Supporting Information

A hexa-herbal TCM decoction used to treat skin inflammation: An LC-MS-based phytochemical analysis

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Table S1 Ions present in the HHCF and more than one composing botanical drugs.

(Only ions with abundance > 1.5% of the ion which was present in the greatest amount were listed.)

R_t (min)	Ionization mode	Measured (m/z)	Source	Proposed identity
2.00	Positive	110	DIC, RHE, SCU, KOC	NA
2.34	Negative	195	RHE, SOP, SCU, PHE	Gluconic acid/Galactonic acid
2.58	Positive	136	DIC, RHE, SOP, SCU, KOC	Adenine
2.58	Positive	130	DIC, RHE, SOP, SCU, KOC	Pyroglutamic acid
2.77	Negative	133	RHE, SOP, SCU, PHE	Malic acid
2.77	Negative	115	RHE, SOP, SCU, PHE	Fumaric acid
3.25	Negative	191	RHE, SOP, SCU, PHE	Citric acid/Isocitric acid
3.25	Negative	111	RHE, SOP, SCU, PHE	Fragment from citric acid/isocitric acid
3.36	Positive	137	SCU, PHE, KOC	Hypoxanthine/4-Hydroxyacetophenone
3.36	Positive	154	RHE, SCU, KOC	Dopamine
3.75	Positive	132	DIC, RHE, SOP, SCU, PHE, KOC	Hydroxyproline/Isoleucine /Leucine/Norleucine
16.48	Negative	113	RHE, SOP, SCU, PHE	NA
17.01	Negative	113	RHE, SOP, SCU, PHE	NA
19.46	Negative	113	RHE, SCU, PHE	NA
26.65	Negative	113	RHE, SOP, SCU, PHE	NA
52.60	Negative	113	RHE, SOP, SCU, PHE	NA
88.26	Negative	113	RHE, SCU, PHE	NA
88.26	Negative	103	SCU, PHE	NA

Table S2 Putatively identified compounds in the HHCF by LC-MS/MS in positive ionization mode.

R_t (min)	No.	*m/z*	Adduct ion(s)	MS/MS fragment ions (*m/z*)	Source	Identity	Reported MS/MS fragments (CE=collision energy)
3.36	**P1**	191	$[M+H]^+$	191 (100%), 148 (25.73%), 162 (0.26%)	SOP	Cytisine	$MS^{n=2-4}$ [191] (CE: 50%): 148(100) [1]
3.36	**P2**	196	$[M+NH_4]^+$	196 (100%), 119 (67.72%), 137 (57.19%), 109 (2.33%), 151 (2.14%), 178 (0.83%), 114 (0.63%), 153 (0.41%), 107 (0.3%), 110 (0.29%)	PHE	Aesculetin	NA
	P3	205	$[M+H]^+$	205 (100%), 108 (1.79%), 110 (1.6%), 146 (1.57%), 162 (0.82%), 157 (0.67%), 990 (0.63%), 164 (0.48%), 160 (0.42%), 147 (0.28%), 204 (0.26%), 134 (0.25%), 144 (0.21%), 133 (0.18%), 161 (0.15%), 122 (0.13%), 148 (0.13%), 176 (0.13%)	SOP	N-Methylcytisine	MS^2 [205](CE: 10-30eV): 205, 162, 146, 108, 58 [2] $MS^{n=2-4}$ [205](CE: 50%): 146(91), 108(100) [1]
	P4	215	$[M+2Na-H]^+$	215 (100%), 169 (54.49%), 142 (11.88%), 141 (9.18%), 125 (8.06%), 171 (7.82%), 107 (5.42%), 112 (4.97%), 214 (3.64%), 136 (2.96%), 130 (2.47%)	RHE	Gallic acid	MS^2 (CE:45 V): 171 [3]
3.75	**P5**	261	$[M+H]^+$	261 (100%), 114 (29.86%), 243 (3.4%), 164 (1.57%), 146 (0.6%), 166 (0.41%), 110 (0.31%), 134 (0.31%), 148 (0.29%), 215 (0.25%), 122 (0.23%), 113 (0.22%), 162 (0.2%), 108 (0.19%), 150 (0.17%), 152 (0.16%), 241 (0.15%), 156 (0.14%), 132 (0.13%), 131 (0.12%), 120 (0.12%), 171 (0.11%), 260 (0.1%), 160 (0.09%), 172 (0.09%), 200 (0.08%), 129 (0.07%), 138 (0.07%), 136 (0.05%), 109 (0.04%), 168 (0.04%), 135 (0.04%), 133 (0.04%), 104 (0.03%), 225 (0.03%)	SOP	Baptifoline	$MS^{n=2-4}$[261](CE: 50%): 243(44), 164(24), 114(100) [1]
	P6	265	$[M+H]^+$	265 (100%), 247 (2.98%), 263 (2.5%), 112 (2.49%), 164 (2.17%), 264 (2.1%), 245 (1.92%), 166 (1.78%), 176 (1.59%), 236 (1.44%), 262 (1.44%), 148 (1.32%), 175 (1.18%), 120 (0.93%), 163 (0.92%), 121 (0.79%), 131 (0.78%), 154 (0.75%), 124 (0.73%), 123 (0.7%), 150 (0.65%), 136 (0.59%), 162 (0.54%), 219 (0.52%), 190 (0.36%), 109 (0.33%), 122 (0.3%), 138 (0.26%)	SOP	5α-Hydroxymatrine OR 9α-Hydroxymatrine	5α-Hydroxymatrine: EI-MS [265]: 264(87), 263(29), 247(100), 246(24), 222(6), 221(26), 208(4), 193(10), 166(15), 112(3), 120(35), 98(4), 96(36) [4] EI-MS (CE: NA): 264(59), 248(12), 247(100), 245(45), 235(6), 222(12), 221(29), 208(5), 193(12), 178(3), 166(16), 153(6), 152(10), 148(12), 125(6), 112(30), 96(36), 55(20), 41(18) [5] 9α-Hydroxymatrine: $MS^{n=2-4}$ [265] (CE: 50%): 247(52), 150(63), 148(100), 112(20) [1] EI-MS (CE: NA): 264(100), 263(67), 247(16), 246(5), 235(9), 222(10), 221(13), 219(21), 208(15), 205(84), 193(19), 178(8), 166(35), 164(22), 153(10), 152(10), 114(11), 112(18), 98(9), 96(43), 55(28), 41(24).[5]
4.15	**P7**	265	$[M+H]^+$	265 (100%), 247 (7.28%), 150 (5.59%), 148 (5.25%), 112 (2.24%), 176 (1.29%), 122 (1.15%), 188 (0.54%), 110 (0.49%), 120 (0.39%), 245 (0.36%), 136 (0.35%), 242 (0.3%), 152 (0.29%), 162 (0.26%), 230 (0.25%), 202 (0.24%), 134 (0.23%), 217 (0.22%), 201 (0.22%), 133 (0.22%), 263 (0.22%), 190 (0.2%), 127 (0.2%), 229 (0.19%), 146 (0.18%), 219 (0.18%), 173 (0.16%), 131 (0.15%), 193 (0.15%), 145 (0.15%), 161 (0.14%), 124 (0.14%), 138 (0.13%), 218 (0.13%), 121 (0.13%), 174 (0.12%), 164 (0.12%), 168 (0.12%), 264 (0.12%), 204 (0.11%), 160 (0.1%), 179	SOP	14β-Hydroxymatrine	EI-MS(CE: NA): 247, 246, 192, 177, 150, 137, 136, 96 [6] EI-MS(CE: NA): 265(19), 264(100), 263(72), 247(3), 246(4), 235(13), 222(48), 221(55), 218(30), 193(57), 192(26), 178(20), 177(19), 162(10), 150(29),

Table S2 Putatively identified compounds in the HHCF by LC-MS/MS in positive ionization mode.

R_t (min)	**No.**	***m/z***	**Adduct ion(s)**	**MS/MS fragment ions (*m/z*)**	**Source**	**Identity**	**Reported MS/MS fragments** (CE=collision energy)
				(0.06%), 132 (0.05%), 163 (0.05%), 153 (0.05%), 246 (0.05%), 108 (0.04%), 111 (0.03%), 206 (0.03%), 200 (0.03%)			149(15), 148(17), 137(14), 136(21), 122(12), 109(8), 98(12), 96(33), 80(8), 55(9), 41(11) [5]
4.40	**P8**	180	$[M+H]^+$	121 (100%), 180 (16.62%), 103 (2.44%), 120 (0.11%), 151 (0.08%), 119 (0.05%)	PHE	Candicine	MS^2[180] (CE:NA): 150, 133, 122, 119, 70 [7] MS^2[180] (CE:NA): 121, 60; MS^3(180→121): 121, 103, 95, 93, 91, 77 [8]
4.75	**P9**	245	$[M+H]^+$	245 (100%), 150 (4.52%), 199 (3.76%), 162 (3.75%), 148 (3%), 158 (2.26%), 110 (2.14%), 122 (2%), 124 (1.6%), 145 (1.54%), 175 (1.54%), 228 (1.33%), 105 (1.26%), 174 (1.23%), 191 (1.2%), 136 (1.03%), 177 (0.94%), 125 (0.94%), 118 (0.93%), 217 (0.89%), 160 (0.63%), 202 (0.52%), 227 (0.38%)	SOP	Anagyrine	$MS^{n=2-4}$ [245] (CE: 50%): 148(100), 98(23) [1]
	P10	265	$[M+H]^+$	265 (100%), 168 (28.79%), 247 (8.6%), 150 (8.32%), 112 (3.93%), 148 (3.42%), 122 (0.87%), 188 (0.81%), 176 (0.57%), 136 (0.53%), 230 (0.53%), 206 (0.29%), 131 (0.25%), 160 (0.22%), 220 (0.21%), 134 (0.2%), 216 (0.2%), 124 (0.19%), 105 (0.19%), 167 (0.18%), 263 (0.18%), 190 (0.17%), 140 (0.16%), 107 (0.16%), 135 (0.16%), 204 (0.16%), 120 (0.15%), 195 (0.15%), 143 (0.13%), 248 (0.13%), 162 (0.13%), 184 (0.13%), 166 (0.13%), 165 (0.12%), 138 (0.12%), 110 (0.12%), 164 (0.12%), 229 (0.11%), 178 (0.11%), 132 (0.11%), 266 (0.1%), 100 (0.08%), 264 (0.08%), 183 (0.06%), 159 (0.06%), 192 (0.05%), 175 (0.04%)	SOP	5α-Hydroxymatrine OR 9α-Hydroxymatrine	5α-Hydroxymatrine: EI-MS: 264(87), 263(29), 247(100), 246(24), 222(6), 221(26), 208(4), 193(10), 166(15), 112(3), 120(35), 98(4), 96(36) [4] EI-MS(CE: NA): 264(59), 248(12), 247(100), 245(45), 235(6), 222(12), 221(29), 208(5), 193(12), 178(3), 166(16), 153(6), 152(10), 148(12), 125(6), 112(30), 96(36), 55(20), 41(18) [5] 9α-Hydroxymatrine: HPLC-IT-TOF, $MS^{n=2-4}$(CE: 50%): 247(52), 150(63), 148(100), 112(20) [1] EI-MS(CE: NA): 264(100), 263(67), 247(16), 246(5), 235(9), 222(10), 221(13), 219(21), 208(15), 205(84), 193(19), 178(8), 166(35), 164(22), 153(10), 152(10), 114(11), 112(18), 98(9), 96(43), 55(28), 41(24).[5]
5.00	**P11**	247	$[M+H]^+$	247 (100%), 150 (33.66%), 148 (10.26%), 188 (2.07%), 122 (1.78%), 158 (0.75%), 105 (0.72%), 121 (0.7%), 134 (0.66%), 112 (0.61%), 149 (0.59%), 246 (0.58%), 110 (0.44%), 176 (0.42%), 147 (0.32%), 160 (0.31%), 136 (0.26%), 245 (0.22%), 129 (0.17%), 111 (0.15%)	SOP	5,6-Dehydrolupanine	EI-MS(CE:45eV): 246(25), 148(6), 134(9), 98(100), 97(38) [9]
5.52	**P12**	263	$[M+H]^+$	150 (100%), 263 (41.59%), 148 (4.71%), 245 (3.13%), 128 (2.6%), 166 (2.52%), 125 (1.94%), 175 (1.93%), 153 (1.61%), 122 (1.47%), 191 (1.39%), 164 (1.33%), 110 (1.25%), 227 (1.22%), 119 (1.01%), 107 (0.97%), 235 (0.85%), 165 (0.84%), 146 (0.84%), 171 (0.46%), 103 (0.4%), 130 (0.36%), 188 (0.36%), 121 (0.34%), 186 (0.33%), 147 (0.32%)	SOP	Mamanine	NA

Table S2 Putatively identified compounds in the HHCF by LC-MS/MS in positive ionization mode.

R_t (min)	No.	*m/z*	Adduct ion(s)	MS/MS fragment ions (*m/z*)	Source	Identity	Reported MS/MS fragments (CE=collision energy)
5.72	**P13**	192	$[M+H]^+$	192 (100%), 177 (42.56%), 149 (2.94%), 148 (2.54%), 176 (0.91%), 151 (0.48%), 147 (0.43%), 163 (0.35%), 161 (0.33%), 174 (0.32%), 133 (0.19%), 159 (0.19%), 119 (0.18%), 160 (0.16%), 132 (0.13%)	PHE	Noroxyhydrastinine	MS^2 [192] (CE:NA): 163, 160, 151, 60 [7]
	P14	249	$[M+H]^+$	249 (100%), 247 (1.8%), 148 (1.8%), 150 (0.81%), 112 (0.39%), 176 (0.33%), 110 (0.26%), 136 (0.25%), 138 (0.2%), 152 (0.2%), 218 (0.15%), 231 (0.14%), 190 (0.13%), 122 (0.12%), 166 (0.11%), 114 (0.11%), 204 (0.1%), 162 (0.09%), 232 (0.05%), 199 (0.02%), 120 (0.02%), 134 (0.02%), 158 (0.01%), 149 (0.01%), 133 (0.01%), 250 (0.01%), 147 (0%), 220 (0%)	SOP	Allomatrine OR Isomatrine OR Matrine OR Sophoridine	Allomatrine: EI-MS(CE: NA): 249(8), 248(51), 247(100), 219(2), 205(4), 192(1), 177(37), 162(3), 150(28), 149(10), 148(9), 137(5), 136(15), 122(5), 109(2), 98(3), 96(7), 55(5), 41(4) [5] Matrine: $MS^{n=2-4}$ [249] (CE: 50%): 176(100), 150(10), 148(5) [1] Isomatrine: $MS^{n=2-4}$ [249] (CE: 50%): 176(100), 150(15), 148(10) [1] Sophoridine: $MS^{n=2-4}$ [249] (CE: 50%): 176(100), 150(15), 148(10) [1]
		519	$[2M+Na]^+$	271 (100%), 519 (1.67%), 314 (0.27%), 272 (0.15%)			
		497	$[2M+H]^+$	249 (100%), 351 (0.77%), 247 (0.44%), 150 (0.29%), 121 (0.11%)			
		271	$[M+Na]^+$	No fragment ion			
6.47	**P15**	247	$[M+H]^+$	247 (100%), 179 (6.18%), 245 (5.01%), 136 (3.66%), 150 (2.64%), 148 (0.75%), 229 (0.62%), 138 (0.56%), 110 (0.37%), 152 (0.3%), 122 (0.27%), 108 (0.26%), 230 (0.25%), 174 (0.23%), 149 (0.21%), 176 (0.2%), 134 (0.19%), 112 (0.17%), 162 (0.15%), 164 (0.14%), 188 (0.13%), 146 (0.13%), 216 (0.1%), 228 (0.1%), 226 (0.1%), 204 (0.09%), 218 (0.04%), 144 (0.04%), 178 (0.04%), 227 (0.04%), 131 (0.03%), 105 (0.02%), 201 (0.01%)	SOP	Sophocarpine OR Isosophocarpine	Sophocarpine: $MS^{n=2-4}$ [247] (CE: 50%): 227(19), 179(100), 150(93), 148(40), 136(63) [1] Isosophocarpine: $MS^{n=2-4}$ [247] (CE: 50%): 179(100), 150(90), 148(51), 136(72) [1]
	P16	249	$[M+H]^+$	249 (100%), 150 (0.59%), 152 (0.55%), 247 (0.5%), 112 (0.36%), 148 (0.32%), 180 (0.22%), 136 (0.18%), 178 (0.18%), 176 (0.16%), 110 (0.15%), 190 (0.13%), 122 (0.11%), 218 (0.1%), 138 (0.09%), 220 (0.08%), 135 (0.08%), 231 (0.07%), 120 (0.06%), 162 (0.06%), 114 (0.06%), 124 (0.03%), 106 (0.03%), 166 (0.03%), 195 (0.02%), 149 (0.01%), 174 (0.01%), 131 (0.01%), 186 (0.01%), 177 (0.01%)	SOP	Allomatrine OR Isomatrine OR Matrine OR Sophoridine	Allomatrine: EI-MS(CE: NA): 249(8), 248(51), 247(100), 219(2), 205(4), 192(1), 177(37), 162(3), 150(28), 149(10), 148(9), 137(5), 136(15), 122(5), 109(2), 98(3), 96(7), 55(5), 41(4) [5] Matrine: $MS^{n=2-4}$ [249] (CE: 50%): 176(100), 150(10), 148(5) [1] Isomatrine: $MS^{n=2-4}$ [249] (CE: 50%): 176(100), 150(15), 148(10) [1] Sophoridine:
		519	$[2M+Na]^+$	271 (100%), 272 (1.89%), 519 (1.3%), 273 (1.09%), 270 (0.51%), 269 (0.25%)			
		497	$[2M+H]^+$	249 (100%), 250 (3.68%), 251 (2.71%), 248 (0.82%), 247 (0.6%), 232 (0.59%), 120 (0.42%), 283 (0.24%)			

Table S2 Putatively identified compounds in the HHCF by LC-MS/MS in positive ionization mode.

