Supplementary file

UHPLC-MS metabolome based classification of umbelliferous fruit taxa: A prospect for phyto-equivalency of its different accessions and in response to roasting

Ahmed Serag [a], Mostafa H. Baky [b], Stefanie Döll [c], Mohamed A. Farag [d,e*]

[a] Pharmaceutical Analytical Chemistry Department, Faculty of Pharmacy, Al-Azhar University, Cairo, 11751, Egypt.

[b] Pharmacognosy Department, Faculty of Pharmacy, Egyptian Russian University, Cairo, 11829, Egypt.

[c] Department of Stress and Developmental Biology, Leibniz Institute of Plant Biochemistry, Weinberg 3, D-06120 Halle (Saale), Germany.

[d] Pharmacognosy Department, Faculty of Pharmacy, Cairo University, Cairo, 11562, Egypt

[e] Chemistry Department, School of Sciences & Engineering, The American University in Cairo, New Cairo, Egypt

*Corresponding author email address: Mohamed.farag@pharma.cu.edu.eg (M.A. Farag)

Suppl. Code S1

R script used for extracting the UHPLC-MS features of the examined umbelliferous fruits

loading xcms library####

```
library(xcms)
```

Setting working directory and assigning the UHPLC-MS files

```
setwd("F:\\ umbelliferae ") ### for Windows
lpath<-"."
files <- list.files(lpath, full.names = T, pattern = ". mzXML ", recursive = T)
```

####Peak detection of the chromatographic features in each sample using "centwave" algorithm#####

```
  xset <- xcmsSet(files=files, method='centWave', ppm=25, peakwidth=c(5,12), snthr=3,
 verbose.columns=F, scanrange=c(100,1800), prefilter=c(3,500),nSlaves=10)
```

####Grouping the peaks across all the samples#####

```
xset_group1 <- group(xset, minfrac = 0.5, bw = 5, mzwid = 1, max = 50)
```

####Retention time alignment#####

```
xset_retcor1 <- retcor(xset_group1, plottype ="mdevden", span = 1, missing = 1, extra = 1)
```

####Regrouping after alignment#####

```
xset_group2 <- group(xset_retcor1, minfrac = 0.5, bw=2, mzwid=0.05)
```

####Filling the missing data using the raw data files#####

```
xset_filled <- fillPeaks(xset_group2)
```

####Generating the final raw data matrix of the detected EICs#####

```
values <- groupval(xset_filled, value="into")
```

####Saving the matrix in a csv file for further processing#####

```
write.csv(values, file=" umbelliferae _neg_minfrac0.5.csv")
```

Suppl. Table S1. Metabolites identified in methanol extracts of investigated umbelliferous fruits *via* UHPLC-PDA-ESI-QToF/MS in negative and positive ionization modes. Confidence levels of annotation are reported according to the guidelines of the Metabolomics Society and coded as follow: 1. Match to reference standard or full 2D structure elucidation. 2. Probable structure based on MS/MS information and data base search. 3. Possible structure or class or isomers. 4. Unknown.

Peak No.	**RT (sec)**	**UV (nm)**	**Mol. ion m/z (±)**	**Molecular formula**	**error (ppm)**	**Name**	**Class**	**MS/MS**	**Confidence level of annotation**
1	29.1	255	377.0853	$C_{18}H_{17}O_9^-$	6.8	Unknown lignan	Lignan	341, 195	3
2	31.6	257	278.1236	$C_{11}H_{20}NO_7^+$	-0.8	*N*-rhamnosyl proline	Acylated amino acid	260, 242	2
3	39.8	257	280.1394	$C_{11}H_{22}NO_7^+$	-1.1	Fructosyl-*O*-valine	Acylated amino acid	262,244, 216,118	2
4	48.2	254	294.1553	$C_{12}H_{24}NO_7^+$	-1.9	Isoleucyl-*O*-hexose	Acylated amino acid	276, 258, 230, 132	3
5	58.8	252	205.0336	$C_7H_9O_7^-$	8.7	Homo(iso)citric acid	Organic acid	111	2
6	66.7	251	328.1399	$C_{15}H_{22}NO_7^+$	-2.4	Fructosyl-*O*-phenylalanine	Acylated amino acid	310, 292, 264, 166	2
7	98.5	nd	315.0715	$C_{13}H_{15}O_9^-$	2	Di-hydroxybenzoic acid-*O*-hexoside	Phenolic acid	153, 109,108	3
8	106.2	254	329.0877	$C_{14}H_{17}O_9^-$	0.2	Vanillic acid-*O*-hexoside	Phenolic acid	167,152, 123,108	3

9	109.1	250	431.1185	$C_{18}H_{23}O_{12}^-$	2.3	Unknown	Unknown	231, 216,128, 192, 137, 93	4
10	119.1	nd	347.1713	$C_{16}H_{27}O_8^-$	-0.5	p-Menth-ene-triol-*O*-hexoside	Terpene	----	3
11	120.45	323	353.0878	$C_{16}H_{17}O_9^-$	0.2	*O*-caffeoyl quinic acid (Chlorogenic acid)	Phenolic acid	315, 299, 277, 191	1
12	139.7	nd	359.0973	$C_{15}H_{19}O_{10}^-$	3	Syringic acid-*O*-hexoside	Phenolic acid	197, 182, 153	3
13	142.6	nd	380.1547	$C_{15}H_{26}NO_{10}^-$	3.9	Pantothenic acid-*O*- hexoside	Nitrogenous compound	200, 146	3
14	149	nd	341.0894	$C_{15}H_{17}O_9^-$	-4.8	Caffeic acid-*O*-hexoside	Phenolic acid	179, 135	3
15	153.3	287	205.0954	$C_{11}H_{13}N_2O_2^+$	8.4	Tryptophan	Amino acid	188, 146	1
16	159.4	nd	325.0944	$C_{15}H_{17}O_8^-$	-4.6	Coumaric acid-*O*-hexoside	Phenolic acid	163, 119	3
17	165.1	nd	517.1538	$C_{22}H_{29}O_{14}^-$	4.7	Feruloyl-*O*-dihexoside	Phenolic acid	193	3
18	166.6	255	339.0718	$C_{15}H_{15}O_9^-$	1.1	Esculetin-*O*-glucoside (Esculin)	Coumarin	177	1
19	173.2	319	299.0771	$C_{13}H_{15}O_8^-$	0.4	Hydroxybenzoic	Phenolic acid	137, 93	2

						acid-*O*-hexoside			
20	179.2	323	353.0881	$C_{16}H_{17}O_9^-$	-0.9	*O*-Caffeoyl quinic acid isomer	Phenolic acid	191	3
21	181.4	290	355.1023	$C_{16}H_{19}O_9^-$	3.1	Dihydrocaffeoyl-quinic acid	Phenolic acid	191	2
22	192	264	325.0929	$C_{15}H_{17}O_8^-$	-0.1	Coumaric acid-*O*-hexoside isomer	Phenolic acid	163, 119	3
23	193	264	417.1388	$C_{18}H_{25}O_{11}^-$	3.4	Sinapoyl alcohol derivative	Phenolic acid	209, 194	3
24	194.4	nd	357.1183	$C_{16}H_{21}O_9^-$	2.1	Dihydroferuloyl-*O*-hexoside	Phenolic acid	195	3
25	194.5	255	425.165	$C_{17}H_{29}O_{12}^-$	3.4	Unknown	Unknown	353, 246, 191, 163	4
26	198.1	323	353.0879	$C_{16}H_{17}O_9^-$	-0.4	*O*-caffeoyl quinic acid isomer	Phenolic acid	191	3
27	201.2	290.5	475.1457	$C_{20}H_{27}O_{13}^-$	0.4	Unknown phenolic acid	Phenolic acid	279, 191, 163, 113, 77	3-4
28	204	nd	503.1776	$C_{22}H_{31}O_{13}^-$	-1.1	Sinapyl-*O*-pentosyl hexoside	Phenolic acid	173, 129, 113	3
29	211.2	nd	355.1012	$C_{16}H_{19}O_9^-$	6.2	Feruloyl-*O*-hexoside	Phenolic acid	193, 134	3
30	215	nd	379.0692	$C_{17}H_{15}O_{10}^-$	-5.7	Unknown	Unknown	241,97	4
31	215.5	nd	455.1173	$C_{20}H_{23}O_{12}^-$	4.7	Hydroxycoumarin-*O*-pentosyl	Coumarin	249, 234, 205,190,175	3

