.	tricaffeoylhexaric acid[b] 2	$C_{33}H_{28}O_{17}$	695.1254	695.1262 (24.3), 533.0942 (34.6), 371.0622 (20.3), 353.0510 (1.7), 209.0295 (100), 191.0148 (15.6), 179.0341 (2.9), 161.0230 (2.1), 147.0287 (4.7), 135.0436 (4.7), 129.0179 (5.3), 111.0072 (2.2), 85.0279 (43.7)	6.32	1.219	2	
77.	tricaffeoylhexaric acid[b] 3	$C_{33}H_{28}O_{17}$	695.1254	695.1262 (21.2), 533.0941 (44.3), 371.0620 (20.5), 209.0294 (100), 191.0188 (18.6), 179.0338 (5.5), 161.0231 (2.0), 147.0285 (3.9), 135.0437 (8.0), 129.0179 (10.8), 111.0072 (2.1), 85.0279 (45.0)	6.44	1.133	2	
78.	tricaffeoylhexaric acid[b] 4	$C_{33}H_{28}O_{17}$	695.1254	695.1268 (19.2), 533.0936 (51.1), 371.0621 (24.2), 209.0295 (100), 191.0188 (17.8), 179.0339 (5.4), 173.0448 (2.5), 161.0230 (4.1), 147.0285 (4.4), 135.0437 (10.6), 129.0179 (7.7), 85.0279 (45.1)	6.53	2.011	2	
79.	hydroxybutanyl-trcaffeoylhexaric acid[b] 1	$C_{37}H_{34}O_{19}$	781.1622	781.1623 (34.0), 619.1307 (44.6), 457.0989 (38.4), 353.0515 (0.8), 295.0670 (52.9), 209.0291 (2.9), 191.0187 (78.8), 179.0338 (10.9), 173.0077 (5.3), 161.0232 (6.6), 147.0285 (16.4), 135.0437 (19.0), 129.0178 (17.4), 111.0073 (5.4), 85.0278 (100)	6.53	0.177	2	
80.	hydroxybutanyl-trcaffeoylhexaric acid[b] 2	$C_{37}H_{34}O_{19}$	781.1622	781.1634 (42.3), 619.1310 (54.7), 457.0990 (36.0), 353.0516 (0.6), 295.0670 (65.8), 209.0289 (0.8), 191.0187 (66.9), 179.0337 (9.7), 173.0079 (4.1), 161.0234 (7.3), 147.0286 (16.6), 135.0437 (19.1), 129.0179 (17.9), 111.0072 (6.4), 85.0279 (100)	6.66	1.585	2	
81.	isobutanyl-tricaffeoylhexaric acid[b]	$C_{37}H_{34}O_{18}$	765.1672	765.1686 (59.7), 603.1352 (50.7), 441.1042 (35.0), 279.0720 (92.3), 191.0188 (68.4), 179.0337 (13.7), 173.0078 (4.4), 161.0231 (8.1), 147.0288 (10.5), 135.0437 (25.3), 129.0179 (14.2), 111.0073 (6.5), 85.0278 (100)	8.54	1.755	2	

82.	2-methyllbutanyl/ isovaleryl-tricaffeoylhexaric acid[b]	$C_{38}H_{36}O_{18}$	779.1829	779.1841 (49.7), 617.1520 (41.8), 455.1198 (28.0), 293.0880 (76.2), 191.0187 (62.2), 179.0330 (15.1), 173.0079 (5.5), 161.0233 (6.7), 147.0286 (12.3), 135.0437 (27.8), 129.0179 (0.7), 111.0070 (7.1), 85.0278 (100)	9.21	1.531	2	
				Flavonoids				
83.	myricetin *O*-hexoside	$C_{21}H_{20}O_{13}$	479.0831	479.0832 (77.0), 359.0386 (0.4), 317.0301 (100), 287.0189 (2.0), 271.0252 (3.1), 243.0300 (1.9), 227.0343 (1.2), 215.0343 (0.4), 199.0387 (1.1), 178.9977 (2.0), 151.0025 (0.8)	4.55	0.159	2	[1, 2]
84.	myricetin *O*-acetylhexoside	$C_{23}H_{22}O_{14}$	521.0939 (	521.0939 (76.9), 461.0714 (0.2), 317.0301 (100), 287.0197 (2.2), 271.0249 (3.5), 243.0295 (2.2), 227.0341 (1.5),	5.19	0.483	2	[1]
85.	hyperoside[a]	$C_{21}H_{20}O_{12}$	463.0885	463.0884 (100), 301.0348 (44.3), 300.0275 (71.3), 271.0247 (37.4), 255.0296 (16.5), 243.0296 (8.6), 227.0340 (2.8), 178.9973 (2.6), 163.0024 (2.2), 151.0023 (6.0), 121.0275 (1.5), 107.0121 (1.8)	5.29	0.520	1	[1, 2]
86.	luteolin-7-*O*-glucoside[a,b]	$C_{21}H_{20}O_{11}$	447.0934	447.0934 (100), 285.0401 (39.5), 284.0326 (57.5), 255.0299 (0.8), 239.0346 (0.6), 227.0340 (3.2), 211.0392 (2.4)	5.31	0.213	1	
87.	patuletin *O*-hexoside[b]	$C_{22}H_{22}O_{13}$	493.0987	493.0992 (100), 331.0460 (78.6), 316.0222 (17.3), 287.0199 (20.4), 271.0246 (7.6), 259.0250 (4.0), 243.0303 (2.9), 215.0340 (2.3), 199.03962 (1.2), 181.0132 (4.5), 165.9895 (5.1), 139.0020 (2.3), 136.9866 (2.6), 121.0280 (3.7)	5.50	0.783	2	
88.	quercetin *O*-acetylhexoside[b] 1	$C_{23}H_{22}O_{13}$	505.0988	505.0991 (100), 463.0863 (1.1), 301.0345 (33.8), 300.0275 (79.9), 271.0247 (34.5), 255.0296 (15.0), 243.0295 (9.23), 227.0346 (2.5), 211.0396 (0.8), 199.0392 (0.5), 178.9968 (2.5), 163.0026 (1.7), 151.0024 (4.8), 135.0070 (0.5), 121.0270 (0.9), 107.0123 (1.8)	5.61	0.666	2	
89.	nepetin *O*-hexoside[b]	$C_{22}H_{22}O_{12}$	447.1038	477.1038 (100), 357.0618 (0.6), 315.0465 (26.0), 300.0271 (15.1), 299.0197 (18.6), 271.0251 (2.9), 255.0299 (1.4), 243.0296 (2.9), 227.0343 (2.8), 165.9898 (0.6), 163.0024 (1.8), 164.9816 (1.6), 136.9867 (1.3), 133.0280 (12.2)	5.68	-0.061	2	
90.	kaempferol 3-*O*-glucoside[a]	$C_{21}H_{20}O_{11}$	447.0934	447.0934 (100), 285.0396 (23.9), 284.0326 (55.8), 255.0296 (44.0), 227.0344 (42.4), 211.0397 (1.5), 178.9980 (0.4), 163.0022 (0.4), 151.0023 (2.2), 107.0120 (0.9)	5.88	0.258	1	[1, 2]