R_t (min)	No.	*m/z*	Adduct ion(s)	MS/MS fragment ions (*m/z*)	Source	Identity	Reported MS/MS fragments (CE=collision energy)
							HPLC-IT-TOF, $MS^{n=2-4}$(CE: 50%): 176(100), 150(15), 148(10) [1]
8.02	**P17**	263	$[M+H]^+$	263 (100%), 245 (16.22%), 150 (4.09%), 136 (3.05%), 138 (2.57%), 246 (2.44%), 203 (2.43%), 177 (1.41%), 110 (1.33%), 137 (1.14%), 148 (0.88%), 159 (0.79%), 149 (0.72%), 122 (0.58%), 134 (0.55%), 162 (0.49%), 217 (0.48%), 231 (0.48%), 227 (0.47%), 195 (0.44%), 228 (0.39%), 160 (0.38%), 161 (0.36%), 174 (0.35%), 218 (0.34%), 109 (0.32%), 146 (0.31%), 124 (0.3%), 186 (0.3%), 135 (0.29%), 191 (0.27%), 151 (0.27%), 178 (0.26%), 163 (0.19%), 202 (0.19%), 189 (0.19%), 147 (0.19%), 187 (0.18%), 108 (0.18%), 112 (0.18%), 131 (0.15%), 166 (0.15%), 188 (0.15%), 176 (0.15%), 190 (0.15%), 132 (0.15%), 123 (0.15%), 175 (0.14%), 164 (0.13%), 200 (0.12%), 111 (0.11%), 216 (0.11%), 205 (0.1%), 204 (0.1%), 229 (0.1%), 243 (0.1%), 120 (0.1%), 168 (0.09%), 130 (0.08%), 172 (0.08%), 125 (0.08%), 133 (0.07%), 265 (0.05%), 121 (0.04%), 139 (0.03%), 201 (0.02%), 165 (0.02%), 262 (0.01%), 261 (0.01%), 157 (0.01%), 106 (0.01%), 158 (0.01%), 142 (0.01%), 235 (0.01%)	SOP	Oxysophocarpine	$MS^{n=2-4}$ [263] (CE: 50%): 245(100), 150(53), 138(39) [1]
		525	$[2M+H]^+$	263 (100%), 525 (1.69%), 245 (0.44%), 465 (0.24%), 246 (0.14%), 265 (0.14%), 150 (0.12%), 393 (0.09%), 136 (0.07%), 149 (0.06%), 203 (0.05%), 331 (0.04%), 138 (0.04%)			
	P18	265	$[M+H]^+$	265 (100%), 247 (6.37%), 205 (4.4%), 148 (3.69%), 136 (2.5%), 248 (2.21%), 137 (1.65%), 150 (1.57%), 162 (0.97%), 206 (0.92%), 220 (0.91%), 176 (0.86%), 177 (0.74%), 219 (0.61%), 112 (0.59%), 161 (0.41%), 120 (0.4%), 192 (0.36%), 149 (0.33%), 133 (0.33%), 124 (0.29%), 122 (0.23%), 190 (0.23%), 110 (0.2%), 134 (0.18%), 138 (0.18%), 178 (0.17%), 233 (0.16%), 188 (0.15%), 108 (0.14%), 151 (0.14%), 164 (0.14%), 189 (0.13%), 135 (0.13%), 204 (0.12%), 109 (0.12%), 163 (0.11%), 235 (0.11%), 174 (0.1%), 160 (0.1%), 191 (0.1%), 230 (0.09%), 202 (0.08%), 146 (0.04%), 152 (0.03%), 139 (0.03%), 245 (0.02%), 111 (0.02%), 264 (0.02%), 179 (0.01%), 217 (0.01%), 123 (0.01%), 107 (0.01%), 105 (0.01%), 229 (0.01%), 207 (0.01%), 175 (0.01%), 203 (0.01%)	SOP	Oxymatrine OR Oxysophoridine	Oxymatrine: $MS^{n=2-4}$ [265] (CE: 50%): 265(100), 247(26), 205(35), 148(53) [1]
		529	$[2M+H]^+$	265 (100%), 529 (1.03%), 247 (0.34%), 248 (0.26%), 176 (0.2%), 264 (0.2%), 205 (0.17%), 266 (0.17%), 263 (0.15%), 206 (0.15%), 220 (0.11%), 148 (0.1%), 136 (0.07%), 137 (0.07%), 267 (0.04%)			
	P19	266	$[M+NH_4]^+$	266 (100%), 248 (6.66%), 206 (4.05%), 249 (2.99%), 137 (2.95%), 149 (2.86%), 148 (1.78%), 151 (1.43%), 205 (1.37%), 138 (1.31%), 177 (1.24%), 136 (1.21%), 150 (1.1%), 221 (1.05%), 207 (0.96%), 220 (0.85%), 178 (0.8%), 162 (0.69%), 265 (0.63%), 163 (0.59%), 112 (0.5%), 110 (0.45%), 121 (0.41%), 193 (0.38%), 134 (0.36%), 120 (0.32%), 189 (0.3%), 123 (0.29%), 176 (0.28%), 113 (0.28%), 133 (0.25%), 124 (0.24%), 234 (0.23%), 161 (0.23%), 122 (0.2%), 135 (0.2%), 192 (0.19%), 165 (0.19%), 247 (0.19%), 139 (0.19%), 106 (0.19%), 164 (0.18%), 219 (0.17%), 179 (0.17%), 236 (0.17%), 204 (0.16%), 231 (0.15%), 152 (0.15%), 111 (0.14%), 107 (0.14%), 190 (0.13%), 108 (0.13%), 175 (0.13%), 171 (0.11%), 125 (0.11%), 109 (0.11%), 147 (0.11%), 167 (0.1%), 232 (0.1%), 230 (0.1%), 132 (0.09%), 153 (0.08%)	SOP	Lupanine	EI-MS(CE:45eV): 248(45), 150(38), 149(58), 136(100), 98(28) [9]
10.42	**P20**	247	$[M+H]^+$	247 (100%), 148 (76.77%), 176 (14.81%), 150 (7.33%), 110 (2.34%), 179 (2.13%), 229 (2.11%), 218 (1.57%), 190 (1.49%), 120 (1.48%), 230 (1.46%), 206 (1.42%), 188 (1.38%), 121 (1.35%), 146 (1.06%), 109 (1.04%), 219 (1.01%), 122 (1.01%), 112	SOP	(+)-7,11-Dehydromatrine	$MS^{n=2-4}$ [247] (CE: 50%): 176(100), 148(13) [1]

Table S2 Putatively identified compounds in the HHCF by LC-MS/MS in positive ionization mode.

R_t (min)	No.	*m/z*	Adduct ion(s)	MS/MS fragment ions (*m/z*)	Source	Identity	Reported MS/MS fragments (CE=collision energy)
				(1.01%), 134 (0.91%), 165 (0.86%), 212 (0.84%), 157 (0.81%), 133 (0.72%), 204 (0.69%), 160 (0.61%), 132 (0.59%), 174 (0.57%), 186 (0.54%), 164 (0.52%), 216 (0.51%), 202 (0.49%), 105 (0.48%), 127 (0.47%), 111 (0.41%), 123 (0.4%), 124 (0.39%), 136 (0.37%), 162 (0.36%), 131 (0.35%), 245 (0.33%), 130 (0.32%), 113 (0.3%), 138 (0.28%), 161 (0.27%), 147 (0.26%), 159 (0.22%), 203 (0.2%), 119 (0.19%), 135 (0.19%), 173 (0.19%), 189 (0.18%), 137 (0.16%), 108 (0.15%), 106 (0.15%)			
11.30	**P21**	263	$[M+H]^+$	263 (100%), 245 (20.1%), 112 (9.14%), 235 (5.4%), 246 (5.34%), 195 (2.93%), 204 (2.77%), 149 (2.76%), 136 (2.1%), 218 (1.98%), 148 (1.64%), 162 (1.58%), 120 (1.4%), 138 (1.36%), 135 (1.19%), 122 (1.17%), 110 (1.02%), 180 (1%), 134 (1%), 191 (0.99%), 166 (0.91%), 202 (0.79%), 111 (0.74%), 200 (0.7%), 176 (0.68%), 146 (0.64%), 173 (0.59%), 159 (0.59%), 106 (0.57%), 124 (0.57%), 217 (0.57%), 177 (0.55%), 188 (0.54%), 150 (0.5%)	SOP	9α-Hydroxysophocarpine	$MS^{n=2-4}$ [263] (CE: 50%): 245(33), 164 (100) [1] EI-MS(CE: NA): 262(77), 261(100), 245(12), 233(5), 219(6), 217(10), 203(25), 193(19), 166(30), 154(19), 153(6), 152(11),, 136(15), 122(9), 144(6), 112(14), 110(18), 109(8), 98(3), 96(37), 92(2), 68(23), 41(24).[5]
11.48	**P22**	263	$[M+H]^+$	263 (100%), 164 (20.48%), 245 (19.12%), 246 (12.69%), 218 (6.89%), 204 (6.55%), 150 (4.09%), 176 (3.22%), 148 (3.14%), 166 (2.31%), 175 (2.03%), 190 (1.7%), 134 (1.39%), 146 (1.18%), 202 (1.07%), 152 (0.87%), 186 (0.85%), 136 (0.83%), 217 (0.77%), 188 (0.75%), 162 (0.73%), 203 (0.66%), 165 (0.64%), 147 (0.59%), 112 (0.57%), 180 (0.57%), 174 (0.55%), 108 (0.54%), 155 (0.52%), 160 (0.45%), 133 (0.43%), 189 (0.42%), 264 (0.42%), 122 (0.4%), 231 (0.39%), 138 (0.37%), 178 (0.26%), 179 (0.24%), 243 (0.2%), 200 (0.17%), 130 (0.16%), 161 (0.15%), 124 (0.15%), 132 (0.15%), 135 (0.14%), 220 (0.13%)	SOP	Leontalbinine N-oxide	$MS^{n=2-4}$ [263] (CE: 50%): 195(82), 166(100) [1]
		525	$[2M+H]^+$	NA			
	P23	265	$[M+H]^+$	265 (100%), 247 (17.02%), 205 (6.84%), 248 (5.94%), 150 (3.38%), 177 (2.27%), 137 (2.04%), 206 (1.61%), 220 (1.57%), 136 (1.53%), 148 (1.48%), 151 (1.35%), 149 (0.82%), 162 (0.74%), 219 (0.73%), 152 (0.71%), 138 (0.46%), 192 (0.4%), 176 (0.38%), 124 (0.38%), 161 (0.35%), 112 (0.32%), 122 (0.29%), 120 (0.28%), 165 (0.23%), 133 (0.23%), 175 (0.22%), 160 (0.19%), 166 (0.18%), 164 (0.18%), 204 (0.18%), 191 (0.18%), 111 (0.16%), 109 (0.16%), 194 (0.16%), 135 (0.14%), 110 (0.13%), 218 (0.12%), 134 (0.11%), 189 (0.1%), 168 (0.1%)	SOP	Oxymatrine OR Oxysophoridine	Oxymatrine: $MS^{n=2-4}$ [265] (CE: 50%): 265(100), 247(26), 205(35), 148(53) [1]
		529	$[2M+H]^+$	NA			
11.88	**P24**	243	$[M+H]^+$ OR $[M]^+$	No fragment ions	DIC	Dasycarpusenester A	NA
						O-Ethylnor-γ-fagarine	NA
20.08	**P25**	342	$[M+H]^+$	192 (100%), 342 (19.81%), 177 (6.11%)	PHE	Tetrahydrojatrorrhizine	MS^2 [342] (CE:NA): 342, 298, 249, 192, 177, 145 [7]
21.12	**P26**	344	$[M+NH_4]^+$	107 (100%), 165 (15.81%), 145 (7.02%), 403 (6.68%), 192 (5.09%), 344 (4.14%), 193 (3.43%), 180 (2.66%), 127 (1.91%)	RHE	4-(4'-Hydroxylphenyl)-2-butanone 4'-O-β-D-glucoside	NA

Table S2 Putatively identified compounds in the HHCF by LC-MS/MS in positive ionization mode.

R_t (min)	**No.**	***m/z***	**Adduct ion(s)**	**MS/MS fragment ions (*m/z*)**	**Source**	**Identity**	**Reported MS/MS fragments** (CE=collision energy)
	P27	349	$[M+NH_4]^+$	349 (100%), 185 (1.85%), 187 (1.53%), 291 (0.65%), 257 (0.35%), 259 (0.29%), 247 (0.22%), 127 (0.21%), 189 (0.2%), 350 (0.08%), 159 (0.07%)	RHE	Epicatechin	NA
22.08	**P28**	344	$[M+H]^+$	344 (100%), 175 (16.68%), 299 (15.38%), 137 (14.51%), 301 (7.39%), 151 (6.26%), 143 (5.14%), 267 (2.52%), 269 (1.98%), 192 (1.42%), 312 (1.38%), 177 (1.24%), 107 (1.2%), 207 (1.1%), 193 (1.08%), 241 (1.05%), 239 (1.04%), 115 (0.66%), 235 (0.65%), 194 (0.6%), 145 (0.46%), 206 (0.44%), 237 (0.43%), 160 (0.43%), 163 (0.41%), 179 (0.41%), 119 (0.35%), 117 (0.35%), 329 (0.31%), 284 (0.31%), 209 (0.3%), 213 (0.29%), 294 (0.29%), 162 (0.28%), 205 (0.28%), 149 (0.26%), 272 (0.26%), 123 (0.24%), 131 (0.24%), 251 (0.23%), 180 (0.2%), 176 (0.2%), 118 (0.19%), 271 (0.19%), 109 (0.19%), 153 (0.18%), 122 (0.18%), 182 (0.17%), 187 (0.16%), 178 (0.15%), 161 (0.15%), 268 (0.15%), 125 (0.15%), 252 (0.14%), 223 (0.14%), 255 (0.14%), 188 (0.14%), 174 (0.13%), 165 (0.13%), 253 (0.13%), 181 (0.13%), 142 (0.12%), 225 (0.12%)	PHE	Methyl-N-{[(2-methyl-2-propanyl)oxy]carbonyl}glycylprolylglycinate	MS^2 [344] (CE:NA): 343, 222, 209, 192, 163, 95 [7]
22.91	**P29**	342	$[M+H]^+$	342 (100%), 192 (65.27%), 130 (44.39%), 265 (38.79%), 297 (30.11%), 116 (23.34%), 203 (18.44%), 298 (16.58%), 300 (15.05%), 237 (7.11%), 282 (6.16%), 107 (5.29%), 299 (4.9%), 177 (4.72%), 132 (3.32%), 167 (2.84%), 279 (2.44%), 129 (2.43%)	PHE	2-{3,3-Bis[(2-hydroxyethyl)amino]-2-nitroprop-2-en-1-ylidene}-5,5-dimethylcyclohexane-1,3-dione	MS^2[342] (CE:NA): 325, 313, 311, 298, 293, 290, 287 [7]
24.33	**P30**	592	$[2M+NH_4+H]^+$	592 (100%), 163 (13.44%), 286 (5.69%), 382 (3.82%)	PHE	Rutecarpine	NA
26.84	**P31**	314	$[M+H]^+$	314 (100%), 107 (333.67%), 269 (204.1%), 143 (95.44%), 137 (82.51%), 121 (56.43%), 115 (41.17%), 175 (26.19%), 271 (28.98%), 145 (11.62%), 237 (30.37%), 147 (16.78%), 191 (29.59%), 251 (7.9%), 194 (7.67%), 163 (11.95%), 146 (12.06%), 177 (5.97%), 193 (5.82%), 178 (4.46%), 209 (4.43%)	PHE	Evoeuropine	NA
31.32	**P32**	356	$[M+H]^+$	356 (100%), 247 (47.81%), 311 (24.45%)	PHE	2-Amino-N-(3-amino-2-hydroxypropyl)adenosine	MS^2 [356] (CE:NA): 261, 260, 242, 177 [7]
52.87	**P33**	366	$[M]^+$	336 (100%), 321 (26.43%), 320 (14%), 292 (13.06%), 306 (2.64%), 335 (1.54%), 304 (1.41%), 278 (1.37%), 275 (1.11%), 318 (0.51%)	PHE	Berberine	MS^2 [336] (CE:NA): 321, 306, 278 [10] MS^2 [336] (CE:35V): 320, 292 [11]

Table S3 Putatively identified compounds in the LC-MS/MS in negative ionization mode.