						hexoside			
32	215.7	nd	371.0969	$C_{16}H_{19}O_{10}^-$	3.9	Hydroxyferuloyl-*O*-hexoside	Phenolic acid	209, 135	3
33	215.7	nd	507.2065	$C_{22}H_{35}O_{13}^-$	3.5	Unknown	Unknown	361, 199, 113	4
34	217.2	nd	483.2081	$C_{20}H_{35}O_{13}^-$	0.4	Unknown	Unknown	307, 113	3/4
35	221.6	nd	505.1922	$C_{22}H_{33}O_{13}^-$	0.8	Dihydrosinapyl-*O*-pentosyl hexoside	Phenolic acid	173, 113	3
36	223.3	shd 300	337.0934	$C_{16}H_{17}O_8^-$	-1.4	*O*-Coumaroylquinic acid	Phenolic acid	191, 163	2
37	224.2	nd	385.1166	$C_{17}H_{21}O_{10}^-$	-6.7	Sinapic acid-*O*-hexoside	Phenolic acid	223, 208 ,193, 134	2/3
38	224.7	271,330	593.1514	$C_{27}H_{29}O_{15}^-$	-0.4	Apigenin di-*C*-hexoside	*C*-flavonoid	473, 413, 383, 353	2/3
39	228.9	nd	433.2079	$C_{20}H_{33}O_{10}^-$	0.7	Unknown	Unknown	328, 268, 189, 264	4
40	229.8	nd	411.1318	$C_{19}H_{23}O_{10}^-$	-5.3	Unknown	Unknown	257, 241, 97	3
41	231	nd	509.2212	$C_{22}H_{37}O_{13}^-$	5.5	Hydroxy-dimethyl-octenoic acid-di-*O*-hexoside	Fatty acid	441, 113	3
42	235	nd	341.1259	$C_{16}H_{21}O_8^-$	-4.9	Cuminoid C	Terpene	161,119	2

43	237.6	nd	371.0973	$C_{16}H_{19}O_{10}^-$	2.9	Feruloylgluconic acid	Phenolic acid	249,121	2
44	238.1	nd	423.0958	$C_{19}H_{19}O_{11}^-$	-5.9	Unknown	Unknown	241, 97	4
45	239.7	316	413.1445	$C_{19}H_{25}O_{10}^-$	1.9	Unknown phenolic acid	Phenolic acid	241, 97	3
46	240.5	270, 336	367.1027	$C_{17}H_{19}O_9^-$	1.9	*O*-feruloyl quinic acid	Phenolic acid	275, 191	2
47	242.1	nd	343.1406	$C_{16}H_{23}O_8^-$	-2.1	Cuminoid D	Terpene	163	2
48	242.4	nd	387.1329	$C_{17}H_{23}O_{10}^-$	-8.5	Unknown feruloyl derivative	Phenolic acid	191	3
49	243.1	nd	361.1503	$C_{16}H_{25}O_9^-$	0.2	Dihydroxy-dimethyl-octadienoic acid-*O*-hexoside	Fatty acid	199, 155	3
50	243.1	269, 338	579.1327	$C_{26}H_{27}O_{15}^-$	5	Luteolin-6-*C*-hexosyl-8-*C*-pentoside	*C*-flavonoid	459, 429, 357, 298	3
51	248.3	345	447.0947	$C_{21}H_{19}O_{11}^-$	-3.2	Luteolin-*C*-hexoside	*C*-flavonoid	357, 327	3
52	250.6	nd	249.119	$C_{32}H_{34}O_5^+$	3.1	Unknown	Unknown	227, 205, 183, 161	4
53	254.2	326	623.1262	$C_{27}H_{27}O_{17}^-$	-1.4	Luteolin-*O*-hexosyl	*O*-flavonoid	447, 285	3

						hexauronide			
54	258.7	323	385.1145	$C_{17}H_{21}O_{10}^-$	-1.4	Sinapic acid-*O*-hexoside isomer	Phenolic acid	209, 193, 161, 134	3
55	263.7	323	425.142	$C_{20}H_{25}O_{10}^-$	7.9	Dihydroxy-methylbutyl-hydroxycoumarin hexoside	Coumarin	263, 245, 219,161	3
56	268.9	320	389.1218	$C_{20}H_{21}O_8^-$	6.1	Polydatin, Piceid, 3,4,5-Trihydroxystilbene-3-beta-monoglucoside	Stilbene	227, 185	1
57	270.2	322	471.1507	$C_{21}H_{27}O_{12}^-$	0.2	Coumaroyl-*O*-rutinose	Phenolic acid	431, 325, 161, 133	3
58	270.3	342	533.132	$C_{25}H_{25}O_{13}^-$	-3.7	Apigenin di-*C*-pentoside	*C*-flavonoid	473, 443, 383, 353	3
59	270.7	266,335	607.1343	$C_{27}H_{27}O_{16}^-$	-6.3	Apigenin-*O*-hexosyl hexauronide	*O*-flavonoid	431, 269	3
60	271.3	326	331.178	$C_{16}H_{27}O_7^-$	-5.3	p-Menth-ene-diol-*O*-hexoside	Terpene	----	3
61	271.4	nd	609.1427	$C_{27}H_{29}O_{16}^-$	5.5	Rutin	*O*-flavonoid	301,300,270,269	1
62	272.9	270, 238	431.0969	$C_{21}H_{19}O_{10}^-$	-1.3	Apigenin-*C*-	*C*-flavonoid	341, 311, 283,	3

						hexoside		269	
63	276	252, 342	637.1439	$C_{28}H_{29}O_{17}^-$	-4.5	Chrysoeriol-*O*-hexosyl hexauronide	*O*-flavonoid	461, 299, 284	3
64	277.6	255, 353	477.0668	$C_{21}H_{17}O_{13}^-$	1.4	Quercetin-*O*-hexauronide	*O*-flavonoid	301	3
65	279.1	255, 353	463.0854	$C_{21}H_{19}O_{12}^-$	6.1	Quercetin-3-glucoside, Isoquercitrin	*O*-flavonoid	301, 300, 271	1
66	286.4	297	264.0875	$C_{13}H_{14}NO_5^-$	0.9	unknown	Unknown	234, 202	4
67	290	nd	549.0886	$C_{24}H_{21}O_{15}^-$	3.3	Quercetin-*O*-hexosyl malonate	Acylated-*O*-flavonoid	300, 271	3
68	291.1	264, 339	447.0916	$C_{21}H_{19}O_{11}^-$	3.7	Kampferol-*O*-hexoside	*O*-flavonoid	285,284, 255, 227	3
69	292.1	320	515.1186	$C_{25}H_{23}O_{12}^-$	1.7	di-*O*-Caffeoylquinic acid	Phenolic acid	191, 179, 173, 135	2
70	301.2	327	461.0706	$C_{21}H_{17}O_{12}^-$	4.1	Luteolin-*O*-hexauronide	*O*-flavonoid	285	3
71	301.4	327	601.1176	$C_{28}H_{25}O_{15}^-$	3.8	Methoxyoxalyl-dicaffeoylquinic acid	Phenolic acid	335, 233,215, 191,135,179,161	2
72	303.3	267, 330	593.1542	$C_{27}H_{29}O_{15}^-$	-5.1	Apigenin-*O*-dihexoside	*O*-flavonoid	269	3