91.	isorhamnetin 3-*O*-glucoside[a]	$C_{22}H_{22}O_{12}$	477.1038	477.1038 (100), 357.0618 (1.9), 315.0496 (12.6), 314.0434 (54.8), 299.0197 (4.4), 271.0248 (20.3), 257.0456 (4.5), 243.0293 (23.6), 227.0340 (3.0), 215.0349 (3.2), 199.0391 (3.0), 151.0020 (2.6)	6.03	-0.124	1	[1, 2]
92.	quercetin *O*-acetylhexoside isomer[b] 2	$C_{23}H_{22}O_{13}$	505.0988	505.0983 (100), 301.0352 (97.8), 271.0247 (2.4), 255.0292 (1.9), 243.0298 (1.3), 227.0339 (1.6), 211.0392 (0.7), 161.0232 (4.8), 151.0023 (35.2), 121.0280 (8.2), 107.0123 (14.5)	6.06	-0.859	2	
93.	quercetin O-malonylhexoside	$C_{24}H_{22}O_{15}$	549.0886	549.0860 (0.7), 505.0995 (100), 463.0898 (0.5), 343.0456 (2.8), 313.0360 (2.3), 301.0354 (90.3), 271.0247 (1.2), 255.0295 (1.0), 243.0303 (0.5), 227.0342 (0.8), 178.9978 (1.9), 175.0023 (4.2), 151.0023 (32.2), 121.0280 (7.1), 107.0123 (13.3)	6.06	-4.722	2	[1]
94.	6-methoxykaempferol *O*-hexoside[b]	$C_{22}H_{22}O_{12}$	477.1038	477.1032 (100), 357.0626 (0.8), 314.0434 (39.7), 315.0508 (29.9), 299.0198 (19.6), 271.0247 (13.3), 255.0295 (1.6), 243.0295 (4.1), 227.0346 (2.5), 215.0343 (6.9), 199.0393 (1.5), 181.0132 (5.2), 165.9896 (14.2), 109.9993 (4.2)	6.25	-1.340	2	
95.	kaempferol *O*-acetylhexoside	$C_{23}H_{22}O_{12}$	489.1038	489.1040 (100), 285.0401 (73.9), 255.0296 (45.1), 227.0344 (29.6), 211.0392 (2.8), 199.0388 (0.6), 163.0025 (1.3), 151.0020 (1.6)135.0070 (1.5), 107.0122 (2.0)	6.28	0.308	2	[1]
96.	hispidulin *O*-hexoside[b]	$C_{22}H_{22}O_{11}$	461.1089	461.1093 (100), 299.0555 (8.1), 284.0313 (9.2), 283.0247 (43.5), 255.0297 (10.0), 211.0396 (1.5), 183.0441 (3.2), 163.0023 (10.1), 135.0073 (2.3), 117.0330 (7.5)	6.32	0.792	2	
97.	jaceosidine *O*-hexoside[b]	$C_{23}H_{24}O_{12}$	491.1195	491.1197 (100), 329.0664 (4.6), 314.0421 (8.6), 313.0355 (11.8), 298.0118 (11.8), 270.0167 (13.2), 257.0074 (0.9), 242.0217 (2.4), 214.0268 (1.6), 198.0312 (1.2), 165.9886 (0.4), 164.9817 (1.1), 163.0022 (2.1), 147.0437 (2.0), 136.9867 (2.0), 132.0200 (1.8)	6.50	1.875	2	
98.	quercetin *O*-coumaroylhexoside isomer	$C_{30}H_{26}O_{14}$	609.1250	609.1254 (100), 463.0888 (23.6), 301.0350 (42.5), 300.0276 (60.9), 271.0248 (36.9), 255.0297 (17.6), 243.0294 (9.1), 227.0344 (2.7), 211.0400 (0.7), 199.0392 (0.6), 178.9976 (2.7), 163.0023 (1.9), 151.0023 (7.9), 121.0280 (1.5), 107.0122 (2.9)	7.07	0.643	2	[1, 2]
99.	quercetin *O*-feruloylhexoside[b]	$C_{31}H_{28}O_{15}$	639.1355	639.1357 (100), 463.0883 (11.5), 301.0349 (29.9), 300.0276 (55.5), 271.0248 (34.5), 255.0298 (16.3), 243.0297 (9.2), 227.0342 (2.8), 211.0397 (0.9), 199.0398	7.20	0.308	2	