Rt (min)	**No.**	***m/z***	**Adduct ion(s)**	**MS/MS fragment ions (*m/z*)**	**Source**	**Identity**	**Reported MS/MS fragments** (CE=collision energy)
2.34	**N1**	193	$[M-H]^-$	113 (100%), 103 (39.1%), 101 (15.01%)	SCU	Glucuronic acid	NA
2.46	**N2**	191	$[M-H]^-$	191 (100%), 127 (7.66%), 111 (4.1%), 173 (3.01%), 109 (2.98%), 145 (2.25%), 190 (2.16%), 171 (1.96%), 103 (1.05%), 129 (0.97%), 143 (0.79%)	PHE	Quinic acid	MS^2 [191] (CE:NA): 173, 127, 111, 93, 85 [12]
	N3	223	$[M-H]^-$	129 (100%), 111 (79.45%), 205 (47.14%), 101 (46.72%), 125 (37.99%), 223 (26.17%)	SOP	Sinapiic acid	NA
3.50	**N4**	191	$[M-H]^-$	111 (100%), 131 (7.5%), 129 (2.94%), 191 (2.19%), 190 (1.49%), 155 (1.41%)	PHE	Citric acid	MS^2 [191] (CE:NA): 173, 111 [12]
	N5	331	$[M-H]^-$	169 (100%), 211 (76.8%), 331 (43.3%), 125 (29.19%), 124 (21.17%), 123 (11.69%), 151 (9.12%), 167 (8.78%), 193 (8.31%), 168 (8.19%), 271 (8.09%), 112 (7.95%), 113 (7.03%), 119 (5.65%), 128 (4.98%), 183 (4.9%), 241 (4.72%), 101 (4.19%), 286 (2.89%), 107 (2.07%), 210 (1.41%), 270 (1.41%), 137 (1.13%)	RHE	Galloylglucose (i.e. 1-*O*-Galloyl-β-D-glucose or 6-*O*-Galloyl-β-D-glucose) OR Glucopyranosyloxyl gallic acid (i.e. Gallic acid-3-O-β-D-glucoside or Gallic acid-4-O-β-D-glucoside)	Glucopyranosyloxyl gallic acid: MS^2 [331] (CE:30-50V): 271, 211, 169, 125 [13] 1-O-Galloylglucose: MS^2 [331] (CE:50%):169(100) [14] Galloylglucose: MS^2 [331] (CE:NA): 169, 125 [15]
4.08	**N6**	331	$[M-H]^-$	169 (100%), 123 (38.65%), 331 (38.36%), 151 (34.32%), 125 (27.77%), 211 (26.08%), 271 (20.32%), 113 (8.98%), 183 (8.02%), 124 (5.04%), 241 (4.82%), 168 (4.77%), 101 (4.67%), 119 (3.85%), 107 (3.65%), 210 (3.33%), 153 (3.14%), 197 (2.41%), 167 (2.12%), 193 (2.06%), 162 (1.17%), 152 (0.76%), 165 (0.57%)	RHE		
4.61	**N7**	331	$[M-H]^-$	211 (100%), 271 (96.85%), 169 (84.6%), 125 (24.42%), 168 (19.07%), 124 (16.25%), 107 (9.53%), 331 (7.91%), 241 (4.09%), 165 (4.05%), 123 (3.53%), 151 (3.14%), 197 (1.89%), 139 (1.59%), 167 (1.58%), 270 (1.56%), 183 (1.31%), 101 (1.03%), 113 (0.88%)	RHE		
5.35	**N8**	125	$[M-H]^-$	125 (100%), 124 (13.85%)	RHE	Pyrogallol	NA
	N9	169	$[M-H]^-$	125 (100%), 169 (8.42%), 107 (3.58%), 124 (3.27%)	RHE	Gallic acid	MS^2 [169] (CE:30-50V): 125, 107 [13]
	N10	331	$[M-H]^-$	211 (100%), 169 (66.81%), 271 (62.68%), 125 (21.96%), 331 (15.26%), 193 (12.23%), 124 (11.97%), 151 (10.94%), 241 (10.24%), 123 (7.63%), 103 (6.98%), 168 (4.58%), 183 (4.56%), 167 (3.64%), 113 (2.85%), 107 (1.27%)	RHE	Galloylglucose (i.e. 1-*O*-Galloyl-β-D-glucose or 6-*O*-Galloyl-β-D-glucose) OR Glucopyranosyloxyl gallic acid (i.e. Gallic acid-3-O-β-D-glucoside or Gallic acid-4-O-β-D-glucoside)	Glucopyranosyloxyl gallic acid: MS^2 [331] (CE:30-50V): 271, 211, 169, 125 [13] 1-O-Galloylglucose: MS^2 [331] (CE:50%):169(100) [14] Galloylglucose: MS^2 [331] (CE:NA): 169, 125 [15]
8.71	**N11**	255	$[M-H]^-$	165 (100%), 107 (38.58%), 179 (32.86%), 133 (22.4%), 193 (17.87%), 149 (16.97%), 147 (16.65%), 255 (13.5%), 131 (10.06%), 135 (8.43%), 119 (7.46%), 105 (3.15%), 175 (2.9%), 163 (2.02%), 211 (1.85%), 121 (1.8%), 137 (1.56%), 132 (1.55%), 181 (1.4%), 103 (1.23%), 151 (1.06%), 130 (1.05%), 134 (0.98%), 106 (0.98%), 162 (0.62%), 150 (0.6%), 109 (0.31%)	SOP	Piscidic acid	MS^2 [276] (CE:NA): 211(33), 193(96), 179(90), 165(87), 149(57) [16]
		511	$[2M-H]^-$				
13.88	**N12**	577	$[M-H]^-$	289 (100%), 407 (65.72%), 125 (38.87%), 425 (22.46%), 577 (19.45%), 245 (14.76%), 451 (13.65%), 305 (9.9%), 161 (9.42%), 287 (7.36%), 273 (7.08%), 381 (5.51%), 137 (5.37%), 205 (4.92%), 299 (4.55%), 559 (4.07%), 151 (3.55%), 175 (3.43%), 243 (3.16%), 255 (2.83%), 203 (2.77%), 450 (2.51%), 256 (2.43%), 163 (2.25%), 328 (2.19%), 329 (2.1%), 229 (2.05%), 109 (2%), 339 (1.99%), 179 (1.92%), 269 (1.85%), 283 (1.74%)	RHE	Procyanidin B (Catechin dimers)	MS^2 [577] (CE:30-50V): 407, 289, 245, 125, 109 [13]
16.48	**N13**	289	$[M-H]^-$	109 (100%), 123 (91.31%), 203 (82.01%), 151 (66.21%), 245 (56.6%), 125 (55.02%), 137 (47.19%), 205 (40.11%), 289 (35.92%), 149 (31.13%), 121 (30.99%), 221 (30.71%), 179 (29.9%), 188 (29.79%), 161 (25.5%), 165 (22.74%), 175 (22.34%), 187 (21.66%), 164 (20.04%), 202 (17.32%), 227	RHE	Catechin	MS^2 [298] (CE:30-50V): 271, 245, 125, 109 [13]

Table S3 Putatively identified compounds in the LC-MS/MS in negative ionization mode.

Rt (min)	No.	*m/z*	Adduct ion(s)	MS/MS fragment ions (*m/z*)	Source	Identity	Reported MS/MS fragments (CE=collision energy)
				(16.9%), 247 (16.8%), 135 (12.93%), 199 (12.77%), 162 (11.73%), 167 (11.33%), 139 (11.08%), 159 (11.03%), 231 (10.45%), 173 (10.2%), 217 (9.78%), 145 (9.56%), 122 (8.76%), 157 (8.68%), 244 (8.36%), 163 (8.17%), 147 (7.96%), 158 (7.31%), 160 (7.14%), 212 (7.09%), 220 (7.09%), 201 (7%), 230 (6.97%), 117 (6.91%), 204 (6.8%), 138 (5.62%), 150 (5.44%), 177 (5.21%), 178 (5.17%), 185 (5.15%), 174 (4.93%), 107 (4.67%), 131 (4.61%), 271 (4.54%), 184 (4.46%), 166 (4.43%), 186 (3.81%), 183 (3.56%), 108 (2.94%), 226 (2.18%), 146 (2.03%), 211 (2.02%), 209 (1.94%), 229 (1.75%), 176 (1.54%), 113 (1.51%), 133 (1.26%), 111 (1.21%)			MS^2 [298] (CE:50%): 109(100), 152(40), 123(60) [14]
		579	$[2M-H]^-$	289 (100%), 245 (13.19%), 125 (3.06%), 179 (2.62%), 203 (2.41%), 205 (2.13%), 137 (1.79%), 109 (1.52%), 271 (1.19%), 187 (1.04%), 135 (1.01%), 217 (0.98%), 123 (0.96%), 175 (0.9%), 165 (0.85%), 151 (0.75%), 221 (0.74%), 247 (0.6%), 149 (0.51%), 227 (0.44%), 188 (0.44%), 161 (0.43%), 204 (0.41%), 160 (0.37%), 200 (0.3%), 121 (0.25%), 167 (0.19%), 164 (0.19%)			
	N14	353	$[M-H]^-$	191 (100%), 205 (2.98%), 127 (1.69%), 109 (0.83%), 265 (0.79%), 135 (0.63%), 161 (0.62%), 173 (0.49%), 179 (0.29%), 111 (0.24%)	PHE	Chlorogenic acid	MS^2 [353] (CE:20eV): 191, 173, 135, 127, 111 [17]
		707	$[2M-H]^-$	NA			
18.15	**N15**	367	$[M-H]^-$	193 (100%), 134 (52.75%), 149 (8.46%), 117 (6.01%), 191 (3.98%), 173 (3.75%), 155 (3.02%), 367 (2.41%), 109 (1.95%), 116 (1.9%), 111 (1.28%), 154 (0.87%), 190 (0.62%), 148 (0.43%)	PHE	3-*O*-Feruloylquinic acid	MS^2 [337] (CE:NA): 193(100), 191(1.8), 173(3.3), 134(4.5) [18]
21.10	**N16**	325	$[M-H]^-$	NA	RHE	4-(4'-Hydroxylphenyl)-2-butanone 4'-O-β-D-glucoside	MS^2 [325] (CE:50%): 163(100), 57(45) [14] MS^2 [325] (CE:15-35V): 161 [19]
		371	$[M+FA-H]^-$	163 (100%), 121 (39.46%), 162 (12.41%), 113 (8.94%), 101 (7.9%), 161 (4.17%)			
		651	$[2M-H]^-$	NA			
	N17	415	$[M+Na-2H]^-$	NA	RHE	6-Hydroxymusizin-8-O- β-D-glucoside	MS^2 [393] (CE:50%): 231(100) [14]
		439	$[M+FA-H]^-$	231 (100%), 113 (77.31%), 393 (11.6%)			
22.77	**N18**	289	$[M-H]^-$	123 (100%), 109 (99.46%), 125 (63.81%), 203 (60.91%), 245 (45.97%), 205 (42.45%), 151 (36.41%), 289 (32.34%), 137 (31.47%), 221 (31.24%), 188 (24.48%), 159 (23.6%), 161 (23.03%), 175 (21.4%), 121 (19.64%), 163 (17.76%), 146 (17.55%), 122 (17.39%), 149 (14.55%), 187 (14%), 185 (13.59%), 145 (12.8%), 164 (11.92%), 139 (11.92%), 165 (10.61%), 217 (10.16%), 162 (9.71%), 227 (8.78%), 230 (8.05%), 138 (8.01%), 135 (7.29%), 179 (7.27%), 202 (6.52%), 174 (6.35%), 167 (6.1%), 199 (5.73%), 229 (5.42%), 143 (4.53%), 186 (4.17%), 244 (4.17%), 201 (4.02%)	RHE	Epicatechin	MS^2 [289] (CE:30-50V): 245, 125, 109 [13]
	N19	337	$[M-H]^-$	191 (100%), 163 (10.21%), 173 (7.7%), 119 (6.74%), 111 (4.09%), 129 (2.45%), 143 (1.65%), 172 (1.28%), 142 (0.78%)	PHE	*p*-coumaroylquinic acid (not previously reported in Phellodendron)	3-O-*p*-Coumaroylquinic acid MS^2 [337] (CE:NA): 191(7.6), 163(100), 119(3.9) 4-O-*p*-Coumaroylquinic acid MS^2 [337] (CE:NA): 191(6.4), 173(100), 163(7.2) 5-O-*p*-Coumaroylquinic acid

Table S3 Putatively identified compounds in the LC-MS/MS in negative ionization mode.

Rt (min)	**No.**	***m/z***	**Adduct ion(s)**	**MS/MS fragment ions (*m/z*)**	**Source**	**Identity**	**Reported MS/MS fragments** (CE=collision energy)
							MS^2 [337] (CE:NA): 191(100), 163(7.1) [18]
24.72	**N20**	303	$[M-H]^-$	125 (100%), 177 (29.2%), 149 (17.35%), 151 (13.92%), 217 (8.99%), 124 (7.9%), 165 (7.78%), 213 (7.67%), 175 (7.13%), 123 (6.97%), 193 (6.77%), 285 (4.74%), 199 (4.16%), 121 (3.99%), 173 (3.31%), 303 (3.07%), 197 (2.61%), 189 (2.47%), 241 (2.43%), 133 (2.29%), 243 (2.15%), 107 (1.77%), 152 (1.75%), 145 (1.61%), 275 (1.61%), 120 (1.55%), 212 (1.27%), 147 (1.26%), 164 (1.19%), 148 (1.14%), 191 (1.1%), 172 (0.99%), 190 (0.98%)	SCU	2',3,5,6',7-Pentahydroxyflavanone (Ganhuangemin)	MS^2 [303] (CE:NA): 285, 276, 259, 217, 177 [20]
26.26	**N21**	367	$[M-H]^-$	191 (100%), 173 (41.26%), 193 (18.5%), 134 (11.18%), 111 (8.15%), 155 (4.26%), 178 (3.62%), 149 (3.53%), 143 (3.1%), 175 (2.27%), 113 (2.05%), 137 (1.84%), 160 (1.78%), 129 (1.77%), 127 (1.74%), 101 (1.33%), 117 (1.25%), 192 (1%), 136 (0.64%), 116 (0.63%), 115 (0.58%), 171 (0.36%)	PHE	5-*O*-Feruloylquinic acid	MS^2 [337] (CE:NA): 193(6.0), 191(100), 173(2.2), 134(4.5) [18]
26.65	**N22**	389	$[M-H]^-$	NA	RHE	Resveratrol-4'-O-β-D-glucoside OR Resveratrol 3-O-β-glucoside (Pieceid)	MS^2 [389] (CE:15-35V): 227, 185, 143 [19]
		435	$[M+FA-H]^-$	227 (100%), 191 (9.41%), 389 (3.8%), 225 (2.18%), 173 (1.57%), 367 (1.44%), 374 (1.42%), 185 (1.08%), 193 (0.64%), 228 (0.43%)			
		779	$[2M-H]^-$	NA			
		825	$[2M+FA-H]^-$	NA			
	N23	503	$[M-H]^-$	113 (100%), 389 (59.12%), 191 (19.03%)	RHE	Melezitose	MS^2 [503] (CE:30-50V): 179, 161, 131, 113 [13]
		584	$[M+Br]^-$	NA			
28.16	**N24**	229	$[M-H]^-$	229 (100%), 185 (45.31%), 139 (33.76%), 183 (28.24%), 167 (20.83%), 137 (18.63%), 211 (9.9%), 165 (9.23%), 155 (8.91%), 117 (7.3%), 149 (4.12%), 113 (3.63%), 111 (2.36%)	PHE	Osthenol	NA
32.06	**N25**	301	$[M-H]^-$	125 (100%), 149 (66.53%), 151 (64.68%), 148 (35.07%), 301 (29.63%), 175 (26.33%), 283 (24.01%), 107 (22.49%), 147 (18.18%), 152 (14.15%), 201 (8.59%), 171 (8.31%), 192 (8.15%), 121 (8.09%), 135 (7.67%), 229 (7.09%), 213 (6.53%), 187 (6.25%), 215 (5.98%), 119 (5.9%), 177 (5.81%), 257 (5.67%), 163 (5.57%), 105 (5.44%), 109 (5.24%), 211 (5.21%), 239 (5.12%), 205 (4.94%), 227 (4.85%), 176 (3.14%), 161 (2.76%), 153 (2.62%), 159 (2.53%), 189 (2.48%), 195 (2.44%), 203 (2.43%), 273 (2.42%), 120 (2.41%), 272 (2.37%), 185 (2.29%), 214 (2.26%), 137 (2.21%), 233 (1.79%), 245 (1.73%), 216 (1.6%), 255 (1.56%), 160 (1.55%), 186 (1.49%), 133 (1.44%), 173 (1.33%)	SCU	3,5,7,2',6'-Pentahydroxyflavone (Viscidulin I)	MS^2 [345] (CE:NA): 383, 273, 257, 229, 151 [20]
34.57	**N26**	441	$[M-H]^-$	169 (100%), 289 (50.74%), 125 (35.13%), 245 (17.94%), 271 (12.85%), 203 (12.14%), 137 (8.9%), 253 (8.3%), 193 (7.68%), 205 (7.38%), 331 (7.28%), 179 (6.31%), 151 (6.2%), 441 (6%), 124 (5.44%), 303 (5.34%), 166 (4.44%), 288 (4.14%), 287 (3.83%), 168 (3.31%), 227 (2.89%), 175 (2.76%), 259 (2.65%), 145 (2.65%), 109 (2.41%), 123 (2.38%), 221 (2.19%), 204 (1.99%), 397 (1.82%), 150 (1.82%), 167 (1.81%), 184 (1.77%), 185 (1.39%), 165 (1.31%), 315 (1.22%), 192 (1.04%), 188 (1.04%), 161 (0.91%), 164 (0.87%)	RHE	Epicatechin 3-O-gallate	MS^2 [441] (CE:50%): 289(100), 109 [14]
	N27	477	$[M-H]^-$	477 (100%), 169 (40.95%), 313 (35.4%), 125 (11.02%), 151 (7.41%), 124 (5.6%), 289 (3.44%), 123 (3.28%), 168 (3.05%), 441 (2.8%), 161 (2.22%), 163 (1.95%), 245 (1.95%), 241 (1.89%), 211 (1.36%), 167 (1.25%), 101 (1.16%), 295 (1.01%)	RHE	Isolindleyin	MS^2 [477] (CE:50%): 313(100), 169(55), 125(25) [14]
	N28	555	$[M-H]^-$	NA	RHE		MS^2 [555](CE:15-35V): 255, 227 [19]