73	305.9	nd	477.1018	$C_{22}H_{21}O_{12}^-$	4.4	Isorhamnetin-*O*-hexoside	*O*-flavonoid	315, 314, 299, 271	3
74	307.9	nd	505.0965	$C_{23}H_{21}O_{13}^-$	4.5	Quercetin-*O*-hexosyl acetate	Acylated-*O*-flavonoid	300, 271	3
75	310	266, 336	431.1001	$C_{21}H_{19}O_{10}^-$	-3.9	Apigenin-*O*-hexoside	*O*-flavonoid	269, 268	3
76	310.4	288, 320	491.082	$C_{22}H_{19}O_{13}^-$	2.3	Pentahydroxyflavone-*O*-hexouronic acid methyl ether	*O*-flavonoid	315, 300, 271, 255	2
77	311.3	266,341	533.0936	$C_{24}H_{21}O_{14}^-$	0.2	Luteolin-*O*-hexosyl - malonate	Acylated-*O*-flavonoid	447, 285, 284	3
78	314.1	320	531.1705	$C_{23}H_{31}O_{14}^-$	2.7	Ferulic acid derivative	Phenolic acid	193	3-4
79	315	266343	489.1045	$C_{23}H_{21}O_{12}^-$	-1.3	Kaempferol-*O*-hexosyl-acetate	Acylated-*O*-flavonoid	285, 284, 237	3
80	315.6	nd	489.1016	$C_{23}H_{21}O_{12}^-$	4.5	Luteolin-*O*-hexosyl-acetate	Acylated-*O*-flavonoid	447, 243	3
81	315.8	273	463.1233	$C_{22}H_{23}O_{11}^+$	0.4	Trihydroxymethoxy flavone hexoside	*O*-flavonoid	301	3
82	317	268, 339	461.1107	$C_{22}H_{21}O_{11}^-$	-3.9	Chryseriol-*O*-hexoside	*O*-flavonoid	446, 299, 298, 284, 283	3
83	317	nd	475.2174	$C_{22}H_{35}O_{11}^-$	2.2	Unknown	Unknown	353, 273, 189	3

84	317.3	277	359.0767	$C_{18}H_{15}O_8^-$	1.4	Rosmarinic acid	Phenolic acid	197, 161	1
85	320.6	nd	447.0913	$C_{21}H_{19}O_{11}^-$	4.4	Luteolin-*O*-hexoside	*O*-flavonoid	285	3
86	321.3	324	547.1477	$C_{26}H_{27}O_{13}^-$	-3.6	Apigenin-*C*-hexoside-*C*-rhamnoside	*C*-flavonoid	487, 457, 427, 397, 367	3
87	321.4	nd	625.1185	$C_{30}H_{25}O_{15}^-$	2.2	Quercetin-*O*-caffeoyl-hexoside	Acylated-*O*-flavonoid	463, 300, 161	3
88	326.1	nd	477.2345	$C_{22}H_{37}O_{11}^-$	-0.7	Dimethyl-octadienol-di-hexoside	Terpene	301, 113	3
89	326.9	296	499.1232	$C_{25}H_{23}O_{11}^-$	2.9	O-(Dihydroxy-cinnamoyl),-O-(hydroxy-cinnamoyl) quinic acid	Phenolic acid	191, 163, 135, 119	2
90	328.5	280	473.1469	$C_{24}H_{25}O_{10}^-$	-3.4	Cuminoid E	Chalcone	311, 279, 251, 235	2
91	329.5	nd	479.1195	$C_{22}H_{23}O_{12}^-$	2.1	Pentahydroxyflavanone methyl ether hexoside	*O*-flavonoid	333, 285, 255,211, 153,108	3
92	330.1	nd	431.1012	$C_{21}H_{19}O_{10}^-$	-6.6	Luteolin-*O*-rhamnoside	*O*-flavonoid	285	3

93	334.2	nd	529.1351	$C_{26}H_{25}O_{12}^-$	0.1	*O*-caffeoyl-*O*-feruloylquinic acid	Phenolic acid	191, 179,161	2
94	337.6	nd	609.1214	$C_{30}H_{25}O_{14}^-$	5.9	Kaempferol-di-*O*-hexoside	*O*-flavonoid	447, 285, 161	3
95	337.9	266, 335	517.1028	$C_{24}H_{21}O_{13}^-$	-7.7	Apigenin-*O*-hexosyl-malonate	Acylated-*O*-flavonoid	431, 269	3
96	338.5	285	473.1095	$C_{23}H_{21}O_{11}^-$	-1.1	unknown flavonoid	Flavonoid aglycone	263, 219,110	3-4
97	340.4	220, 284	499.1248	$C_{25}H_{23}O_{11}^-$	-0.4	*O*-(Dihydroxy-cinnamoyl),-*O*-(hydroxy-cinnamoyl) quinic acid isomer	Phenolic acid	191, 163, 119	3
98	340.8	284	841.2511	$C_{48}H_{41}O_{14}^-$	-1.1	Miyabenol C glucoside	Stilbene	679, 345	2
99	344.5	218	529.1294	$C_{26}H_{25}O_{12}^-$	2.7	*O*-caffeoyl-*O*-feruloylquinic acid isomer	Phenolic acid	193, 191, 173, 135	3
100	352.6	nd	521.1658	$C_{25}H_{29}O_{12}^-$	1.3	Unknown caffeoyl derivative	Phenolic acid	269, 179,135	3-4
101	356.6	220	339.0859	$C_{19}H_{15}O_6^-$	4.5	p-Coumaric acid-	Phenolic acid	307, 263, 235	2

						O-dihydroxy-cinnamoyl methyl ester			
102	367.1	nd	301.035	$C_{15}H_9O_7^-$	1.2	Quercetin	Flavonoid aglycone	151, 285, 179, 273	1
103	367.4	220	447.2236	$C_{21}H_{35}O_{10}^-$	-2.5	Dimethyl-octadienol-pentosyl-hexoside	Terpene	379, 301, 161	3
104	370.5	268, 349	285.0412	$C_{15}H_9O_6^-$	-2.5	Luteolin; 3',4',5,7-Tetrahydroxyflavone	Flavonoid aglycone	285, 199, 151, 217, 241	1
105	370.7	nd	623.1371	$C_{31}H_{27}O_{14}^-$	5.6	Luteolin-*O*-feruloyl hexoside	Acylated-O-flavonoid	284, 255	3
106	375.8	337	473.1079	$C_{23}H_{21}O_{11}^-$	2.3	Apigenin-*O*-hexosyl acetate	Acylated-O-flavonoid	269, 268	3
107	394.3	nd	245.0444	$C_{13}H_9O_5^-$	4.5	Pimpinellin	Coumarin	245, 213, 185	2
108	396.8	220	245.0449	$C_{13}H_9O_5^-$	2.7	Pimpinellin isomer	Coumarin	213, 185	3
109	397.2	220	298.1803	$C_{19}H_{24}NO_2^+$	-0.6	Unknown	Unknown	133	4
110	397.3	nd	491.2851	$C_{24}H_{43}O_{10}^-$	2.3	Trihydroxy-octadecaenoic acid-hexoside	Hydroxy fatty acid	329, 229, 211	3
111	404	220, 320	453.1329	$C_{28}H_{21}O_6^-$	3.3	Trihydroxystilbene	Stilbene	345, 225	3