				(1.8), 161.0231 (9.6), 151.0024 (7.9), 135.0438 (7.9), 121.0283 (1.3), 107.0122 (2.8)				
100.	quercetin *O*-coumaroylhexoside 2	$C_{30}H_{26}O_{14}$	609.1250	609.1254 (100), 463.0885 (26.0), 301.0350 (51.3), 300.0275 (78.1), 283.0245 (0.3), 271.0248 (43.7), 255.0298 (19.1), 243.0295 (10.5), 227.0345 (2.6), 211.0392 (1.4), 199.0394 (0.5), 178.9975 (3.6), 163.0025 (2.2), 151.0023 (9.3), 121.0281 (1.9), 107.0123 (3.2)	7.30	0.643	2	[1, 2]
101.	luteolin[a,b]	$C_{15}H_{9}O_{7}$	285.0406	285.0402 (100), 267.0292 (0.2), 257.0443 (0.2), 241.0499 (0.8), 223.0388 (0.2), 217.0499 (0.9), 199.0394 (1.7), 175.0390 (2.8), 151.0024 (4.4), 133.0280 (21.6), 107.0123 (4.1)	7.58	-0.952	1	
102.	quercetin[a]	$C_{15}H_{10}O_{7}$	301.0354	301.0353 (100), 273.0406 (3.2), 257.0459 (1.1), 243.0297 (0.3), 229.6005 (0.7), 211.0389 (0.3), 178.9975 (21.6), 151.0023 (47.4), 175.0391 (0.3), 121.0280 (12.3), 107.0123 (12.9)	7.62	-0.252	1	[2]
103.	kaempferol *O*-coumaroylhexoside 1	$C_{30}H_{26}O_{13}$	593.1301	593.1307 (100), 447.0934 (2.7), 285.0401 (75.2), 255.0297 (42.7), 227.0343 (28.3), 211.0391 (2.5), 163.0388 (1.3), 151.0024 (3.2), 107.0121 (2.5)	7.69	1.039	2	[1, 2]
104.	patuletin[b]	$C_{16}H_{12}O_{8}$	331.0464	331.0458 (100), 316.0223 (62.3), 287.0198 (12.6), 271.0245 (7.0), 259.0246 (3.7), 243.0303 (1.2), 242.0211 (1.2), 181.0129 (5.2), 165.9895 (18.3), 139.0023 (9.5), 136.9858 (0.6), 121.0280 (1.2), 109.9994 (11.5)	7.72	-0.304	2	
105.	herbacetin methyl ether	$C_{16}H_{12}O_{7}$	315.0510	315.0512 (82.8), 300.0276 (100), 271.0251 (0.4), 255.0295 (1.7), 243.0290 (2.0), 227.0346 (2.3)	7.76	0.679	2	[1]
106.	nepetin[b]	$C_{16}H_{12}O_{7}$	315.0510	315.0512 (82.8), 300.0276 (100), 271.0251 (1.2), 255.0295 (1.7), 243.0290 (2.0), 227.0346 (2.3), 201.0184 (3.7), 165.9897 (1.2), 136.9866 (9.7), 109.9904 (1.2)	7.76	0.679	2	
107.	isorhamnetin *O*-*p*-coumaroylhexoside isomer[b] 1	$C_{31}H_{28}O_{14}$	623.1406	623.1412 (100), 477.1039 (1.4), 315.0511 (69.2), 299.0197 (15.7), 300.0271 (10.4), 271.0248 (24.4), 255.0298 (8.9), 243.0295 (14.4), 227.0345 (4.0), 199.0395 (3.6), 151.0023 (5.0), 145.0281 (10.0), 107.0125 (1.3)	7.88	0.981	2	
108.	kaempferol *O*-coumaroylhexoside isomer 2	$C_{30}H_{26}O_{13}$	593.1301	593.1307 (100), 447.0934 (1.7), 285.0403 (69.5), 255.0296 (34.2), 227.0343 (25.2), 211.0394 (2.2), 161.0232 (2.0), 151.0021 (2.6), 135.0430 (0.7), 107.0122 (2.3)	7.95	1.072	2	[1, 2]
109.	kaempferol *O*-caffeoylhexoside[b]	$C_{30}H_{26}O_{14}$	609.1250	609.1252 (100), 429.0809 (0.5), 447.0910 (0.8), 285.0404 (59.1), 255.0295 (10.2), 227.0344 (9.7), 179.0339 (24.8), 161.0232 (48.9), 135.0437 (28.8), 151.0023 (3.2), 107.0123 (1.6)	7.99	0.364	2	