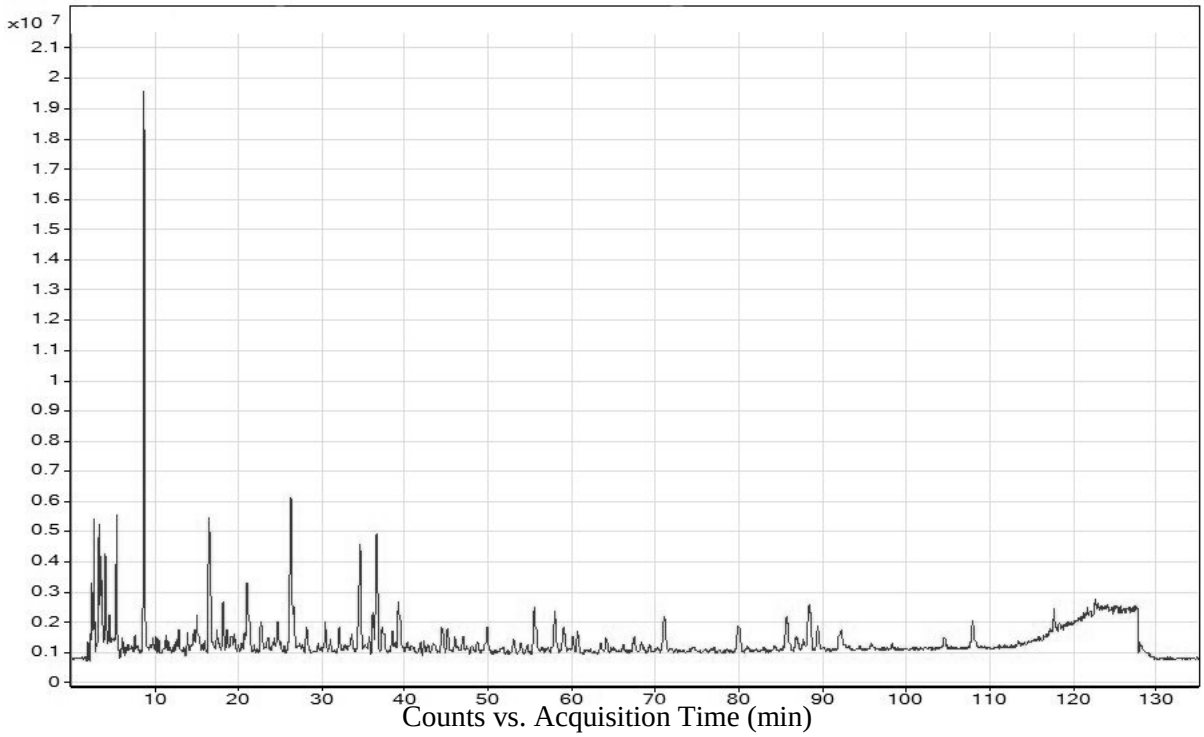
Table S3 Putatively identified compounds in the LC-MS/MS in negative ionization mode.

Rt (min)	No.	*m/z*	Adduct ion(s)	MS/MS fragment ions (*m/z*)	Source	Identity	Reported MS/MS fragments (CE=collision energy)
		591	$[M+Cl]^-$	477 (100%), 137 (12.97%)		Desoxyrhaponticin-6"-O-gallate	
	N29	547	$[M-H]^-$	547 (100%), 337 (30.32%), 457 (14.43%), 427 (13.69%), 367 (12.56%), 487 (6.97%), 280 (5.16%), 409 (2.45%), 529 (1.42%), 349 (1.42%)	SCU	Chrysin-6-C-arabinosyl-8-C-glucoside	MS^2 [547] (CE:NA): 529, 487, 457, 427, 367, 337 [20]
36.56	**N30**	477	$[M-H]^-$	313 (100%), 477 (22.45%), 169 (17.33%), 151 (6.47%), 124 (6.44%), 123 (6.14%), 168 (4.76%), 163 (4.52%), 125 (4.31%), 167 (3.65%), 113 (3.28%), 107 (2.31%), 211 (2.14%), 433 (1.87%), 223 (1.16%), 268 (1.09%), 101 (1.06%), 253 (1.03%), 269 (0.89%), 153 (0.54%), 209 (0.52%), 165 (0.43%), 251 (0.4%), 162 (0.39%), 193 (0.32%), 179 (0.32%)	RHE	Lindleyin	MS^2 [477] (CE:50%): 313(100), 169(55), 125(25) [14]
	N31	545	$[M-H]^-$	NA	RHE	Rhein-8-O-D-[6'-O-(3"-methoxylmalonyl)] glucoside	NA
		591	$[M+FA-H]^-$	477 (100%), 313 (90.2%), 507 (25.16%), 330 (18.66%), 476 (10.52%)			
		955	$[2M-H]^-$	477 (100%), 313 (56.56%)			
37.25	**N32**	547	$[2M-H]^-$	547 (100%), 427 (13.87%), 457 (8.35%), 337 (6.72%), 479 (5.77%), 367 (5.04%), 265 (2.76%), 529 (2.12%), 101 (1.98%), 281 (1.6%), 309 (1.19%), 379 (0.82%), 349 (0.73%), 308 (0.68%), 397 (0.6%), 307 (0.57%), 511 (0.51%), 266 (0.5%), 278 (0.5%), 439 (0.5%), 279 (0.48%), 469 (0.45%), 291 (0.41%), 409 (0.41%), 335 (0.41%), 377 (0.41%), 336 (0.4%)	SCU	Chrysin-6-C-glucosyl-8-C-arabonoside	MS^2 [547] (CE:NA): 529, 487, 457, 427, 367, 337 [20]
38.43	**N33**	541	$[M-H]^-$	313 (100%), 227 (20.57%), 169 (18.22%), 541 (17.99%), 151 (9.27%), 312 (4.29%), 123 (3.42%), 124 (2.09%)	RHE	Resveratrol-4'-O-β-D-(2"-O-galloyl) glucoside	MS^2 [541] (CE:50%): 313(100), 227(25), 169(40), 125(10) [14]
39.20	**N34**	541	$[M-H]^-$	541 (100%), 313 (25.58%), 169 (12.97%), 227 (6.46%), 125 (2.62%), 124 (2.14%), 123 (1.46%), 151 (1.22%), 181 (1.07%), 241 (1.02%), 168 (0.74%), 540 (0.69%), 211 (0.62%)		Resveratrol-4'-O-β-D-(6"-O-galloyl) glucoside	MS^2 [541] (CE:50%): 313(100), 227(25), 169(40), 125(10) [14]
45.08	**N35**	301	$[M-H]^-$	139 (100%), 124 (44.12%), 133 (28.08%), 135 (25.92%), 107 (23.4%), 161 (17.74%), 273 (3.81%), 268 (3.35%), 283 (3.32%), 165 (3.24%), 240 (3.04%), 269 (2.94%), 151 (2.73%), 251 (2.55%), 179 (2.35%), 160 (2.3%), 134 (2.27%), 255 (2.08%), 117 (1.99%), 178 (1.72%), 224 (1.71%), 201 (1.32%)	SCU	4',5,7-trihydroxy-6-methoxyflavanone OR (2S)-7,2',6'-trihydroxy-5-methoxyflavanone	NA
46.91	**N36**	431	$[M-H]^-$	269 (100%), 431 (84.39%), 240 (14.94%), 225 (3.77%), 268 (2.54%), 283 (1.82%), 293 (1.06%), 280 (1%), 281 (0.93%)	RHE	Emodin-1-O-β-D-glucoside OR Emodin-8-O-β-D-glucoside OR Aloe-emodin 8-O-β-D-glucoside OR Aloe-emodin-3-CH_2-O-β-D-glucoside.	Aloe emodin 8- O-β-D-glucoside MS^2 [431] (CE:15-35V): 269, 240 [19] Aloe-emodin-3-CH_2-O-β-D-glycoside MS^2 [431] (CE:15-35V): 269, 268 [19] Emodin 1-O-β-D-glucoside MS^2 [431] (CE:15-35V): 269, 240, 225 [19] Emodin 8-O-β-D-glucoside MS^2 [431] (CE:25%): 311, 293, 269, 268; MS^3 [431→269]: 269, 241, 225; MS^4 [431→269→225]: 210, 182 [21]
55.48	**N37**	481	$[M+Cl]^-$	NA	SOP	(-)-Maackiain-3-O-glucoside (Trifolirhizin)	NA
		483	$[M+K-2H]^-$	NA			
		491	$[M+FA-H]^-$	283 (100%), 255 (10.61%), 254 (4.06%)			

Table S3 Putatively identified compounds in the LC-MS/MS in negative ionization mode.

Rt (min)	**No.**	***m/z***	**Adduct ion(s)**	**MS/MS fragment ions (*m/z*)**	**Source**	**Identity**	**Reported MS/MS fragments** (CE=collision energy)
58.94	**N38**	431	$[M-H]^-$	269 (100%), 431 (38.42%), 268 (11.89%), 311 (4.38%), 225 (2.53%), 293 (2.48%), 265 (1.93%), 240 (1.6%), 241 (1.29%), 239 (0.87%), 224 (0.68%), 270 (0.63%), 181 (0.57%), 282 (0.54%), 310 (0.5%)	RHE	Emodin-1-O-β-D-glucoside OR Emodin-8-O-β-D-glucoside OR Aloe-emodin 8-O-β-D-glucoside OR Aloe-emodin-3-CH_2-O-β-D-glycoside.	Aloe emodin 8- O-β-D-glucoside MS^2 [431] (CE:15-35V): 269, 240 [19] Aloe-emodin-3-CH_2-O-β-D-glycoside MS^2 [431] (CE:15-35V): 269, 268 [19] Emodin 1-O-β-D-glucoside MS^2 [431] (CE:15-35V): 269, 240, 225 [19] Emodin 8-O-β-D-glucoside MS^2 [431] (CE:25%): 311, 293, 269, 268; MS^3 [431→269]: 269, 241, 225; MS^4 [431→269→225]: 210, 182 [21]
63.95	**N39**	233	$[M-H]^-$	191 (100%), 233 (74.34%), 147 (16.22%), 175 (13.72%), 173 (9.55%), 190 (5.6%), 149 (5.1%), 217 (5.08%), 215 (4.04%), 123 (3.6%), 145 (2.65%), 189 (2.07%), 172 (2.05%), 148 (1.99%), 158 (1.92%), 129 (1.9%), 132 (1.19%), 131 (1.12%)	RHE	(5Z)-6-Hydroxy-3,4-dioxo-6-phenyl-5-hexenoic acid	MS^2 [233](CE:30-50V): 189, 175, 147 [13]
71.02	**N40**	269	$[M-H]^-$	269 (100%), 223 (11.25%), 241 (9.54%), 251 (7.35%), 169 (7.09%), 195 (6.82%), 197 (5.46%), 137 (5.03%), 167 (4.17%), 139 (3.69%), 179 (3.12%), 141 (2.68%), 171 (2.6%), 213 (2.35%), 207 (2.16%), 225 (2%), 151 (1.89%), 153 (1.52%), 183 (1.48%), 143 (1.46%), 185 (1.34%), 224 (1.28%), 145 (1.25%), 123 (1.24%), 240 (1.05%), 212 (0.98%), 199 (0.95%), 155 (0.92%), 157 (0.92%), 196 (0.9%), 165 (0.88%), 181 (0.86%), 111 (0.83%), 268 (0.72%), 164 (0.64%), 101 (0.61%), 127 (0.57%), 109 (0.51%), 184 (0.51%), 168 (0.47%), 192 (0.45%), 150 (0.41%), 239 (0.4%), 182 (0.38%), 222 (0.37%), 198 (0.36%), 252 (0.36%), 125 (0.35%), 180 (0.33%), 129 (0.31%), 221 (0.28%), 178 (0.27%), 211 (0.26%), 152 (0.25%), 117 (0.24%), 270 (0.24%), 122 (0.24%), 121 (0.2%), 227 (0.19%), 138 (0.18%), 149 (0.17%)	SCU	5,6,7-Trihydroxyflavone (Baicalein) OR 5,7,8-Trihydroxyflavone (Norwogonin)	Baicalein: MS^2 [269](CE:45% of maximum): 251(100), 241(40), 225(40), 223(40); MS^3 [269→251]: 223(100) [22] Norwogonin: MS^2 [269](CE:NA): 251, 241, 223, 197, 195, 179, 169, 167, 151, 137, 123, 117 [23] MS^2 [269](CE:45% of maximum): 251(60), 241(10), 169(5) [22]

a)



b)

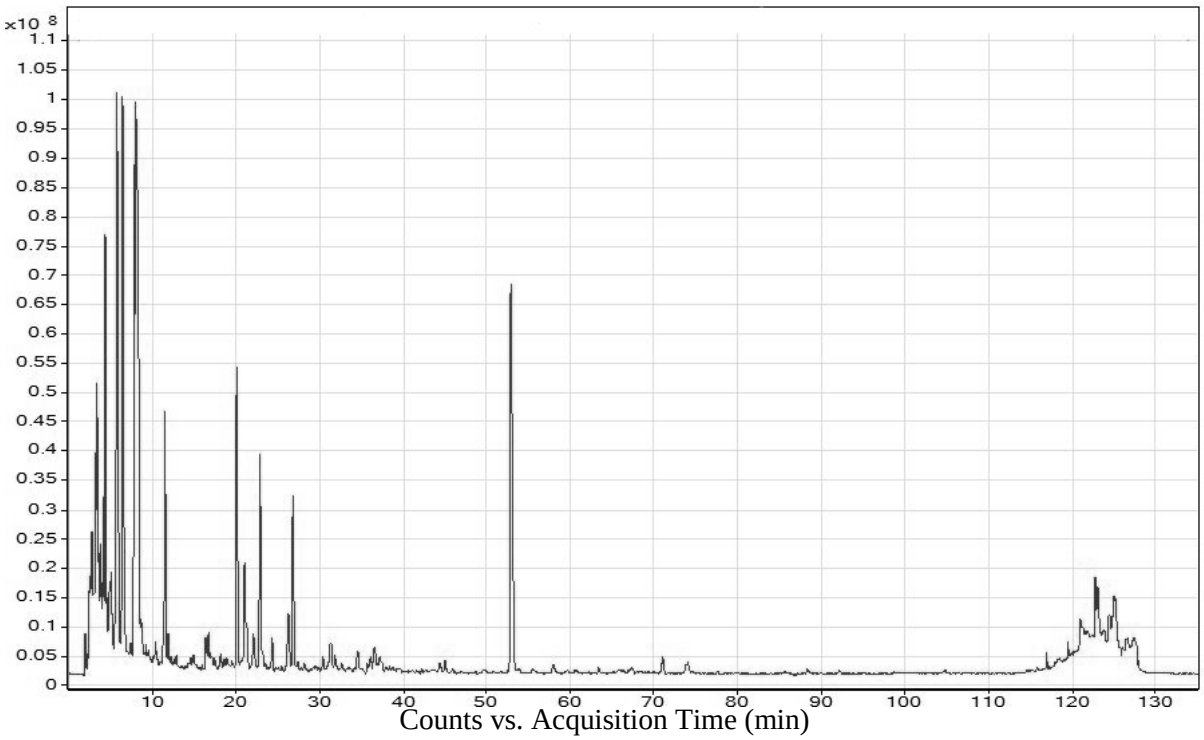


Fig. S1 Total ion chromatogram of HHCF in a) negative and b) positive ionization mode.