						dimer			
112	405.4	220	411.2038	$C_{21}H_{31}O_8^-$	-3.4	Unidentified terpene glycoside	Terpene	331, 97	3
113	409.4	266, 335	269.0467	$C_{15}H_9O_5^-$	-4.3	Apigenin	Flavonoid aglycone	269, 225,201, 151, 117	1
114	410.4	220	215.1289	$C_{11}H_{19}O_4^-$	-0.6	Unknown	Unknown	197, 161	4
115	413	219, 320	679.1994	$C_{42}H_{31}O_9^-$	-3	Miyabenol C	Stilbene	572, 451, 345, 227	2
116	414.8	220	285.0384	$C_{15}H_9O_6^-$	7.3	Kaempferol	Flavonoid aglycone	229, 211, 199, 187	1
117	420.2	nd	327.2181	$C_{18}H_{31}O_5^-$	-1.1	Trihydroxy-octadecadienoic acid	Hydroxy fatty acid	309, 291, 229, 211	3
118	421.2	220	395.1362	$C_{19}H_{23}O_9^-$	-3.7	unknown	Unknown	256, 97	4
119	421.9	nd	299.0559	$C_{16}H_{11}O_6^-$	0.7	Chrysoeriol	Flavonoid aglycone	299, 284	2
120	433	220	301.1071	$C_{17}H_{17}O_5^-$	3.4	Unknown flavonoid	Flavonoid aglycone	285, 264, 230	3
121	446.7	nd	329.2321	$C_{18}H_{33}O_5^-$	3.8	Trihydroxy-octadecaenoic acid	Hydroxy fatty acid	311, 293, 229, 211, 171	3
122	458.5	221	331.248	$C_{18}H_{35}O_5^-$	2.9	Trihydroxy-octadecanoic acid	Hydroxy fatty acid	311, 293,	3
123	465.6	266	163.0765	$C_{10}H_{11}O_2^-$	-0.5	Cumic Acid	Phenolic acid	163, 148, 134,	2

								121	
124	474.6	221	375.1821	$C_{21}H_{27}O_6^-$	-2.1	Unknown	Unknown	329, 281, 227, 101, 97	4
125	479.6	221	313.1079	$C_{18}H_{17}O_5^-$	0.8	Unknown	Unknown	241, 193, 134	4
126	479.7	nd	279.0673	$C_{17}H_{11}O_4^-$	-3.8	Unknown flavonoid	Flavonoid aglycone	279, 251, 235, 117	3
127	480.1	221	309.2055	$C_{18}H_{29}O_4^-$	5.2	Dihydroxy-octadecatrienoic acid	Hydroxy fatty acid	291, 221	3
128	494.4	221	327.2154	$C_{16}H_{31}O_4^-$	7.2	Dihydroxy-palmitic acid	Hydroxy fatty acid	309, 273, 244, 197, 174	3
129	495.1	221	274.274	$C_{16}H_{36}NO_2^+$	0.3	Amino-hexadecanediol	Sphingolipid	230	3
130	497.1	nd	647.1765	$C_{34}H_{31}O_{13}^-$	0.9	Unknown	Unknown	269	4
131	500.5	221	318.2992	$C_{18}H_{40}NO_3^+$	3.2	Amino-methyl-heptadecanetriol	Sphingolipid	256	3
132	501.7	222	307.1907	$C_{18}H_{27}O_4^-$	7	Unknown oxylipid	Oxylipid	235, 185, 121	3
133	513.6	nd	303.1601	$C_{18}H_{23}O_4^-$	0.1	Unknown	Unknown	203, 133	4
134	515.2	222	311.2221	$C_{18}H_{31}O_4^-$	2.5	Dihydroxy-octadecadienoic acid	Hydroxy fatty acid	237, 161	3
135	518	nd	547.2531	$C_{29}H_{39}O_{10}^-$	3.2	Unknown steroid	Steroid	203, 189	3

136	526	221	249.1485	$C_{15}H_{21}O_3^-$	5	Unknown terpene	Terpene	205, 184, 145, 107	3
137	526.8	221	311.1642	$C_{20}H_{23}O_3^+$	-4.3	Unknown	Unknown	293, 264, 175, 121	4
138	533.4	221	293.1765	$C_{17}H_{25}O_4^-$	-2.2	Unknown terpene	Terpene	236, 221	3
139	536.1	320	151.1121	$C_{10}H_{15}O^+$	-2.1	Unknown monoterpene	Terpene	133, 123	3
140	566.9	221	302.3049	$C_{18}H_{40}NO_2^+$	1.5	Amino-octadecanediol	Sphingolipid	284	3
141	586.2	221	313.2383	$C_{18}H_{33}O_4^-$	0.3	Dihydroxy-octadecenoic acid	Hydroxy fatty acid	293, 223, 201, 183	3
142	592.9	222	295.1896	$C_{17}H_{27}O_4^-$	6.3	Unknown terpene	Terpene	251	3
143	594.6	222	313.2384	$C_{18}H_{33}O_4^-$	-1.9	Octadecanedioic acid	Fatty acid	201	3
144	633.9	222	285.2065	$C_{16}H_{29}O_4^-$	2.3	Dihydroxy-hexadecenoic acid	Hydroxy fatty acid	267,223	3
145	640.2	222	564.3269	$C_{27}H_{51}O_9NP^-$	-5.7	Sphingolipid conjugate I	Sphingolipid	279	3
146	658.4	222	297.1535	$C_{16}H_{26}O_3S$	6.7	Unknown	Unknown	265	4
147	663.3	223	540.3273	$C_{25}H_{51}O_9NP^-$	4.7	Sphingolipid conjugate II	Sphingolipid	255	3
148	671.8	222	595.2936	$C_{41}H_{39}O_4^-$	5.9	Unknown	Unknown	315, 279, 241, 152	4

149	674.1	223	315.254	$C_{18}H_{35}O_4^-$	0.4	Dihydroxy-octadecanoic acid	Hydroxy fatty acid	297,269, 253	3
150	675.2	222	595.2877	$C_{34}H_{43}O_9^-$	6	Unknown	Unknown	279, 241, 152	4
151	683.2	223	295.2277	$C_{18}H_{31}O_3^-$	0.6	Hydroxy-octadecadienoic acid	Hydroxy fatty acid	277, 195, 183	3
152	683.5	223	243.1954	$C_{14}H_{27}O_3^-$	4.7	Hydroxy-tetradecanoic acid	Hydroxy fatty acid	-----	3
153	690.2	221	235.1681	$C_{15}H_{23}O_2^+$	4.9	Unknown terpene	Terpene	----	3
154	701.6	223	566.3459	$C_{27}H_{53}O_9NP^-$	4.9	Sphingolipid conjugate III	Sphingolipid	281(-285)	3
155	711.2	nd	293.2112	$C_{18}H_{29}O_3^-$	3.5	Hydroxy-linolenic acid	Hydroxy fatty acid	275, 195, 179	3
156	733.7	223	311.1703	$C_{13}H_{27}O_8^-$	4.1	Unknown	Unknown	205	4
157	788.4	223	325.1829	$C_{21}H_{25}O_3^-$	-6.1	Di-furanyl-dimethyl-undecatrien-ol	Furan	183	3
158	794.2	nd	297.2459	$C_{18}H_{33}O_3^-$	-7.9	Hydroxy-octadecenoic acid	Hydroxy fatty acid	279, 251, 171	3
159	814	nd	271.2273	$C_{16}H_{31}O_3^-$	2.2	Hydroxy-palmitic acid	Hydroxy fatty acid	253, 225	3
160	827	224	227.2008	$C_{14}H_{27}O_2^-$	3.7	Myristic acid	Fatty acid	----	1
161	827.5	nd	277.2184	$C_{18}H_{29}O_2^-$	-3.9	Linolenic acid	Fatty acid	259, 233	2