110.	isorhamnetin *O*-*p*-coumaroylhexoside isomer[b] 2	$C_{31}H_{28}O_{14}$	623.1406	623.1414 (100), 477.1046 (1.5), 315.0510 (74.0), 299.0197 (17.7), 300.0273 (15.6), 271.0248 (30.1), 255.0298 (10.5), 243.0290 (17.4), 227.0345 (4.6), 199.0393 (5.2), 163.0388 (2.6), 151.0023 (5.3), 145.0281 (11.7), 107.0122 (1.6)	8.08	1.174	2	
111.	isorhamnetin *O*-caffeoylhexoside[b]	$C_{31}H_{28}O_{15}$	639.1355	639.1359 (100), 477.1042 (2.0), 315.0512 (68.3), 301.0312 (0.9), 300.0280 (13.4), 271.0247 (17.4), 255.0290 (5.7), 243.0295 (7.9), 227.0347 (1.6), 199.0386 (0.8), 179.0339 (25.8), 161.0232 (70.4), 135.0437 (36.3), 107.0121 (0.9)	8.12	0.496	2	
112.	axillarin[b] (quercetagetin 3,6-dimethylether)	$C_{17}H_{14}O_8$	345.0616	345.0616 (100), 330.0382 (81.6), 315.0148 (69.7), 287.0200 (11.6), 259.0252 (3.6), 243.0298 (3.5), 231.0297 (5.3), 215.0348 (4.2), 175.0026 (3.4), 165.9892 (6.1), 149.0230 (11.2), 139.0387 (5.4), 136.9865 (0.7), 109.9994 (4.8)	8.19	0.027	2	
113.	hispidulin[b]	$C_{16}H_{12}O_6$	299.0561	299.0558 (62.0), 284.0324 (100), 256.0374 (0.8), 255.0310 (16), 227.0346 (13.1), 212.0471 (2.5), 165.9896 (0.9), 136.9866 (13.2)	8.84	0.430	2	
114.	kaempferol[a]	$C_{15}H_9O_7$	285.0406	285.0403 (100), 257.0458 (0.8), 239.0346 (1.3), 229.0446 (0.8), 211.0396 (1.0), 151.0027 (1.5), 117.0329 (1.0), 107.0127 (1.2)	8.84	-0.531	1	[2]
115.	naringenin	$C_{15}H_{12}O_5$	271.0612	271.0611 (100), 253.0504 (6.8), 243.0656 (0.7), 225.0558 (1.8), 215.0708 (1.0), 197.0600 (5.0), 151.0022 (3.4), 119.0490 (0.3), 107.0122 (2.8)	8.86	0.468	1	[1]
116.	isorhamnetin[a]	$C_{16}H_{12}O_7$	315.0510	315.0510 (100), 300.0275 (45.7), 271.0246 (2.9), 255.0293 (1.5), 243.0296 (1.5), 227.0356 (1.2), 215.0344 (0.7), 164.0103 (3.1), 151.0024 (9.7), 107.0123 (7.7)	9.12	0.013	1	[1, 2]
117.	jaceosidin[b] (6-hydroxyluteolin-6,3'-dimethyl ether)[a,b]	$C_{17}H_{14}O_7$	329.0677	329.0668 (83.8), 314.0434 (97.2), 299.0197 (100), 271.0247 (22.1), 255.0287 (0.8), 243.0295 (6.4), 227.0345 (4.0), 215.0341 (17.8), 199.0394 (4.8), 187.0387 (0.6), 165.9895 (16.2), 164.9815 (6.3), 136.9862 (2.0), 133.0278 (9.1)	9.40	0.286	1	
118.	gnaphaliin 1	$C_{17}H_{14}O_6$	313.0718	313.0719 (94.4), 298.0482 (100), 283.0248 (95.5), 255.0296 (52.8), 239.0345 (1.5), 227.0341 (6.3), 211.0391 (3.5), 199.0392 (18.0), 183.0441 (13.1), 167.0488 (7.6), 155.0487 (6.8), 139.0538 (6.9), 127.0539 (2.2), 109.0644 (3.1)	9.52	0.443	2	[1, 2]
119.	quercetagetin-3,6,3'(4')-trimethyl ether[b] 1	$C_{18}H_{16}O_8$	359.0772	359.0774 (100), 344.0538 (59.7), 329.0302 (80.3), 314.0070 (2.6), 301.0354 (7.6), 286.0120 (20.3), 258.0168 (15.4), 230.0213 (8.2), 202.0263 (9.0),	9.66	0.444	2	

120.	quercetin 7,3'(4')-dimethyl ether[b]	$C_{17}H_{13}O_7$	329.0667	165.9895 (2.2), 163.0380 (2.1), 136.9870 (0.5), 118.0155 (1.1), 109.9997 (2.2) 329.0667 (100), 314.0432 (81.6), 299.0196 (88.2), 271.0247 (33.5), 255.0292 (0.8), 243.0295 (12.5), 227.0340 (3.0), 215.0340 (4.9), 199.0393 (13.9), 171.0439 (143.0489 (3.1), 155.0486 (6.5)	9.71	0.073	2	
121.	kaempferid/isokampferid	$C_{16}H_{12}O_6$	299.0561	299.0561 (100), 284.0327 (77.7), 255.0296 (55.5), 239.0346 (43.4), 227.0344 (26.1), 211.0394 (14.5), 199.0388 (0.5), 109.9995 (0.3)	9.99	-0.561	2	[1]
122.	quercetagetin-3,6,3'(4')-trimethyl ether[b] 2	$C_{18}H_{16}O_8$	359.0772	359.0772 (100), 344.0535 (30.5), 329.0302 (48.1), 314.0082 (2.4), 301.0359 (3.1), 286.0120 (8.6), 258.0175 (1.5), 230.0215 (3.7), 194.9925 (25.2), 179.9690 (18.7)	11.18	-0.002	2	
123.	pinocembrin	$C_{15}H_{12}O_4$	255.0663	255.0659 (100), 227.0703 (0.3), 211.0758 (1.8), 183.0808 (0.3), 151.0024 (5.4), 107.0123 (5.9)	11.63	-1.302	2	[1, 2]
124.	galangin	$C_{15}H_{10}O_5$	269.0457	269.0453 (100), 239.0347 (0.6), 227.0348 (0.7), 223.0402 (1.0), 213.0552 (1.5), 195.0446 (1.1), 185.0592 (0.5), 169.0647 (1.9), 143.0489 (1.3), 107.0121 (0.2), 101.0379 (0.2)	11.74	-0.954	2	[2]
125.	gnaphaliin 2	$C_{17}H_{14}O_6$	313.0718	313.0718 (100), 298.0481 (88.6), 283.0246 (74.6), 255.0296 (0.4), 239.0343 (0.5), 227.0343 (4.4), 211.0387 (2.8), 199.0392 (12.6), 183.0441 (7.9), 167.0492 (5.2), 155.0486 (4.7), 139.0538 (4.7), 127.0538 (2.4), 117.0328 (0.3)	12.19	0.123	2	[1, 2]
126.	galangin methyl ether	$C_{16}H_{12}O_5$	283.0612	283.0611 (100), 268.0376 (77.3), 239.0346 (54.3), 211.0393 (76.2), 195.0439 (2.0), 167.0485 (2.3)	12.27	-0.342	2	[1]

Pyrones (phloroglucinol alpha-pyrones)