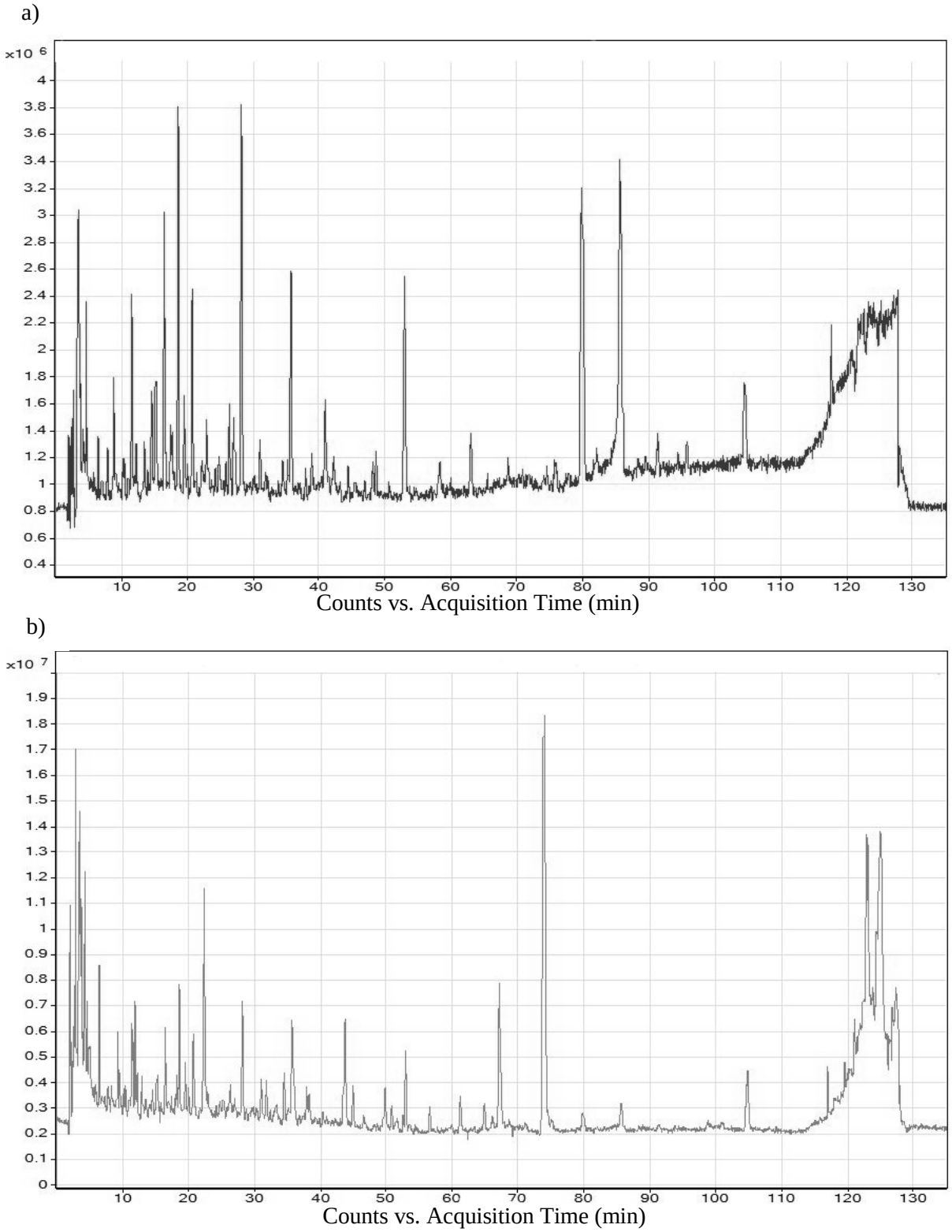
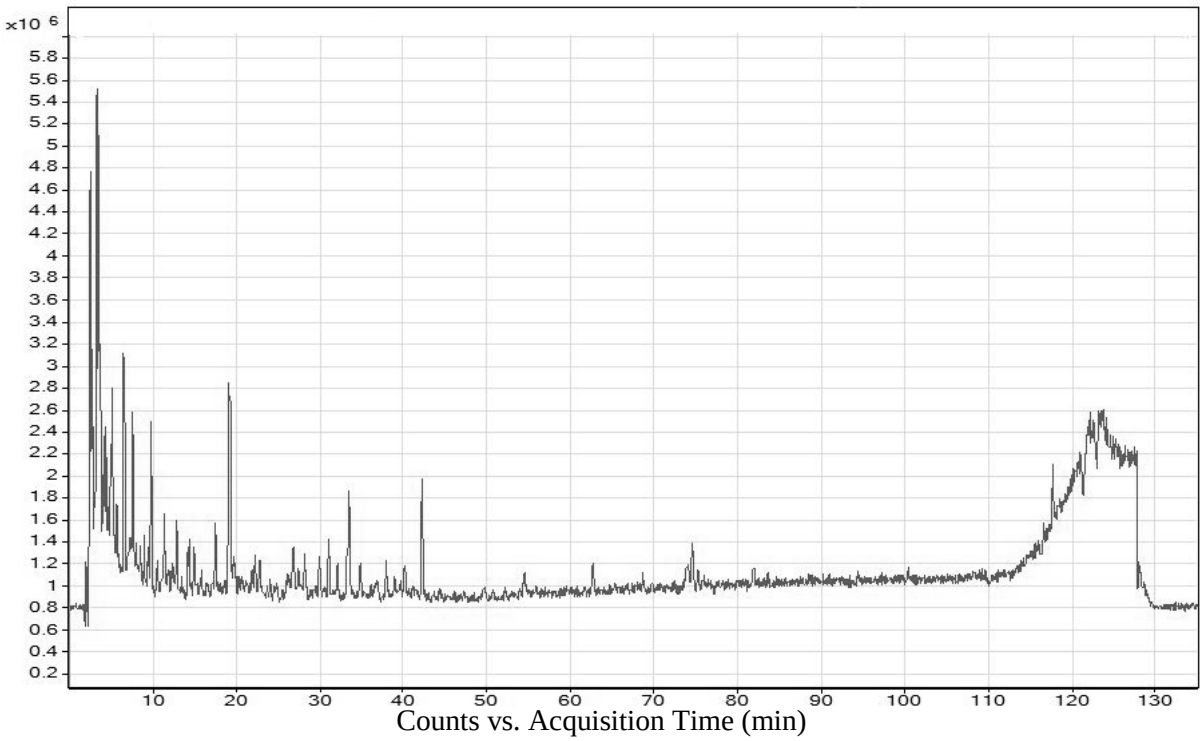


Fig. S2 Total ion chromatogram of DIC in a) negative and b) positive ionization mode.

a)



b)

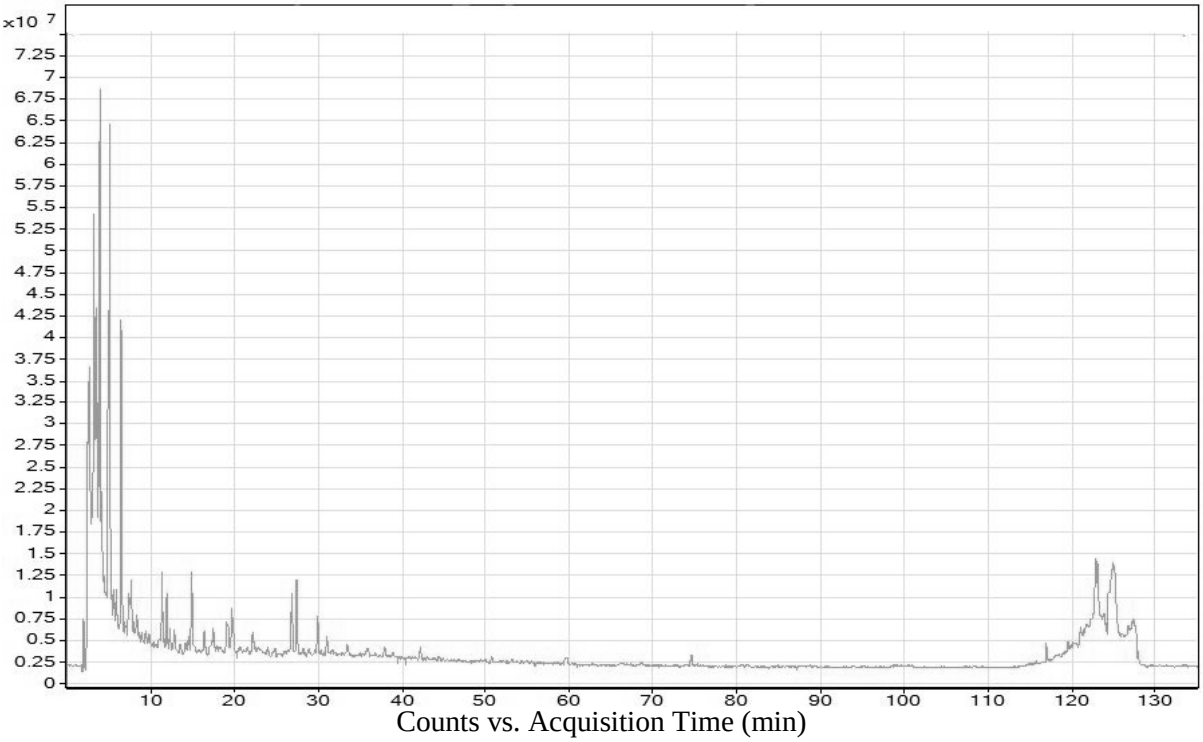
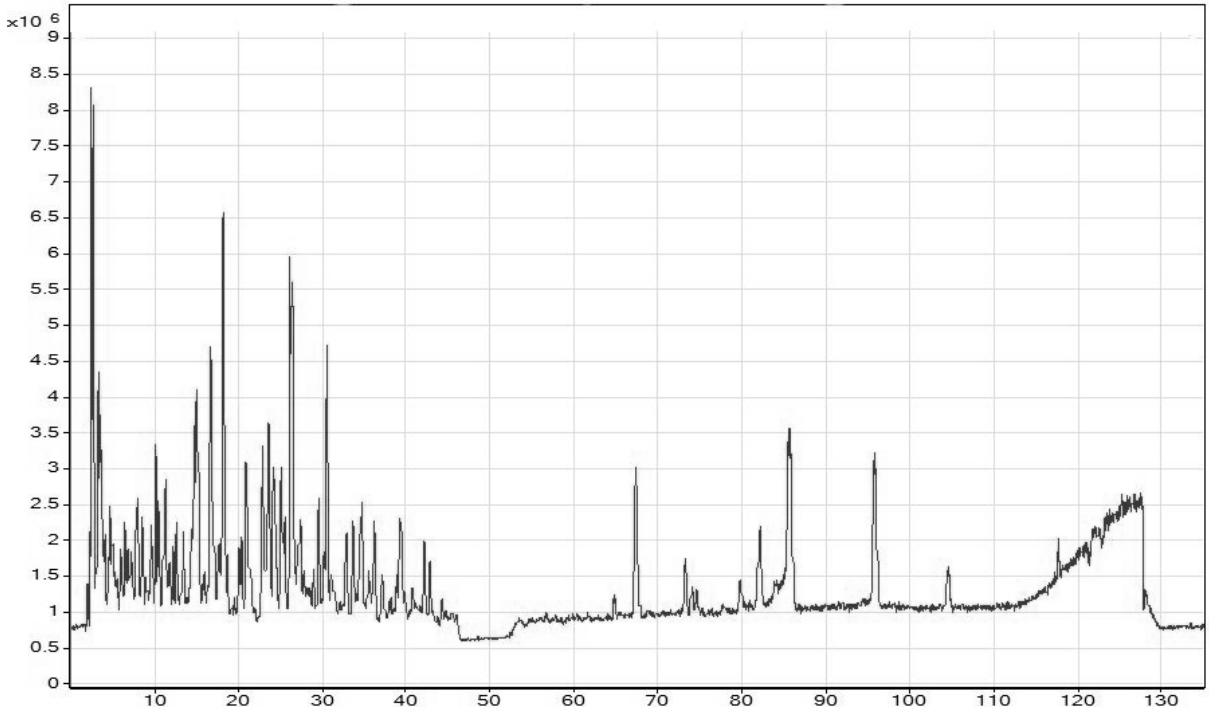


Fig. S3 Total ion chromatogram of KOC in a) negative and b) positive ionization mode.

a)



b)

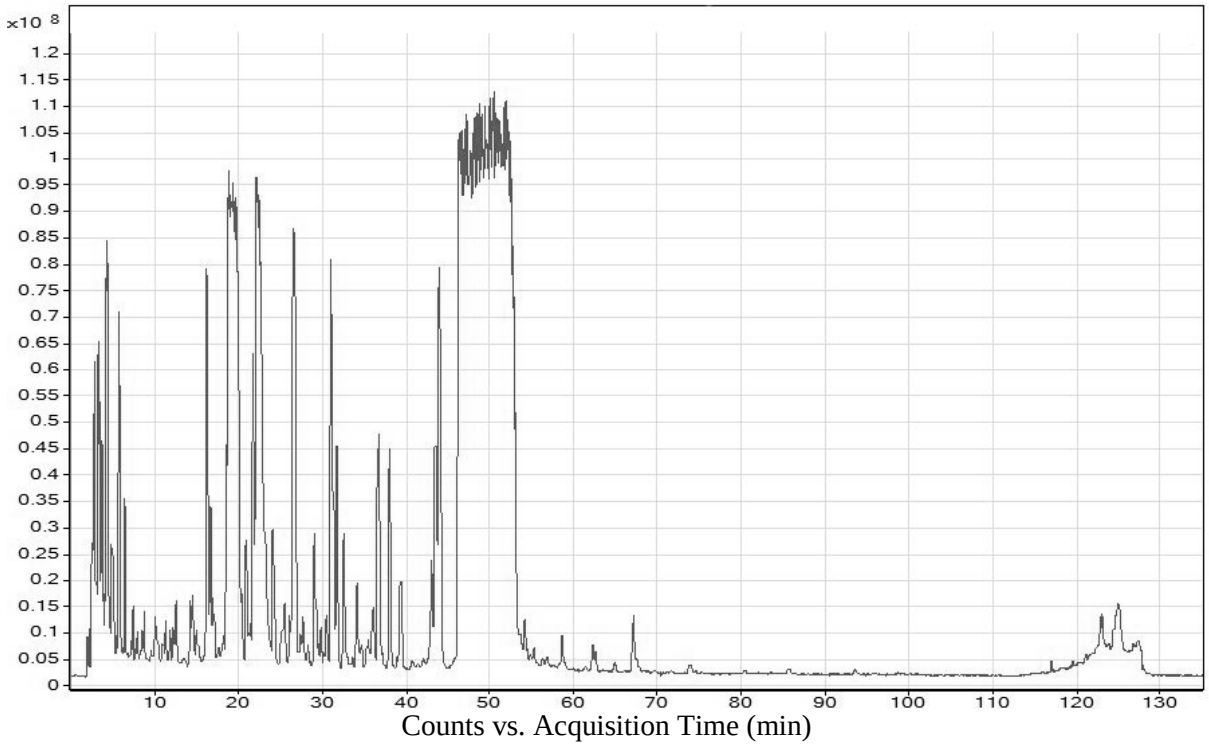
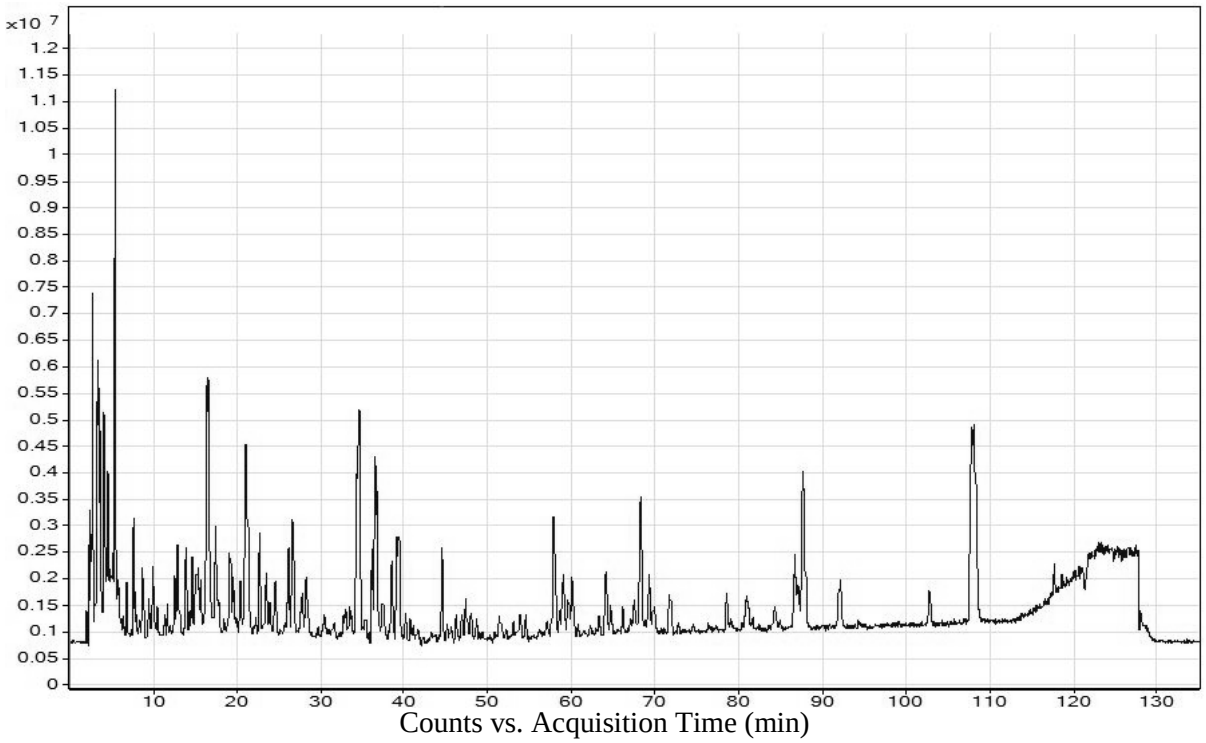