162	836.4	223	415.226	$C_{28}H_{31}O_3^-$	4.6	Hydroxy-octacosadodecenoic acid	Hydroxy fatty acid	279	3
163	847.6	223	455.3522	$C_{30}H_{47}O_3^-$	1.9	Unknown steroid	Steroid	378, 339, 253	3-4
164	849.9	223	439.3551	$C_{30}H_{47}O_2^+$	4.6	Unknown steroid	Steroid	393, 203, 189	3
165	860.2	224	253.2166	$C_{16}H_{29}O_2^-$	2.8	Palmitoleic acid	Fatty acid	---	2
166	860.5	223	282.2767	$C_{18}H_{36}NO^+$	8.8	Oleamide	Nitrogenous compound	265, 247	2
167	870.2	224	343.2826	$C_{20}H_{39}O_4^-$	8.2	Dihydroxy-arachidic acid	Hydroxy fatty acid	---	3
168	874.7	224	241.2158	$C_{15}H_{29}O_2^-$	6	Pentadecanoic acid	Fatty acid	----	2
169	878.3	224	279.2322	$C_{18}H_{31}O_2^-$	2.8	Linoleic acid	Fatty acid	255	1
170	887.9	224	369.3002	$C_{22}H_{41}O_4^-$	2.3	Docosanedioic acid	Fatty acid	351, 307	2
171	909.4	224	453.3354	$C_{30}H_{45}O_3^-$	4.5	Unknown steroid	Steroid	380, 281, 227, 116	3-4
172	909.5	224	299.2579	$C_{18}H_{35}O_3^-$	4.1	Hydroxy-stearic acid	Hydroxy fatty acid	-----	3
173	919.7	224	327.2886	$C_{20}H_{39}O_3^-$	5.7	Hydroxy-arachidic acid	Hydroxy fatty acid	-----	3
174	920.6	224	255.2331	$C_{16}H_{31}O_2^-$	-0.6	Palmitic acid	Fatty acid	-----	1
175	941.7	nd	281.2496	$C_{18}H_{33}O_2^-$	-3.4	Oleic acid	Fatty acid	------	2

176	949.3	224	284.293	$C_{18}H_{38}NO^+$	6.2	Stearamide	Nitrogenous compound	----	3
177	962	224	269.2481	$C_{17}H_{33}O_2^-$	1.8	Heptadecanoic acid	Fatty acid	------	2
178	980.6	224	310.3104	$C_{20}H_{40}NO^+$	-2.7	Eicosenamide	Nitrogenous compound	----	3
179	990	224	327.2885	$C_{20}H_{39}O_3^-$	5.9	Hydroxy-arachidic acid isomer	Hydroxy fatty acid	----	3
180	993.3	224	326.3424	$C_{21}H_{44}NO^+$	-2	Henicosanamide	Nitrogenous compound	256	2
181	998	224	283.2645	$C_{18}H_{35}O_2^-$	-0.8	Stearic acid	Fatty acid	----	1
182	1011.8	224	309.2789	$C_{20}H_{37}O_2^-$	3.4	Eicosenoic acid	Fatty acid	-----	2
183	1024.6	225	341.3046	$C_{21}H_{41}O_3^-$	4.3	Hydroxy-heneicosanoic acid	Hydroxy fatty acid	295, 183	3
184	1029.4	225	312.3245	$C_{20}H_{42}NO^+$	5.2	Eicosanamide isomer	Nitrogenous compound	----	3
185	1057.3	225	355.3191	$C_{22}H_{43}O_3^-$	7.5	Hydroxy-docosanoate	Hydroxy fatty acid	248, 182	3
186	1065.6	225	311.295	$C_{20}H_{39}O_2^-$	1.8	Arachidic acid	Fatty acid	-----	1

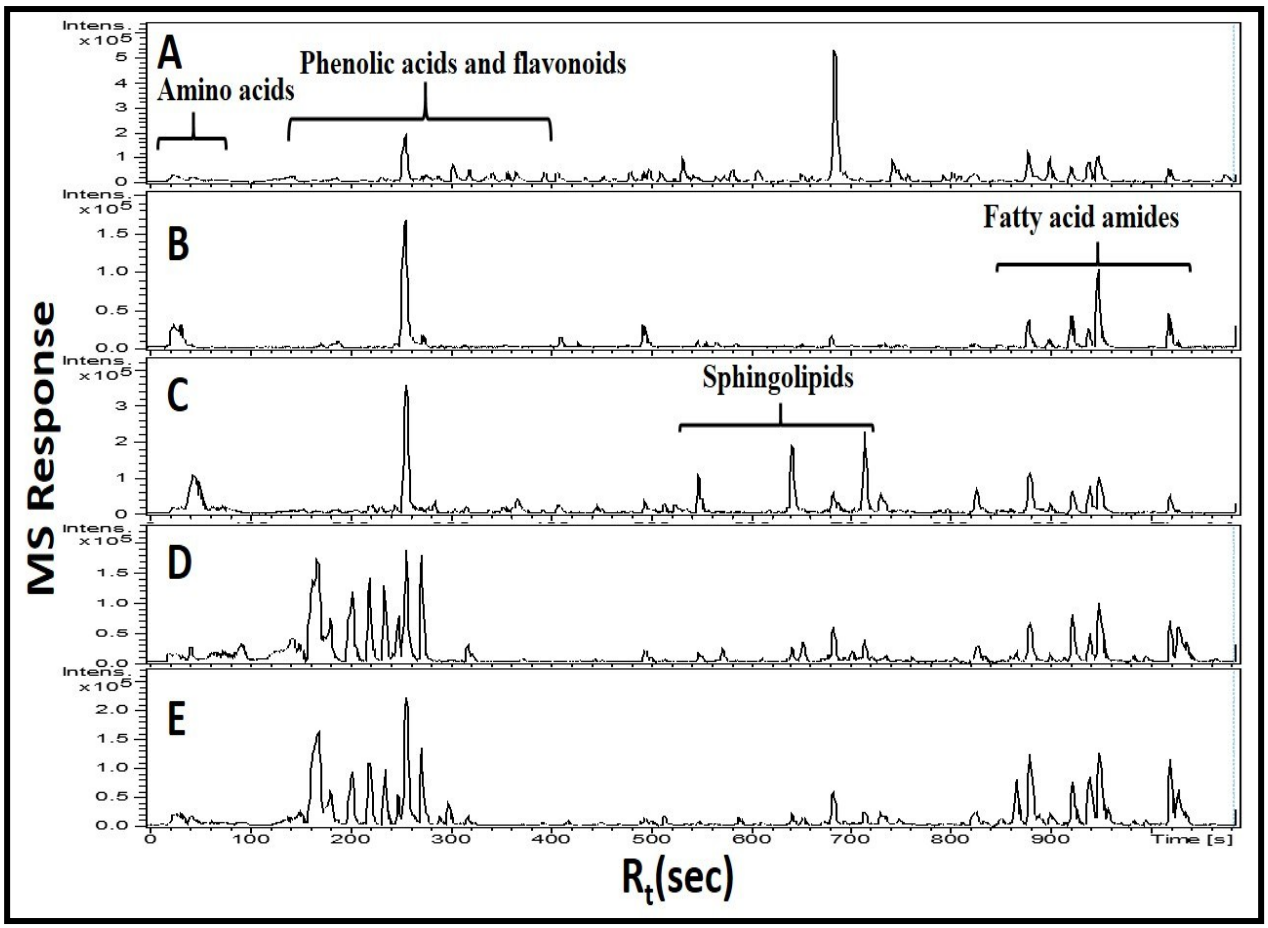

Fig.S1 Representative UHPLC–MS traces analyzed in the positive ion mode of unroasted methanolic extracts of Cumin (A), Fennel (B), Anise (C), Coriander (D) and Caraway (E), characterized by 2 main regions: (150–400 s) with peaks mainly due to amino acids, phenolic acids and flavonoids and a region (550–1000 s) assigned for sphingolipids and fatty acid amides.