№	Subclass (tentatively identified compound)	Molecular formula	Exact mass $[M-H]^-$	Fragmentation pattern in (-) ESI-MS/MS	t_R (min)	Δ ppm	Level of confidence	References
127.	ethylpyrones A[b,c]	$C_{22}H_{26}O_8$	417.1555	417.1557 (42.8), 263.0929 (3.2), 251.0922 (100), 233.0815 (1.4), 205.0496 (0.4), 193.0496 (18.1), 179.0339 (3.1), 153.0544 (73.5), 109.0643 (49.0)	13.15	0.429	3	
128.	ethylpyrones[b,c]	$C_{22}H_{26}O_9$	433.1504	433.1502 (66.6), 378.0953 (4.1), 346.1021 (0.7), 279.0871 (33.1), 267.0872 (100), 261.0765 (1.9), 249.0764 (2.8), 235.0970 (32.1), 223.0969 (49.7), 193.0496 (0.4), 179.0338 (0.4), 179.1065 (17.6), 151.0387 (9.5), 125.0592 (11.0), 109.0643 (4.7)	13.46	-0.475	3	
129.	ethylpyrones[b,c]	$C_{24}H_{28}O_8$	443.1711	443.1710 (100), 289.1081 (81.5), 277.1079 (74.3), 271.0970 (1.6), 259.0973 (19.0), 247.0974 (2.3),	14.15	-0.341	3	

				235.0974 (2.4), 191.0341 (1.7), 179.0336 (6.4), 167.0337 (18.4), 153.0544 (7.5), 123.0435 (7.6), 109.0643 (11.5)				
130.	isopropylpyrones[b,c]	$C_{23}H_{28}O_9$	447.1661	447.1660 (76.3), 279.00872 (28.8), 267.0872 (100), 253.0715 (8.8), 235.0970 (33.6), 223.0970 (56.7), 209.0807 (4.0), 179.1066 (17.3), 167.0703 (2.0), 151.0386 (10.5), 125.0594 (11.0), 97.0278 (3.4)	14.52	-0.147	3	
131.	methylpyrones (arenol)	$C_{21}H_{24}O_7$	387.1449	387.1450 (64.2), 247.0972 (85.5), 235.0970 (100), 205.0860 (6.3), 191.1068 (11.3), 187.0753 (0.7), 166.0262 (4.6), 161.0959 (2.9), 133.0643 (0.8), 123.0435 (2.7), 109.0640 (5.1), 95.0486 (16.1)	14.65	0.087	2	[3]
132.	ethylpyrones[b,c]	$C_{27}H_{34}O_8$	485.2181	485.2183 (100), 331.1552 (57.5), 319.1550 (72.4), 289.1454 (0.4), 277.1455 (1.5), 258.1167 (0.3), 191.0340 (6.2), 179.0340 (10.4), 166.0261 (3.9), 153.0544 (8.7), 137.0229 (3.6), 109.0641 (11.3)	14.89	0.472	3	
133.	unknown[b,c]	$C_{20}H_{26}O_6$	361.1657	361.1660 (95.7), 317.1757 (100), 273.1859 (8.2), 205.0500 (6.2), 193.0497 (22.3), 165.0542 (0.5), 163.0382 (3.9), 151.0388 (6.2), 123.0431 (1.7), 107.0484 (0.9)	15.07	0.937	3	
134.	ethylpyrones [b,c]	$C_{23}H_{28}O_9$	447.1661	447.1659 (100), 293.1031 (61.8), 281.1029 (55.9), 261.0767 (23.3), 249.0765 (49.7), 233.0814 (23.5), 221.0812 (35.1), 153.0544 (7.7), 137.0230 (7.8), 109.0643 (8.0)	15.23	-0.370	3	
135.	ethylpyrones (arzanol)	$C_{22}H_{26}O_7$	401.1606	401.1605 (75.7), 247.0972 (82.9), 235.0970 (100), 219.1019 (0.8), 205.0857 (5.5), 191.1067 (13.4), 187.0760 (0.6), 166.0257 (6.6), 153.0543 (15.1), 123.0436 (1.2), 109.0641 (18.1)	15.76	-0.140	2	[3]
136.	ethylpyrones [b,c]	$C_{27}H_{34}O_8$	485.2181	485.2181 (100), 331.1552 (75.7), 319.1550 (97.9), 277.1438 (3.0), 205.0498 (11.6), 191.0334 (3.2), 179.0335 (2.1), 166.0260 (7.5), 153.0543 (8.8), 123.0437 (4.3), 109.0643 (10.2)	15.81	0.101	3	
137.	ethylpyrones [b,c]	$C_{24}H_{30}O_9$	461.1817	461.1796 (11.4), 307.1194 (13.6), 295.1187 (100), 251.1286 (3.6), 207.0656 (3.4), 153.0544 (32.4), 109.0643 (45.5)	16.30	0.012	3	
138.	ethylpyrones B[b,c]	$C_{25}H_{32}O_8$	459.2024	459.2023 (63.4), 305.1397 (6.7), 293.1394 (100), 279.1239 (4.2), 247.0981 (2.6), 235.0971 (14.0), 221.0806 (2.9), 191.1066 (4.9), 153.0544 (68.2), 109.0643 (55.5)	17.01	-0.307	3	
139.	isopropylpyrones[b,C]	$C_{23}H_{28}O_7$	415.1751	415.1762 (76.3), 247.0972 (78.9), 235.0970 (100), 205.0869 (4.1), 191.1068 (8.9), 167.0701 (12.5), 123.0800 (16.7), 109.0643 (1.0)	17.05	0.033	3	