Fig. S4 Total ion chromatogram of PHE in a) negative and b) positive ionization mode.

a)



b)

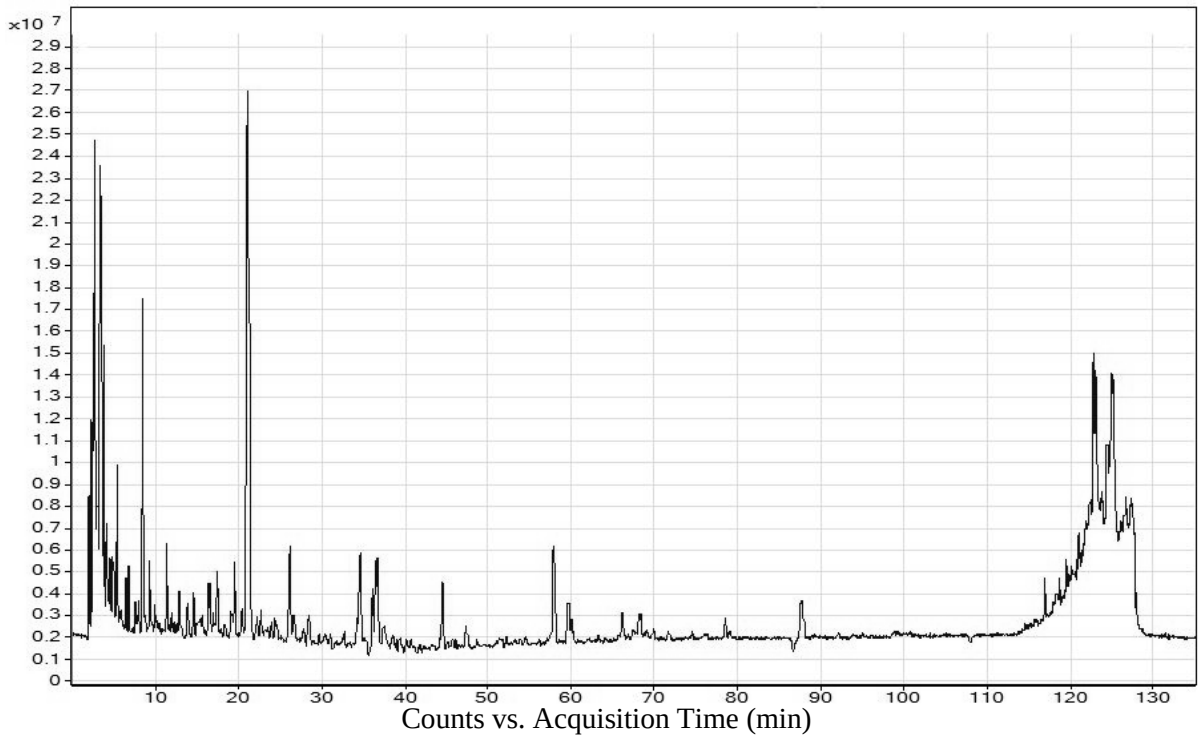
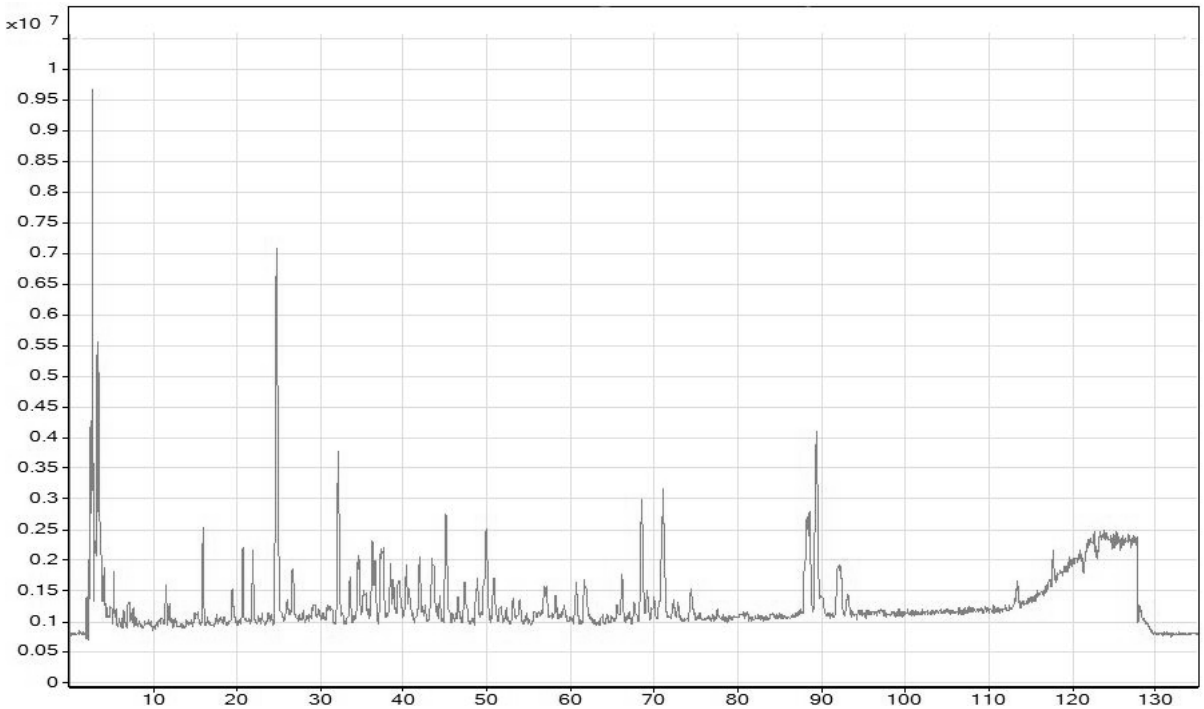


Fig. S5 Total ion chromatogram of RHE in a) negative and b) positive ionization mode.

a)



b)

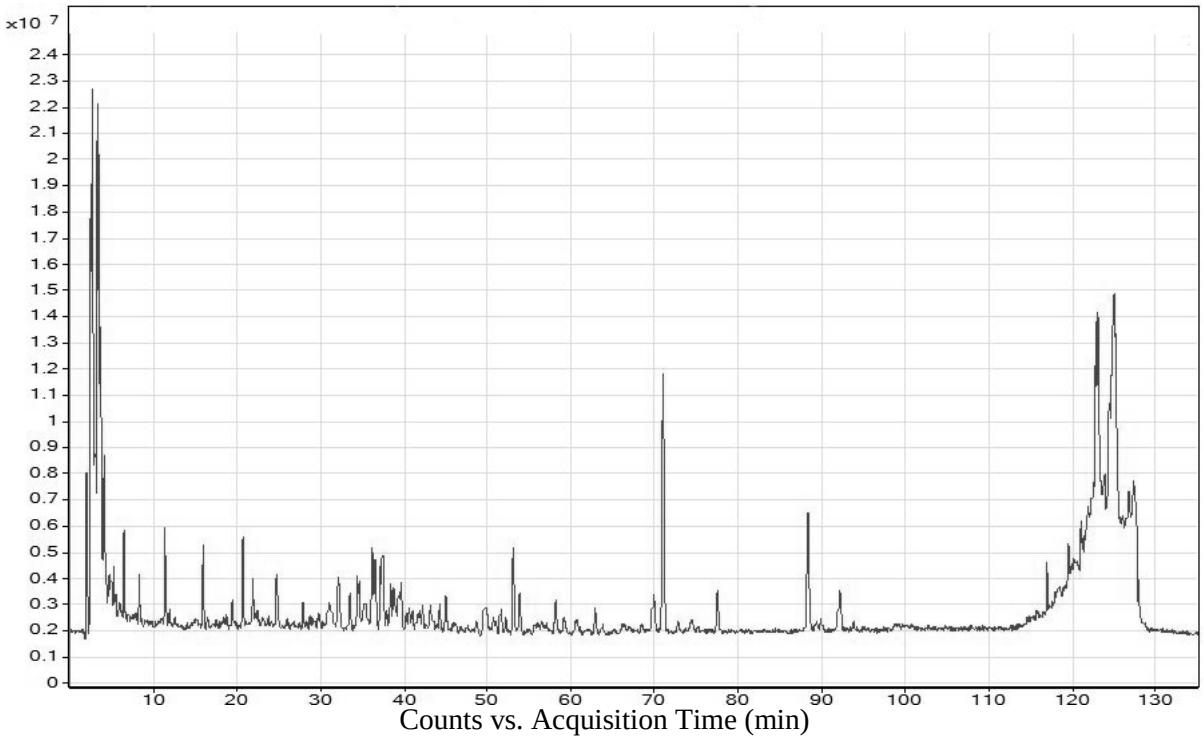
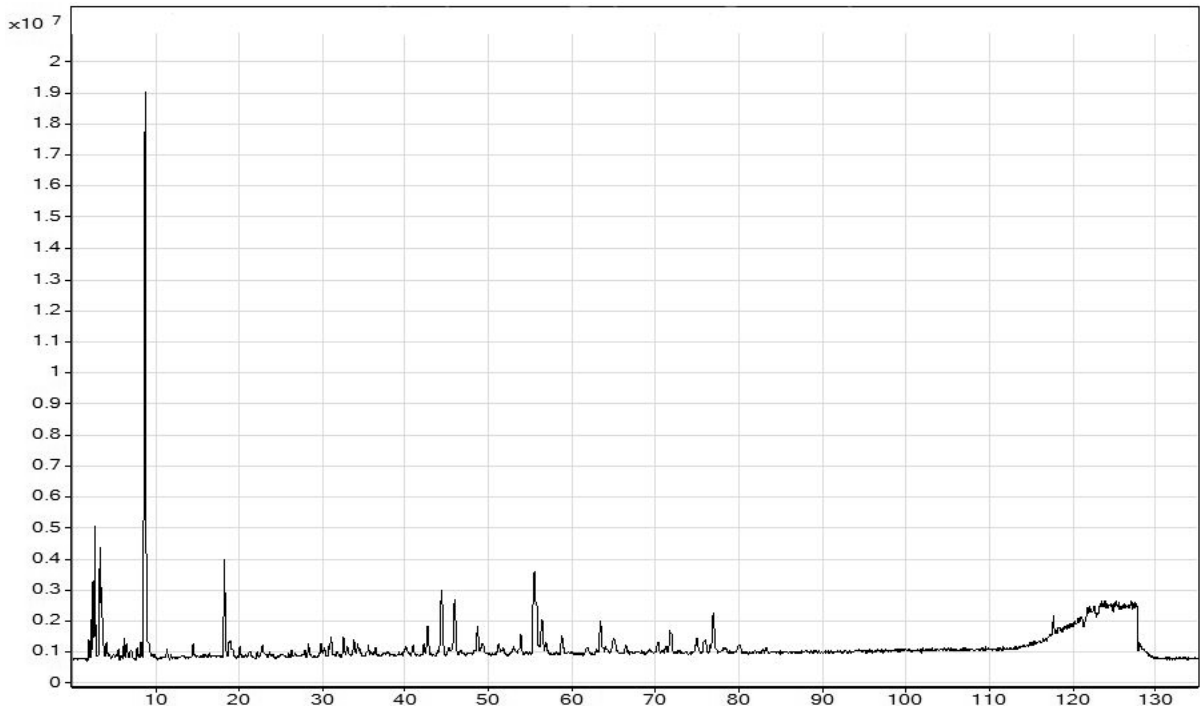


Fig. S6 Total ion chromatogram of SCU in a) negative and b) positive ionization mode.

a)



b)

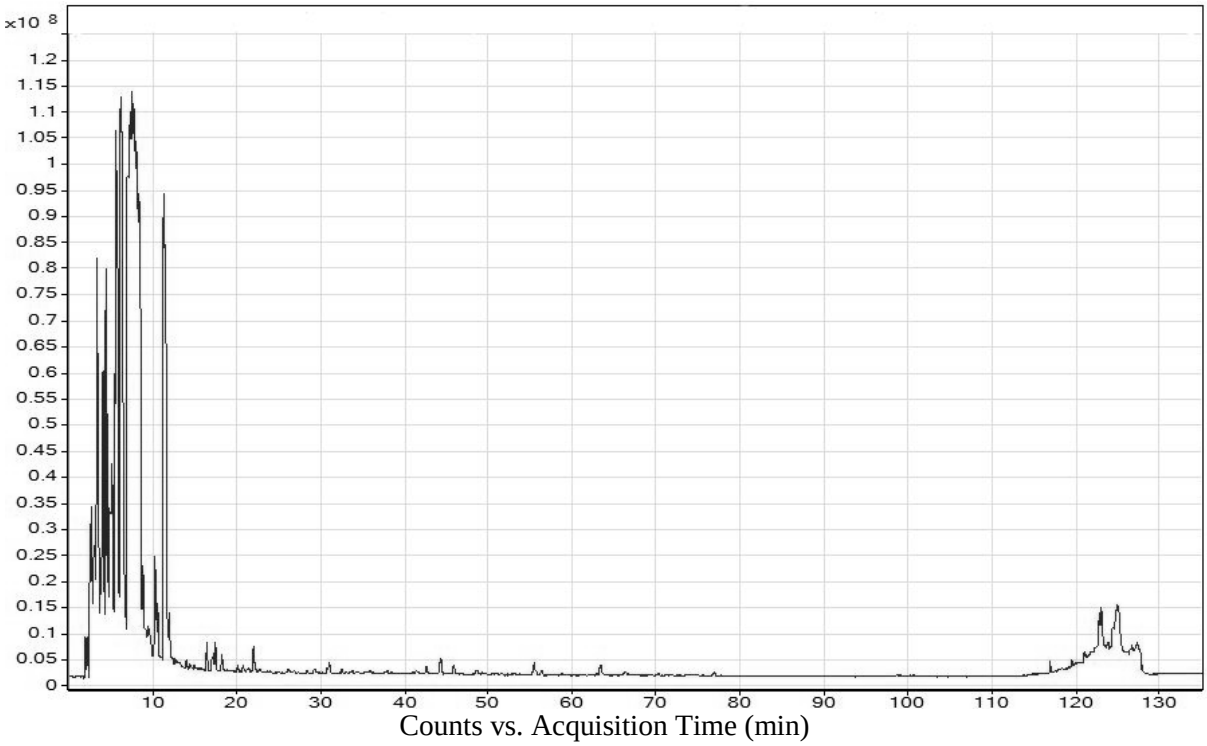


Fig. S7 Total ion chromatogram of SOP in a) negative and b) positive ionization mode.