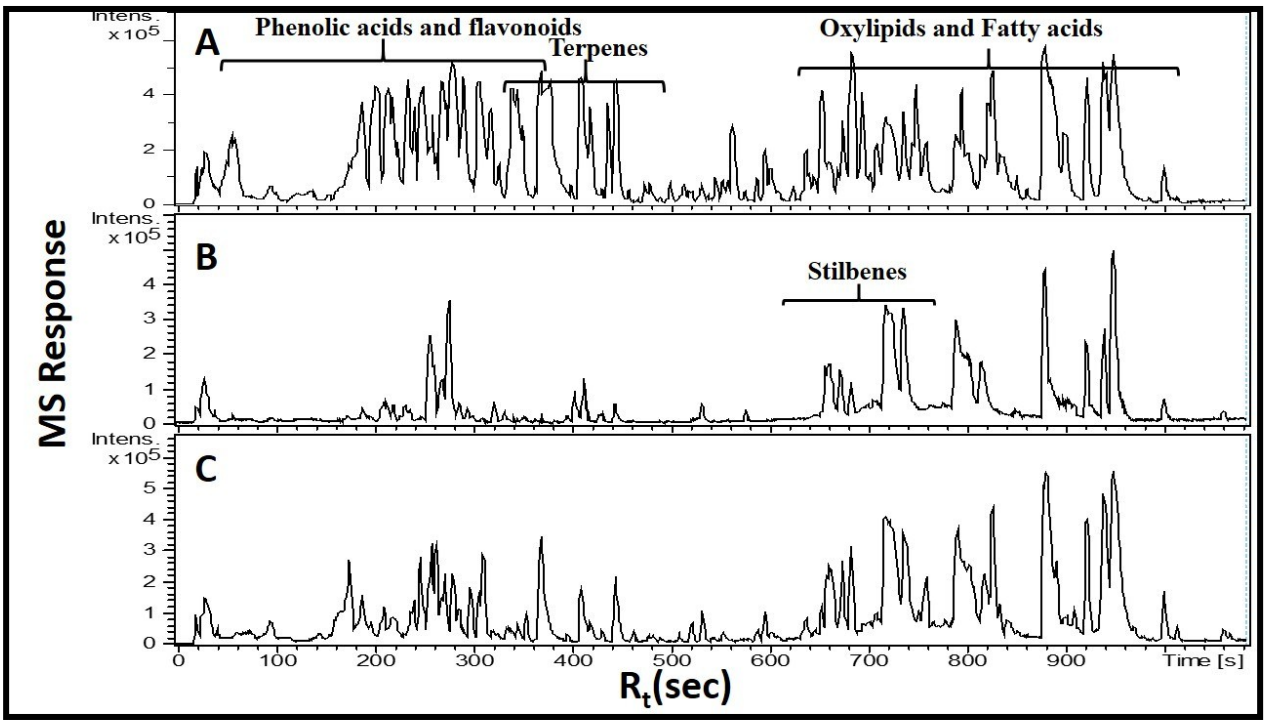

Fig. S2 Representative UHPLC–MS traces analyzed in the negative ion mode of roasted methanol extracts of cumin (A), fennel (B) and anise (C).

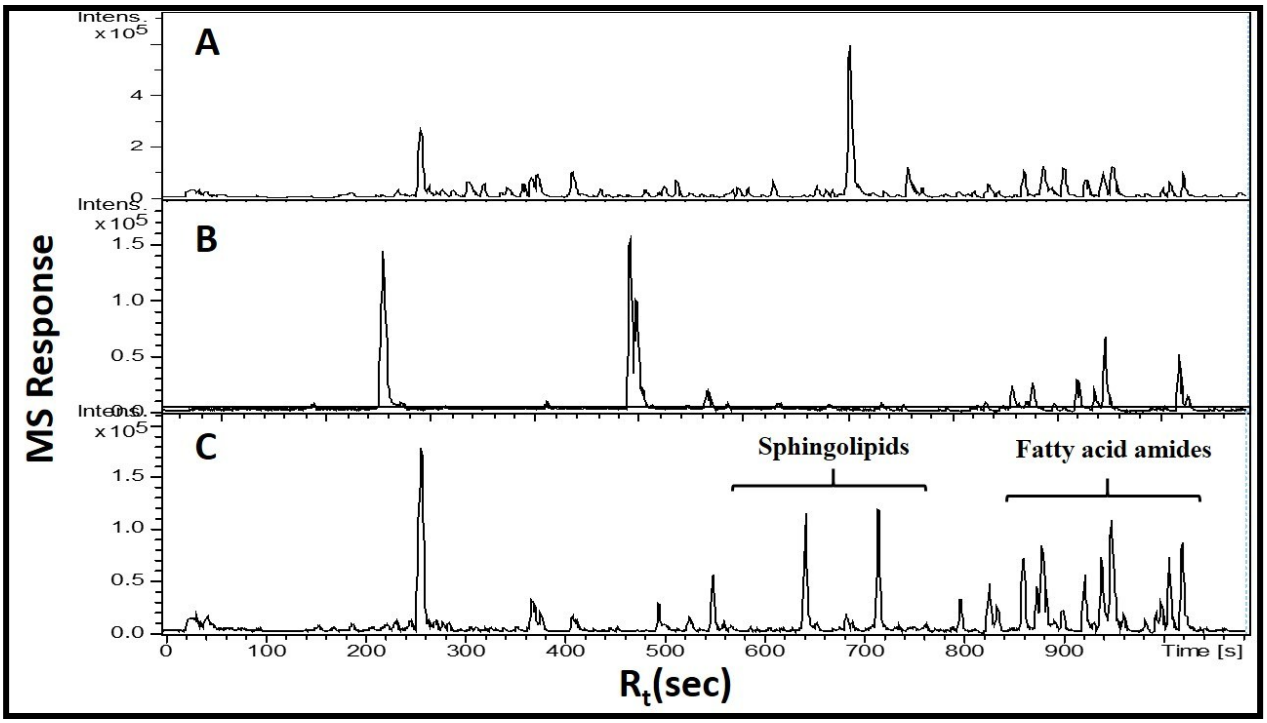

Fig. S3 Representative UHPLC–MS traces analyzed in the positive ion mode of roasted methanol extracts of cumin (A), fennel (B) and anise (C).