140.	ethylpyrones[b,c]	$C_{22}H_{26}O_8$	417.1555	417.1554 (87.9), 263.0923 (76.6), 251.0922 (100), 233.0814 (12.9), 217.0517 (0.4), 209.0815 (1.4), 193.0490 (4.2), 164.0466 (12.3), 179.0341 (3.8), 153.0542 (4.8), 109.0644 (6.6)	17.11	-0.146	3	
141.	ethylpyrones[b,c]	$C_{23}H_{28}O_7$	415.1751	415.1763 (91.5), 261.1131 (78.0), 249.1129 (100), 243.1026 (0.4), 233.1191 (0.4), 217.1221 (0.6), 205.1225 (10.0), 193.0859 (4.8), 180.0418 (3.3), 153.0545 (12.4), 109.0643 (16.4)	17.81	0.177(	3	
142.	ethylpyrone[b,c]	$C_{24}H_{28}O_8$	443.1711.	443.1709 (64.4), 289.1081 (21.4), 277.1079 (64.0), 235.0967 (1.8), 205.0862 (46.3), 193.0860 (100), 153.0543 (7.5), 109.0643 (14.4)	17.89	-0.476	2	
143.	1-methyl-propylpyrones[b,c]	$C_{24}H_{30}O_7$	429.1919	429.1917 (83.2), 247.0972 (77.5), 235.0970 (98.8), 205.0863 (4.9), 191.1069 (12.5), 181.0857 (13.4), 137.0958 (15.7), 150.0314 (3.2), 109.0642 (1.7)	18.55	-0.458	3	
144.	isopropylpyrone[b,c]	$C_{23}H_{28}O_8$	431.1711	431.1769 (95.2), 263.0923 (70.3), 251.0922 (100), 233.0815 (16.4), 209.0800 (1.2), 193.0496 (5.1), 179.0336 (4.8), 167.0701 (5.7), 164.0467 (16.4), 123.0800 (2.1), 109.0646 (0.4)	19.06	-0.489	3	
145.	unknown[b,c]	$C_{23}H_{32}O_6$	403.2126	403.2127 (100), 385.2027 (0.6), 359.2229 (62.3), 315.2324 (5.8), 247.0974 (2.3), 235.0972 (11.8), 217.0857 (1.6), 207.1016 (0.6), 191.0338 (1.5), 151.0388 (4.0), 125.0594 (6.4)	19.22	0.128	3	
146.	ethylpyrones[b] (6-*O*-desmethyl-auricepyrone)	$C_{24}H_{30}O_7$	429.1919	429.1917 (91.5), 275.1288 (82.2), 263.1286 (100), 257.1179 (0.9), 245.1179 (0.8), 229.1234 (0.8), 219.1383 (11.0), 193.0863 (3.5), 153.0543 (14.5), 109.0643 (24.2)	19.57	-0.458	2	[4, 5]
147.	ethylpyrones[b,c]	$C_{23}H_{28}O_8$	431.1711	431.1707 (100), 277.1079 (70.3), 265.1079 (90.6), 247.0973 (13.5), 221.1177 (0.7), 207.0647 (4.5), 193.0496 (4.2), 178.0624 (11.7), 153.0542 (6.9), 109.0642 (10.7),	19.86	-0.976	3	
148.	methylpyrones[b]	$C_{26}H_{32}O_7$	455.2075	455.2078 (100), 315.1602 (73.8), 303.1601 (88.1), 273.1501 (1.3), 259.1696 (4.3), 246.0892 (1.5), 231.0652 (3.1), 218.0939 (0.8), 179.0339 (12.2), 139.0386 (12.2)	20.19	0.513	3	[1, 6, 7]
149.	1-methyl-propylpyrones (heliarzanol/isobar)	$C_{24}H_{30}O_8$	445.1868	445.1865 (97.8), 263.0922 (67.0), 251.0922 (100), 245.0827 (0.5), 233.0813 (14.9), 209.0819 (1.0), 193.0494 (4.6), 181.0861 (6.0), 137.0958 (8.8), 109.0642 (1.5)	20.39	-0.744	3	
150.	1-methyl-propylpyrones[b,c]	$C_{24}H_{28}O_7$	427.1762	427.1737 (19.5), 245.0809 (0.8), 233.0814 (100), 189.0909 (7.5), 181.0859 (59.0), 137.0957 (43.2), 109.0648 (0.4)	20.42	-5.914	3	