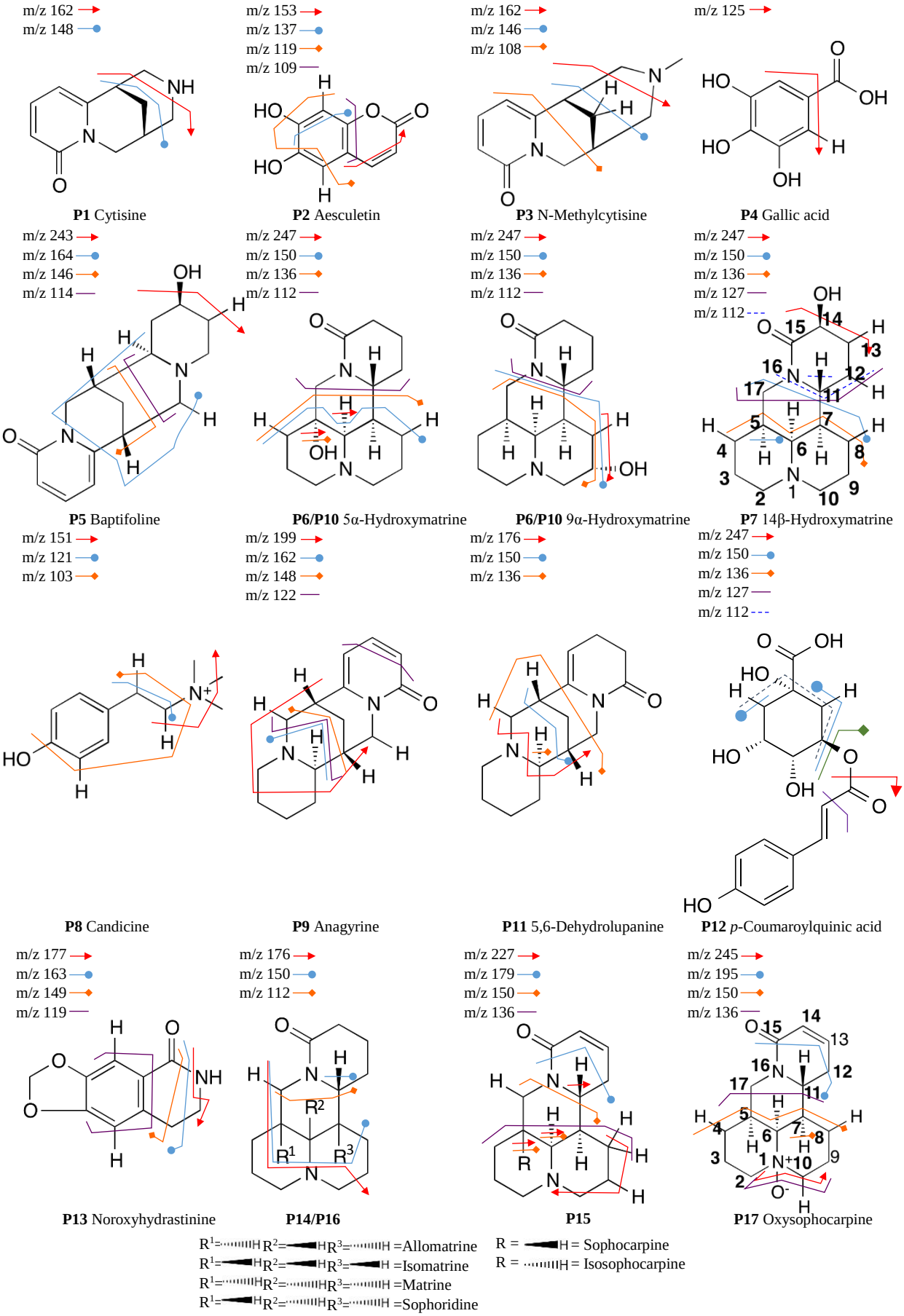


Fig. S8 Fragmentation pathways of putatively identified compounds in positive ionization mode.

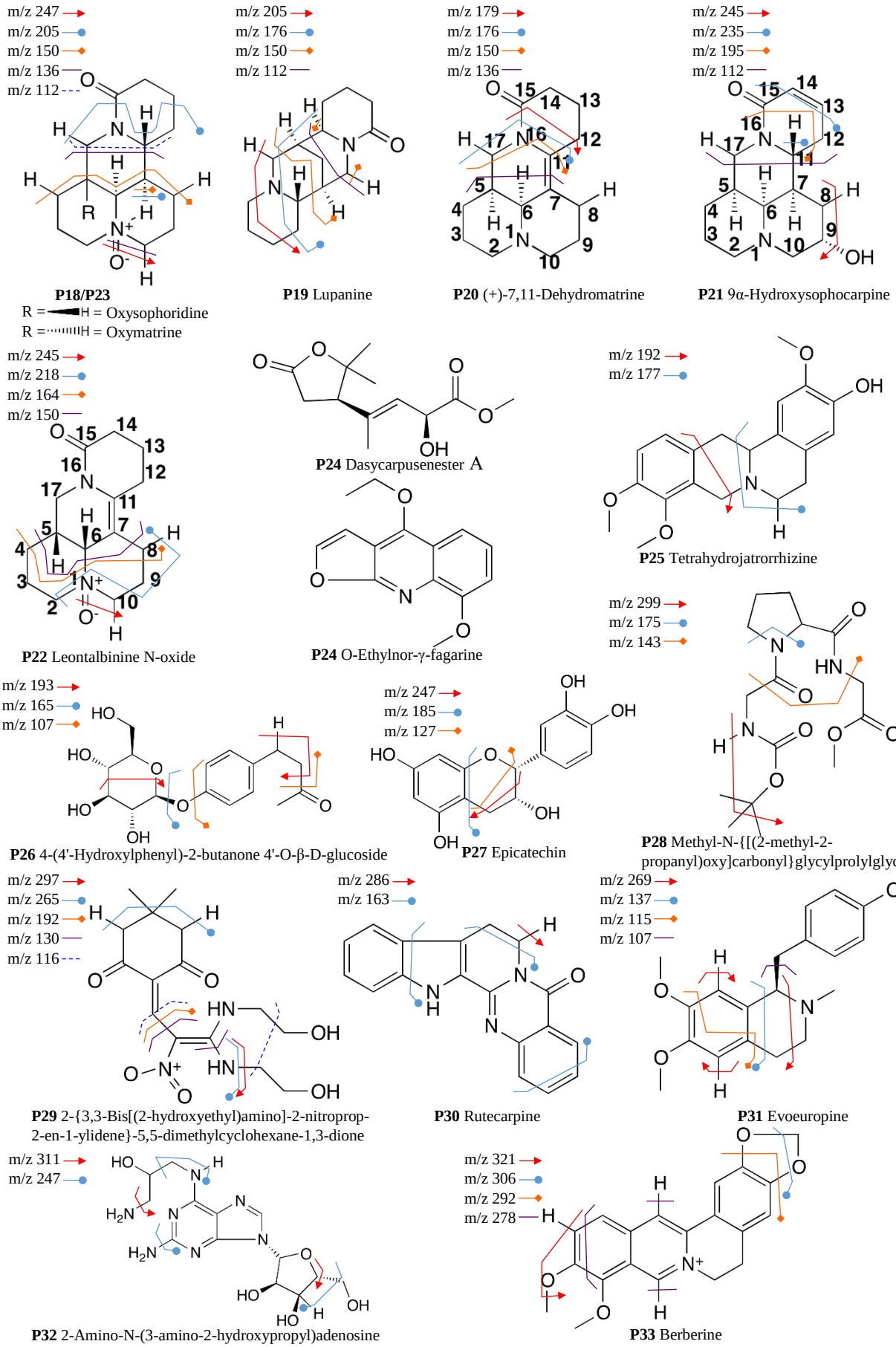


Fig. S8 Fragmentation pathways of putatively identified compounds in positive ionization mode.

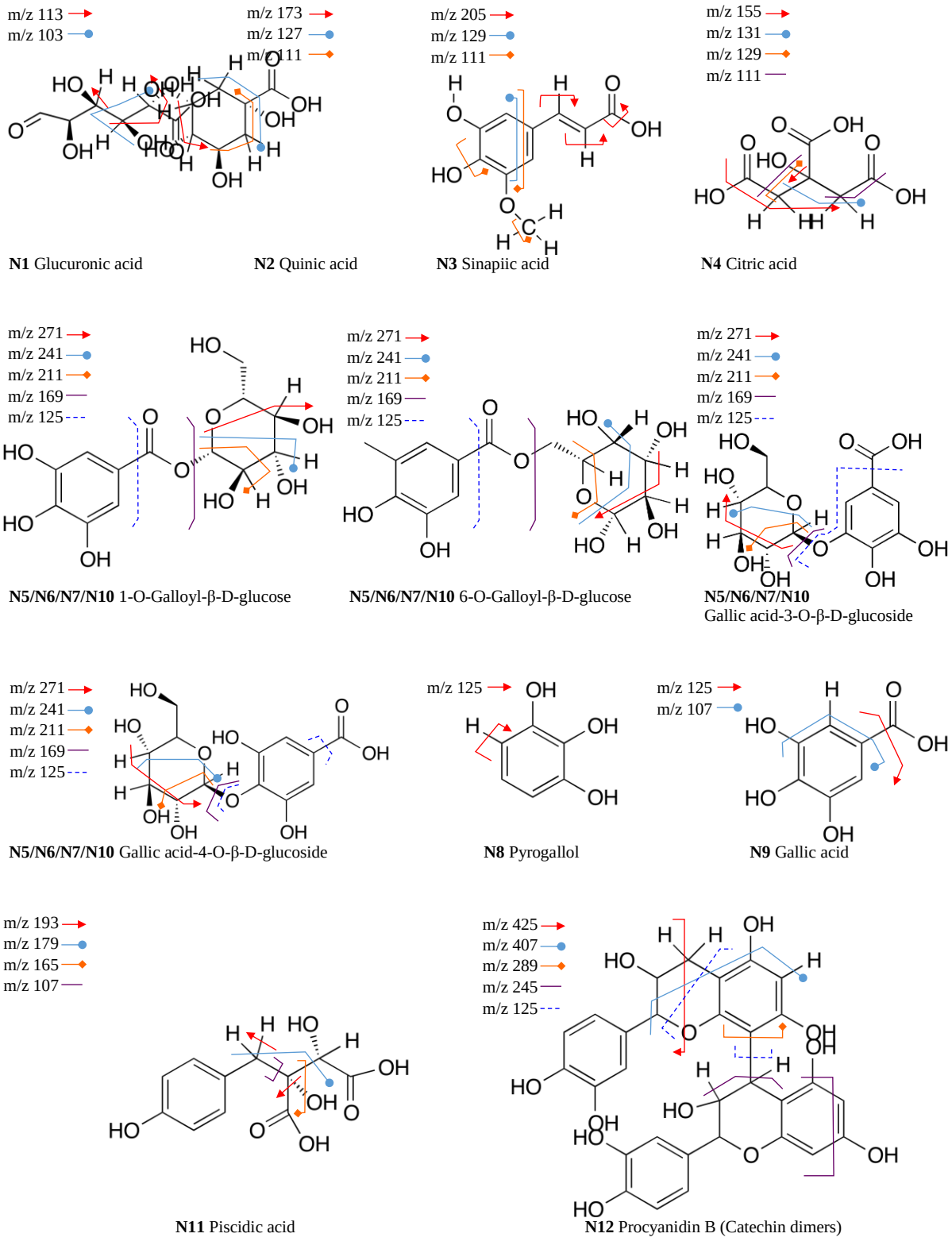
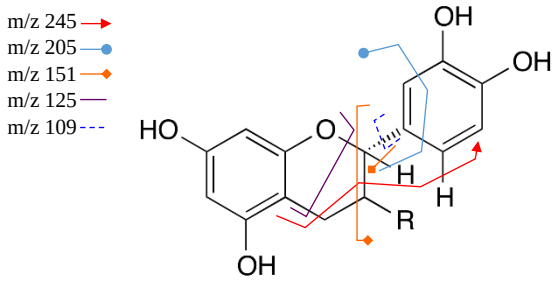
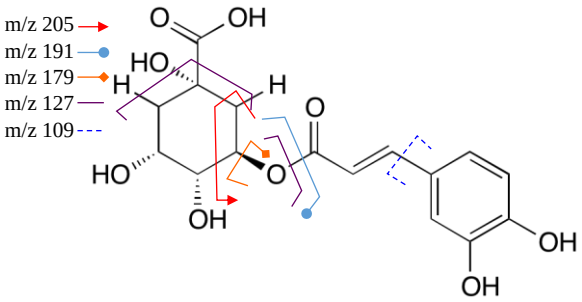


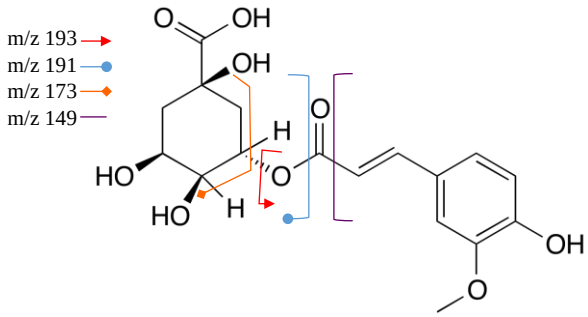
Fig. S9 Fragmentation pathways of putatively identified compounds in negative ionization mode.



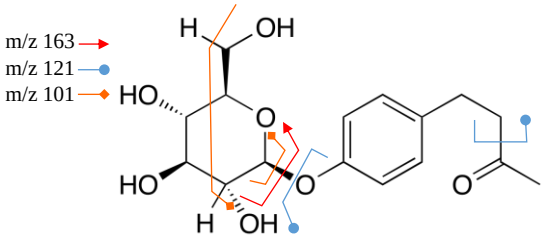
N13/N18 R = OH = Catechin
R = OH = Epicatechin



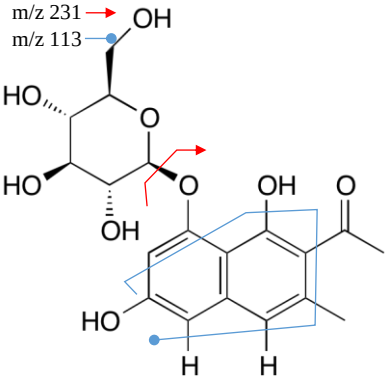
N14 Chlorogenic acid



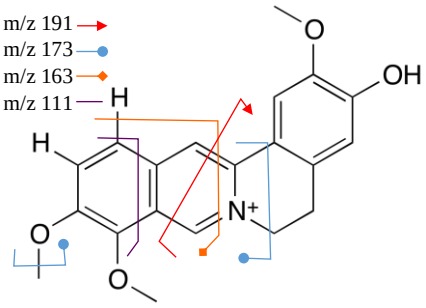
N15 3-*O*-Feruloylquinic acid



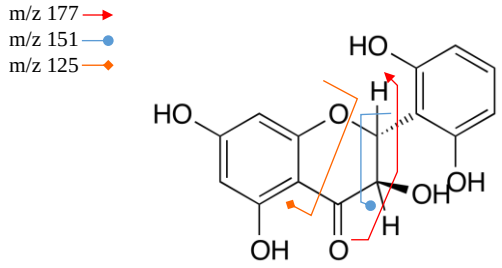
N16 4-(4'-Hydroxylphenyl)-2-butanone 4'-O-β-D-glucoside



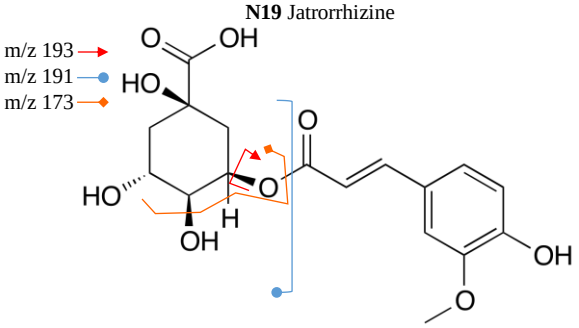
N17 6-Hydroxymusizin-8-O- β-D-glucoside



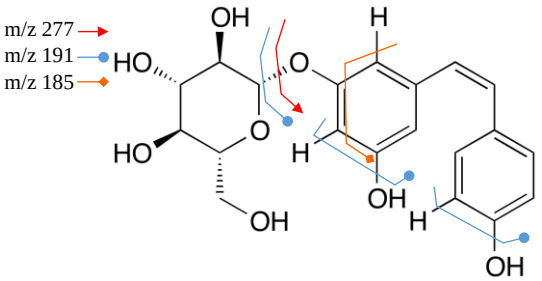
N19 Jatrorrhizine



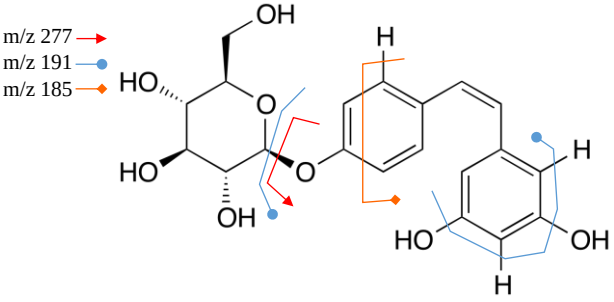
N20 2',3,5,6',7-Pentahydroxyflavanone (Ganhuangemin)