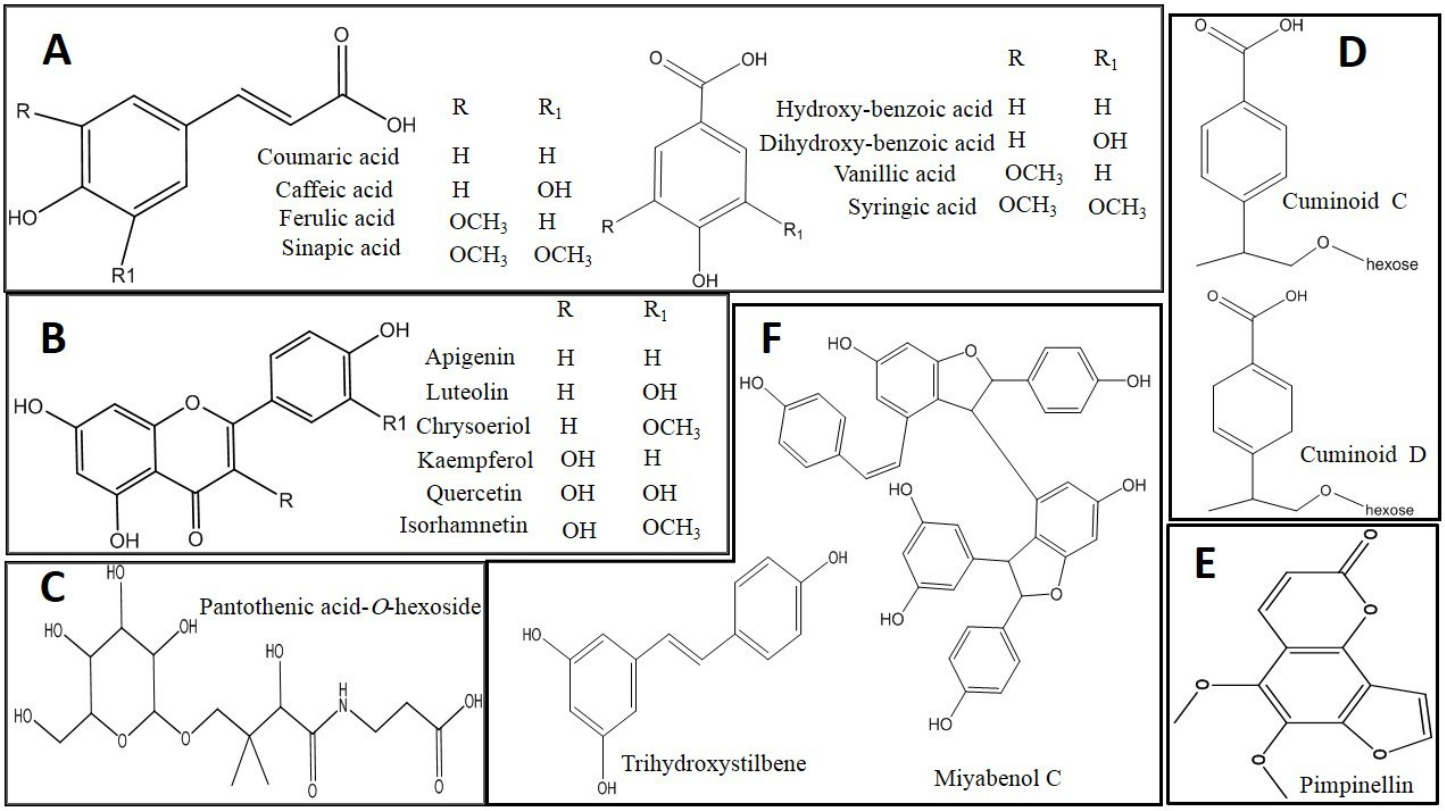

Fig. S4. Major classes of phytochemicals: phenolic acids (A), flavonoids (B), nitrogenous compounds (C), terpenes (D), coumarins (E) and stilbenes (F) detected in the studied umbelliferous fruits.

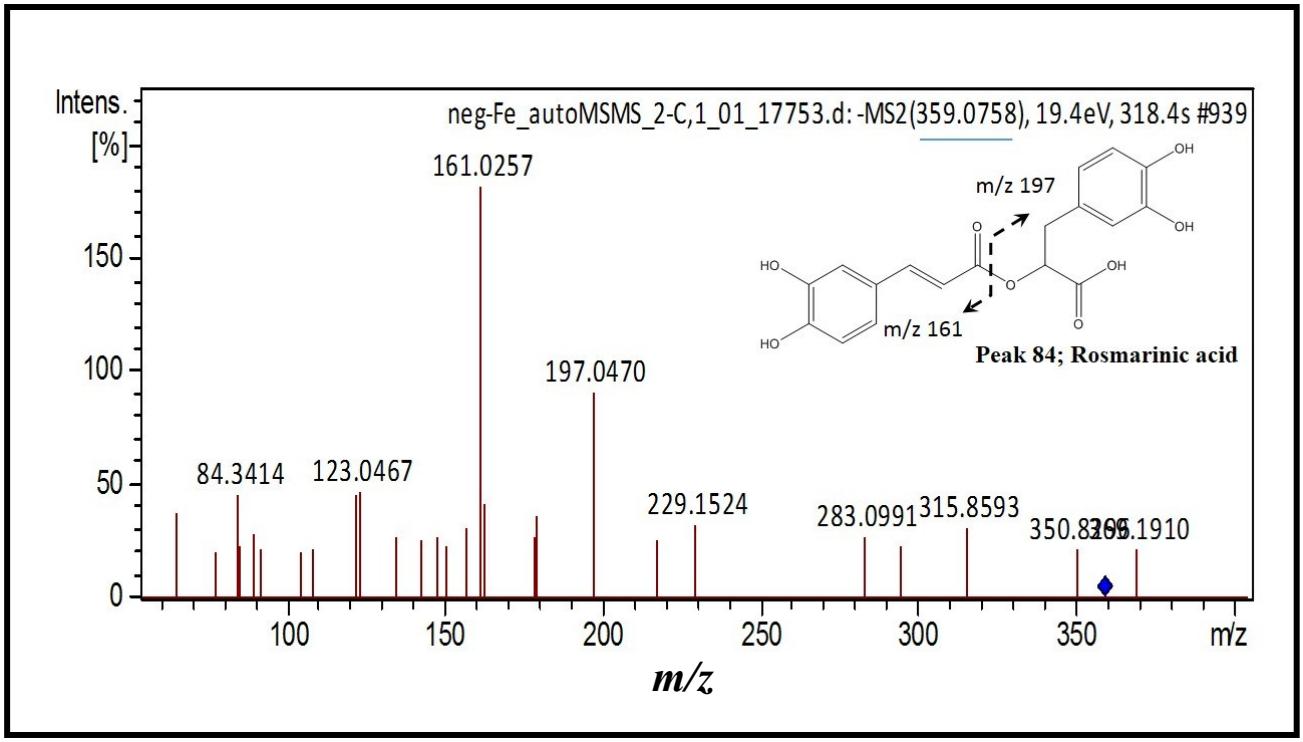

Fig. S5a ESI-MS/MS spectrum of rosmarinic acid (peak 84; $C_{18}H_{15}O_8^-$) in the negative ion mode.

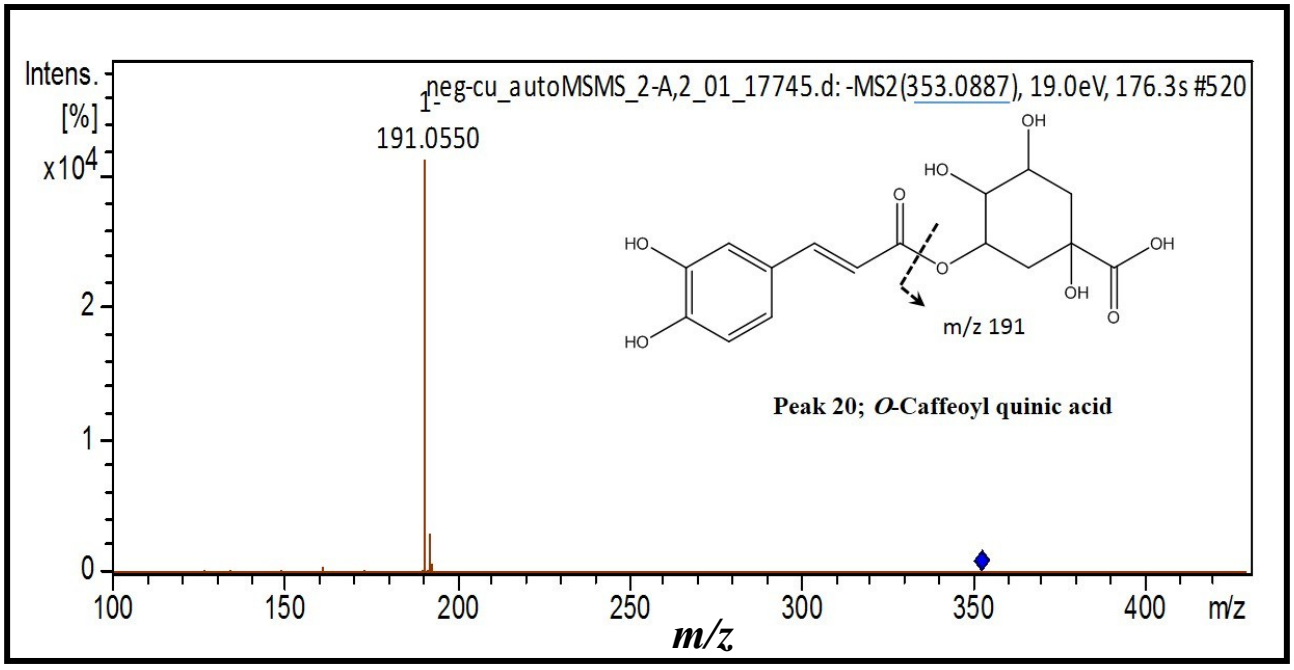

Fig. S5b ESI-MS/MS spectrum of *O*-caffeoyl quinic acid (peak 20; $C_{16}H_{17}O_9^-$) in the negative ion mode.