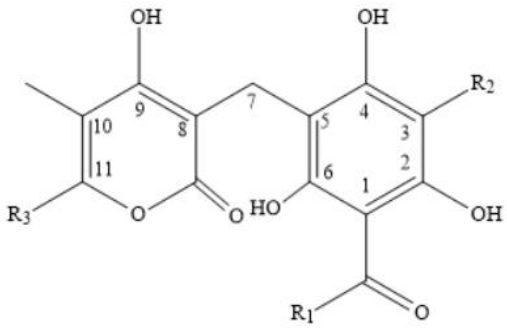
151.	ethylpyrones[b] (23-methyl-6-*O*-desmethylauricepyrone)	$C_{25}H_{32}O_7$	443.2075.	443.2075 (64.4), 289.1445 (78.4), 277.1442 (100), 233.1544 (8.6), 219.0656 (3.8), 205.0496 (4.6), 193.0860 (3.2), 153.0543 (14.0), 109.0643 (16.3	20.73	-0.060	3	[5, 8]
152.	ethylpyrones (heliarzanol/isobar)	$C_{24}H_{30}O_8$	445.1868	445.1867 (100), 291.1237 (61.3), 279.1235 (84.8), 273.1115 (0.6), 261.1133 (11.0), 221.0808 (6.0), 165.0907 (4.7), 153.0546 (5.3), 109.0642 (19.4)	21.00	-0.182	2	[1, 6]
153.	ethylpyrones[b]	$C_{27}H_{34}O_7$	469.2232	469.2232 (100), 315.1600 (49.9), 303.1601 (60.2), 273.1493 (1.0), 259.1696 (3.4), 245.0810 (1.0), 231.0660 (1.9), 191.0338 (5.8), 179.0340 (10.8), 166.0260 (12.6), 153.0546 (7.0), 109.0643 (8.7)	21.23	0.050	2	[7]
154.	ethylpyrones B[b,c]	$C_{25}H_{32}O_8$	459.2024	459.2026 (100), 305.1395 (58.8), 293.1395 (80.5), 275.1289 (9.7), 235.0976 (3.1), 219.0654 (13.9), 191.0704 (0.8), 179.1066 (3.9), 153.0542 (4.5), 109.0642 (8.8)	21.67	0.368	3	
155.	ethylpyrones[b,c]	$C_{27}H_{34}O_8$	485.2181	485.2181 (100), 331.1551 (50.4), 319.1549 (66.3), 301.1446 (6.1), 289.1440 (0.5), 277.1442 (1.3), 219.0649 (0.8), 193.0499 (2.8), 179.0338 (4.7), 153.0541 (4.5), 137.0593 (3.3), 109.0693 (3.7)	21.97	-0.023	3	
156.	Ethylpyrones C [b,c]	$C_{24}H_{28}O_7$	427.1762	427.1763 (22.3), 273.1131 (3.9), 261.1129 (100), 243.1017 (0.4), 217.1223 (4.0), 199.1114 (0.5), 191.0701 (1.6), 153.0543 (46.5), 109.0643 (43.1)	22.13	0.102	2	
157.	isopropylpyrones[b]	$C_{28}H_{36}O_7$	483.2388	483.2388 (89.2), 315.1600 (78.8), 303.1601 (100), 273.1496 (1.8), 259.1699 (4.5), 191.0341 (9.1), 179.0338 (16.9), 167.0701 (3.7), 166.0259 (5.1), 123.0801 (17.0)	22.41	-0.055	3	[8]
158.	Ethylpyrones C [b,c]	$C_{24}H_{28}O_7$	427.1762	427.1762 (40.7), 273.1133 (15.0), 261.1129 (100), 217.1226 (2.6), 191.0702 (18.9), 153.0543 (18.9), 109.0642 (15.9)	23.01	-0.038	2	
				Other compounds				
159.	gnaphaliol *O*-hexoside	$C_{19}H_{24}O_9$	395.1348	395.1323 (8.8), 377.1234 (0.3), 233.0814 (100), 189.0912 (8.1), 173.0595 (1.2), 147.0800 (4.0), 83.0121 (5.5)	8.14	-6.316	2	[1]
160.	micropyrone	$C_{14}H_{20}O_4$	251.1289	251.1286 (48.7), 207.0382 (100), 179.1064 (1.8), 151.1115 (30.0), 113.0956 (90.1), 85.0642 (28.4)	9.12	-1.045	*2*	[6]
161.	italipyrone 1	$C_{22}H_{24}O_7$	399.1449	399.1444 (11.8), 233.0814 (100), 189.0911 (7.1), 173.0594 (0.8), 153.0543 (61.3), 109.0643 (36.9)	17.33	-1.369	2	[1]
162.	Italipyrone 2	$C_{22}H_{24}O_7$	399.1449	399.1440 (14.7), 233.0813 (100), 189.0913 (4.7), 173.0597 (1.1), 153.0543 (49.2), 109.0643 (35.5)	20.39	-2.231	2	[1]
№	**Identified/tentatively annotated compound**	**Molecular formula**	**Exact mass**	**Fragmentation pattern in (+) ESI-MS/MS**	**t_R (min)**	**Δ ppm**	**Level of confidence**	**References**

			[M+H]$^+$					
163.	6-hydroxytremeton	$C_{13}H_{14}O_3$	219.1013	219.1013 (65.9), 201.0911 (14.8), 183.0804 (100), 165.0700 (17.6), 159.0804 (79.7), 157.646 (23.2), 144.0569 (27.6), 141.0697 (12.2), 131.0855 (9.2), 129.0702 (4.3), 115.0546 (7.2), 107.0494 (5.8), 91.0548 (12.7), 57.0343 (3.4)	7.21	-1.373	3	[9]
164.	2-isobutyryl-6-acetylprenylphloroglucinol	$C_{17}H_{22}O_6$	323.1481	323.1481 (22.5), 305.1378 (53.1), 287.1254 (0.5), 277.1429 (62.1), 267.0858 (24.9), 249.0754 (100), 221.0805 (34.7), 203.0701 (66.6), 185.0600 (3.5), 175.0750 (13.6), 161.0595 (10.4), 147.0807 (4.8), 135.0805 (8.6), 109.0284 (1.9), 91.0546 (1.5), 79.0547 (0.5)	13.16	-2.522	3	[10]
165.	2-isobutyryl-4-prenylphloroglucinol	$C_{15}H_{20}O_4$	265.1431	265.1431 (34.3), 209.0807 (100), 191.0701 (32.7), 173.0598 (2.91), 163.0752 (15.8), 149.0597 (4.6), 135.0803 (3.7), 121.0649 (9.2), 113.0600 (2.2), 107.0859 (1.6), 93.0704 (1.3), 79.0548 (1.3)	17.68	-1.379	3	[10]
166.	2-metylvaleryl-4-prenylphloroglucinol	$C_{17}H_{24}O_4$	293.1741	293.1741 (9.8), 237.1118 (100), 219.1013 (28.0), 201.0910 (1.8), 191.1066 (3.6), 177.0909 (0.4), 163.0752 (2.4), 143.0853 (1.0), 131.0856 (1.6), 121.0650 (0.9), 107.0859 (0.7), 93.0705 (1.2), 91.0545 (1.8), 79.0551 (0.2)	18.28	-2.066	3	[10]

[a] identified by comparison with an authentic standard; [b] reported for the first time in *H. italicum*; [c]-undescribed in the literature; A, B, C compounds labeled with the same capital letters share the same fragmentation patterns; Level of confidence: 1-compound identified by comparison to reference standard; 2-putatively annotated compound; 3- putatively characterized compound classes.