N21 5-*O*-Feruloylquinic acid

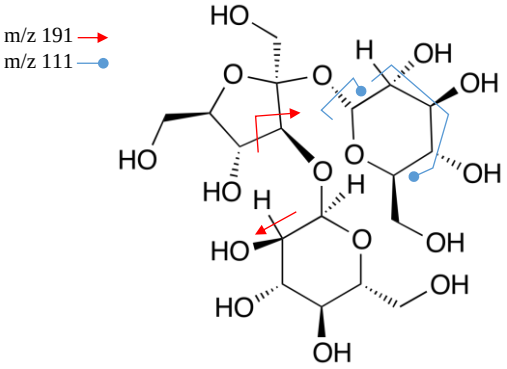


N22 Resveratrol 3-O-ß-glucoside

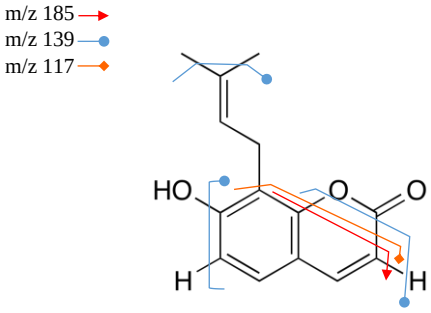


N22_Resveratrol 4'-O-ß-glucoside

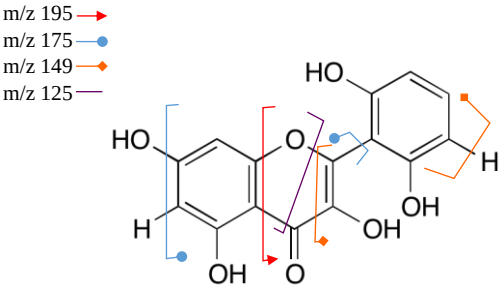
Fig. S9 Fragmentation pathways of putatively identified compounds in negative ionization mode.



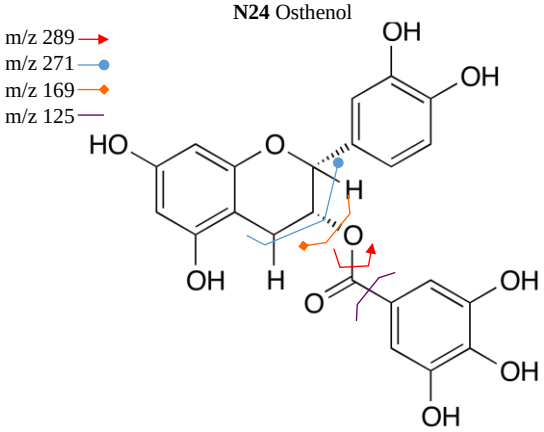
N23 Melezitose



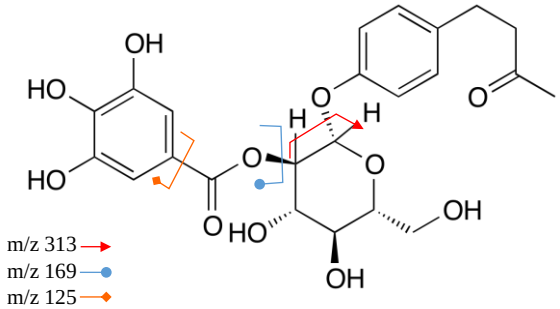
N24 Osthenol



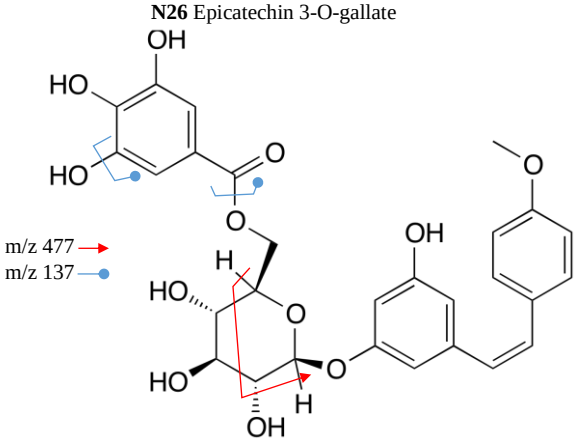
N25 3,5,7,2',6'-Pentahydroxyflavone (Viscidulin I)



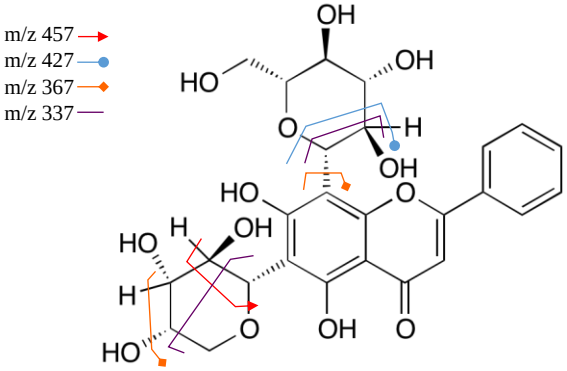
N26 Epicatechin 3-O-gallate



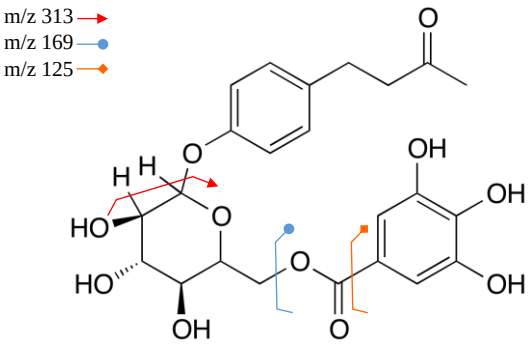
N27 Isolindleyin



N28 Desoxyrhaponticin-6"-O-gallate

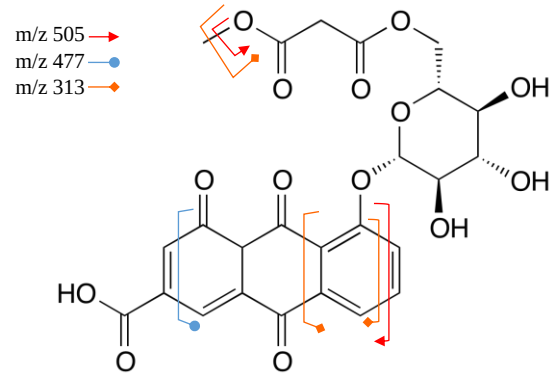


N29 Chrysin-6-C-arabinosyl-8-C-glucoside

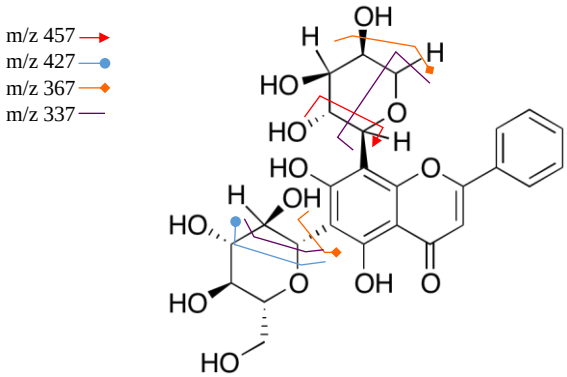


N30 Lindleyin

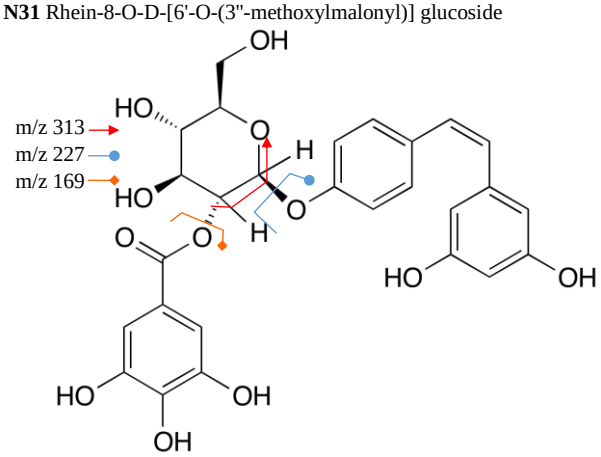
Fig. S9 Fragmentation pathways of putatively identified compounds in negative ionization mode.



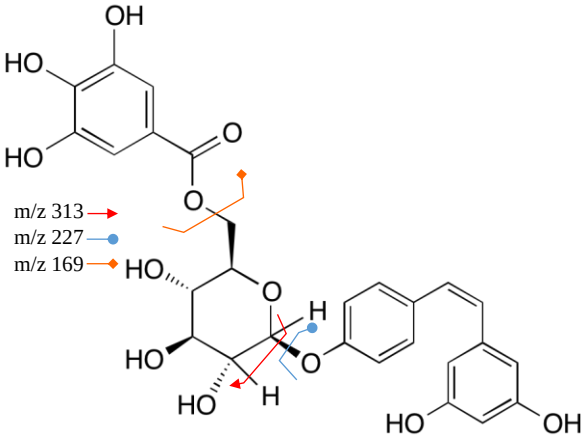
N31 Rhein-8-O-D-[6'-O-(3"-methoxylmalonyl)] glucoside



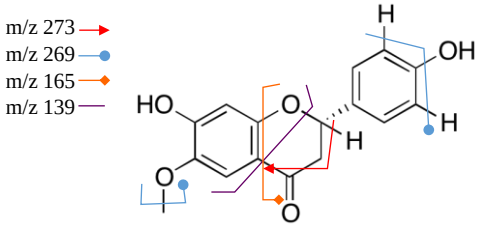
N32 Chrysin-6-C-glucosyl-8-C-arabonoside



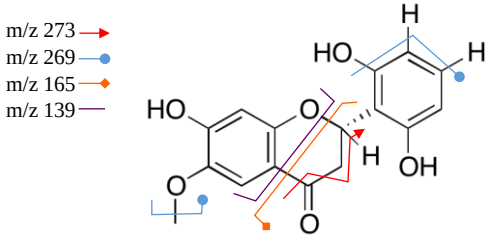
N33 Resveratrol-4'-O-β-D-(2"-O-galloyl) glucoside



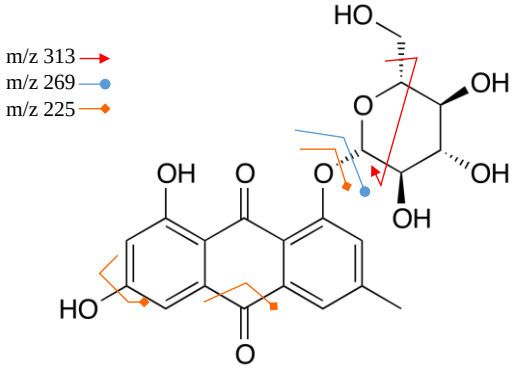
N34 Resveratrol-4'-O-β-D-(6"-O-galloyl) glucoside



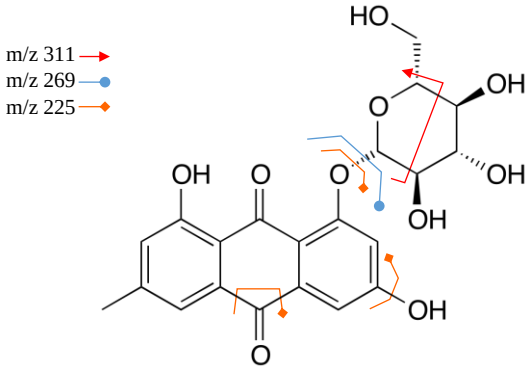
N35_4',5,7-trihydroxy-6-methoxyflavanone



N35_(2S)-7,2',6'-trihydroxy-5-methoxyflavanone



N36/N38_Emodin-1-O-ß-D-glucoside



N36/N38_Emodin-8-O-ß-D-glucoside

Fig. S9 Fragmentation pathways of putatively identified compounds in negative ionization mode.

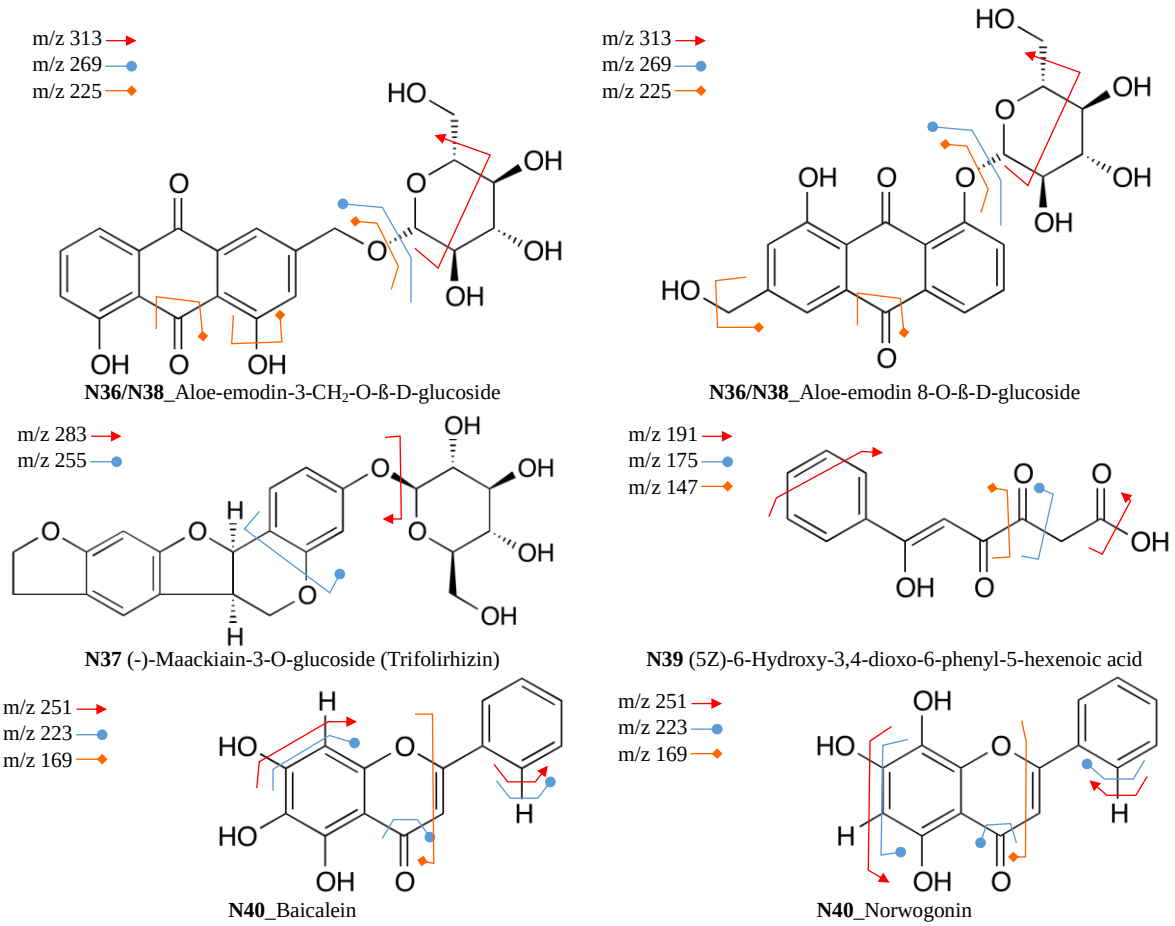


Fig. S9 Fragmentation pathways of putatively identified compounds in negative ionization mode.

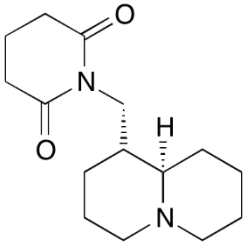


Fig. S10 Chemical structure of Lamprolobine

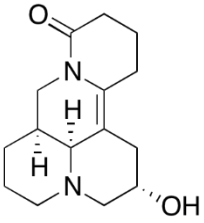


Fig. S11 Chemical structure of (-)-9α-Hydroxy-7, 11-dehydromatrine

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