Table S2. Tentative structures of prenylated phloroglucinol α-pyrones (for numbers and fragmentation patterns, see Table S1).

alpha-pyrone phloroglucinol



N	R_1	R_2	R3	$[M-H]^-$ Exact mass
		Methylpyrones (MP)		
131	CH_3	Prenyl(C_5H_9)	CH_3	387.1449
148	CH_3	Geranyl ($C_{10}H_{17}$)	CH_3	455.2075
		Ethylpyrones (EP)		
135	CH_3	Prenyl	$-CH_2-CH_3$	401.1606
141	$-CH_2-CH_3$	Prenyl	$-CH_2-CH_3$	415.1751
146	$-CH(CH_3)_2$	Prenyl	$-CH_2-CH_3$	429.1919
151	$CH(CH_3)-CH_2-CH_3$	Prenyl	$-CH_2-CH_3$	443.2075
127	CH_3	Hydroxyprenyl	$-CH_2-CH_3$	417.1555
140	CH_3	Hydroxyprenyl	$-CH_2-CH_3$	417.1555
147	$-CH_2-CH_3$	Hydroxyprenyl	$-CH_2-CH_3$	431.1711
152	$-CH(CH_3)_2$	Hydroxyprenyl	$-CH_2-CH_3$	445.1868
138	$-CH(CH_3)-CH_2-CH_3$	Hydroxyprenyl	$-CH_2-CH_3$	459.2024
154	$-CH(CH_3)-CH_2-CH_3$	Hydroxyprenyl	$-CH_2-CH_3$	459.2024
153	CH_3	Geranyl	$-CH_2-CH_3$	469.2232
132	CH_3	Hydroxygeranyl	$-CH_2-CH_3$	485.2181
136	CH_3	Hydroxygeranyl	$-CH_2-CH_3$	485.2181
155	CH_3	Hydroxygeranyl	$-CH_2-CH_3$	485.2181
128	CH_3	Dihydroxyprenyl	$-CH_2-CH_3$	433.1504
134	$-CH_2-CH_3$	Dihydroxyprenyl	$-CH_2-CH_3$	447.1661
156	$-CH(CH_3)_2$	$-C_5H_7$	$-CH_2-CH_3$	427.1762
158	$-CH(CH_3)_2$	$-C_5H_7$	$-CH_2-CH_3$	427.1762
142	$-C_3H_5OH$	Prenyl	$-CH_2-CH_3$	443.1711
		Isopropylpyrones(IPP)		
139	CH_3	Prenyl	$-CH(CH_3)_2$	415.1751
157	CH_3	Geranyl	$-CH(CH_3)_2$	483.2388
144	CH_3	Hydroxyprenyl	$-CH(CH_3)_2$	431.1711

130	CH_3	Dihydroxyprenyl	$-CH(CH_3)_2$	447.1661
1-Methyl-propylpyrones (MPP)				
150	CH_3	C_5H_7	$-CH(CH_3)-CH_2-CH_3$	427.1762
149	CH_3	Hydroxyprenyl	$-CH(CH_3)-CH_2-CH_3$	445.1868
143	CH_3	Prenyl	$-CH(CH_3)-CH_2-CH_3$	429.1919

References

1. Kramberger, K.; Barlič-Maganja, D.; Bandelj, D.; Baruca Arbeiter, A.; Peeters, K.; Miklavčič Višnjevec, A.; Jenko Pražnikar, Z., HPLC-DAD-ESI-QTOF-MS determination of bioactive compounds and antioxidant activity comparison of the hydroalcoholic and water extracts from two Helichrysum italicum species. *Metabolites* **2020,** 10, (10), 403.
2. Pereira, C. G.; Barreira, L.; Bijttebier, S.; Pieters, L.; Neves, V.; Rodrigues, M. J.; Rivas, R.; Varela, J.; Custodio, L., Chemical profiling of infusions and decoctions of Helichrysum italicum subsp. picardii by UHPLC-PDA-MS and in vitro biological activities comparatively with green tea (Camellia sinensis) and rooibos tisane (Aspalathus linearis). *Journal of Pharmaceutical and biomedical analysis* **2017,** 145, 593-603.
3. Appendino, G.; Ottino, M.; Marquez, N.; Bianchi, F.; Giana, A.; Ballero, M.; Sterner, O.; Fiebich, B. L.; Munoz, E., Arzanol, an anti-inflammatory and anti-HIV-1 phloroglucinol α-pyrone from Helichrysum italicum ssp. microphyllum. *Journal of natural products* **2007,** 70, (4), 608-612.
4. Akaberi, M.; Sahebkar, A.; Azizi, N.; Emami, S. A., Everlasting flowers: Phytochemistry and pharmacology of the genus Helichrysum. *Industrial Crops and Products* **2019,** 138, 111471.
5. Jakupovic, J.; Kuhnke, J.; Schuster, A.; Metwally, M.; Bohlmann, F., Phloroglucinol derivatives and other constituents from South African Helichrysum species. *Phytochemistry* **1986,** 25, (5), 1133-1142.
6. Taglialatela-Scafati, O.; Pollastro, F.; Chianese, G.; Minassi, A.; Gibbons, S.; Arunotayanun, W.; Mabebie, B.; Ballero, M.; Appendino, G., Antimicrobial phenolics and unusual glycerides from Helichrysum italicum subsp. microphyllum. *Journal of natural products* **2013,** 76, (3), 346-353.
7. Tomás-Lorente, F.; Iniesta-Sanmartín, E.; Tomás-Barberán, F. A.; Trowitzsch-Kienast, W.; Wray, V., Antifungal phloroglucinol derivatives and lipophilic flavonoids from Helichrysum decumbens. *Phytochemistry* **1989,** 28, (6), 1613-1615.
8. Akaberi, M.; Danton, O.; Tayarani-Najaran, Z.; Asili, J.; Iranshahi, M.; Emami, S. A.; Hamburger, M., HPLC-based activity profiling for antiprotozoal compounds in the endemic Iranian medicinal plant Helichrysum oocephalum. *Journal of natural products* **2019,** 82, (4), 958-969.
9. Bohlmann, F.; Hoffmann, E., Cannabigerol-ähnliche verbindungen aus Helichrysum umbraculigerum. *Phytochemistry* **1979,** 18, (8), 1371-1374.

10. Lourens, A.; Viljoen, A. M.; Van Heerden, F., South African Helichrysum species: a review of the traditional uses, biological activity and phytochemistry. *Journal of Ethnopharmacology* **2008,** 119, (3), 630-652.