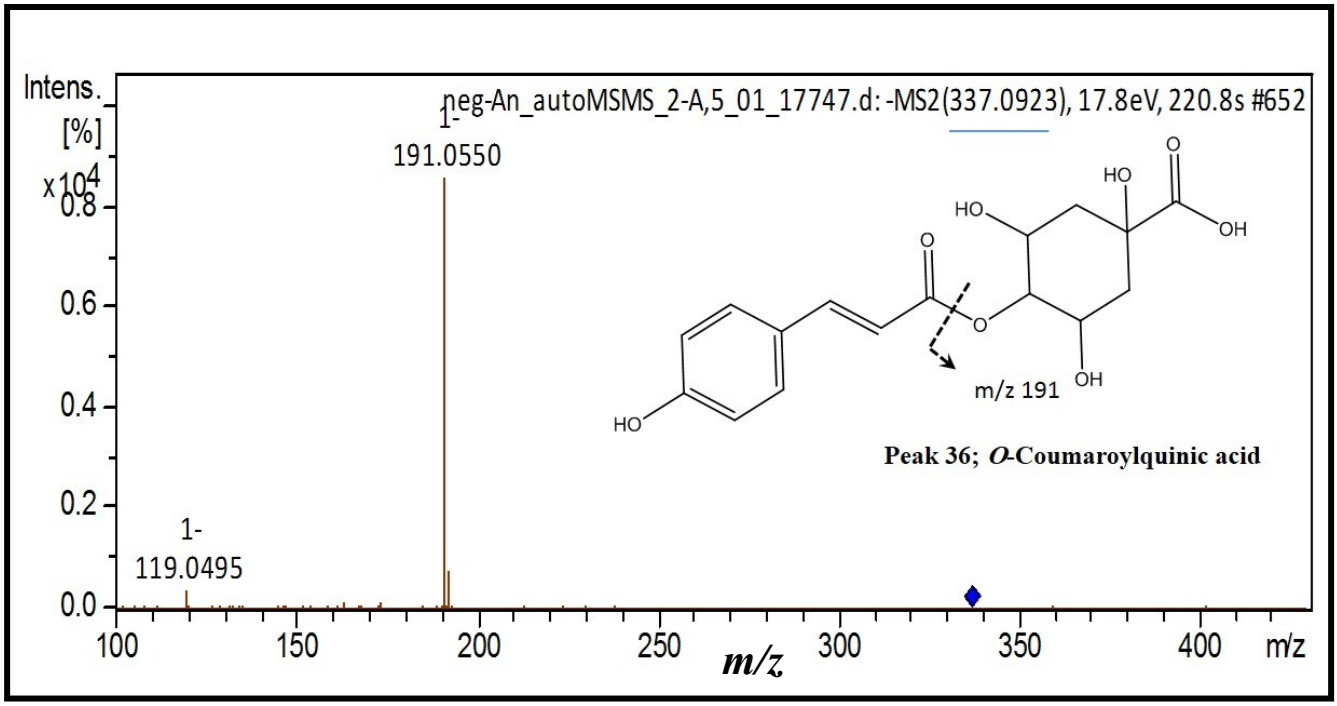

Fig. S5c ESI-MS/MS spectrum of *O*-coumaroylquinic acid (peak 36, $C_{16}H_{17}O_8^-$) in the negative ion mode.

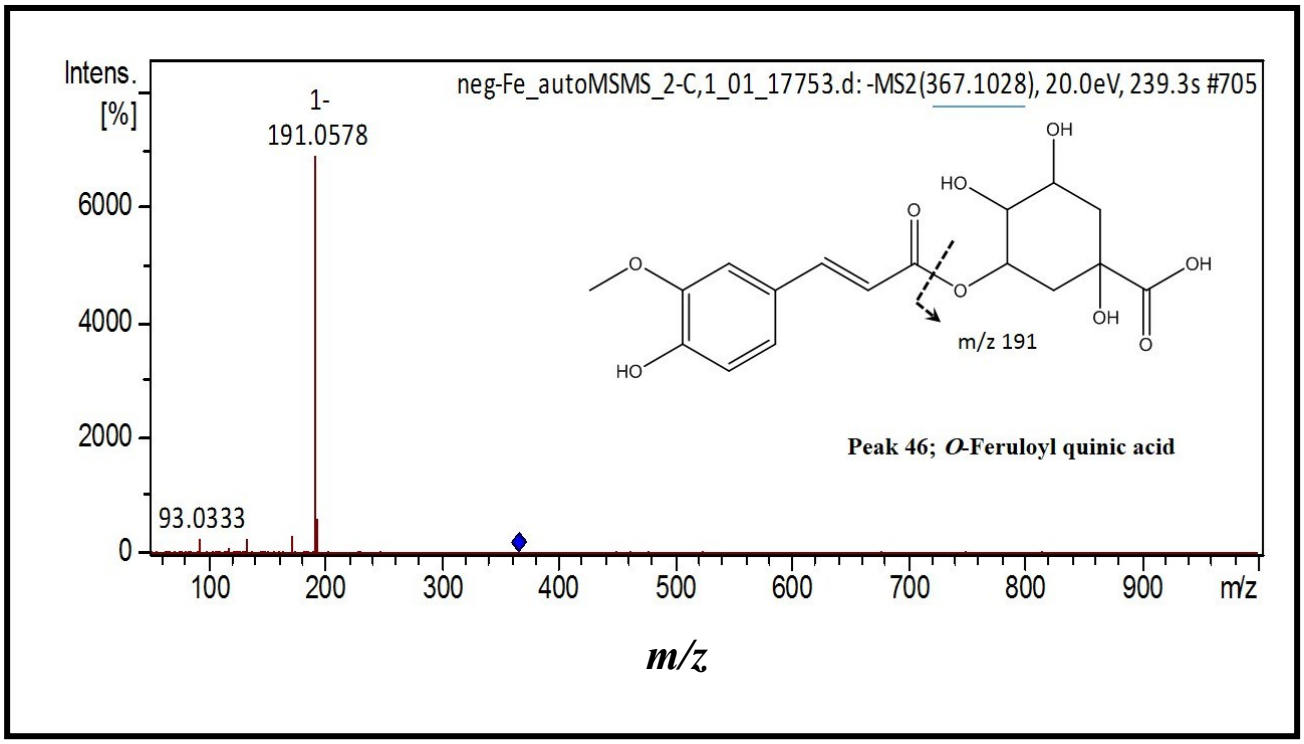

Fig. S5d ESI-MS/MS spectrum of *O*-feruloyl quinic acid (peak 46; $C_{17}H_{19}O_9^-$) in the negative ion mode.

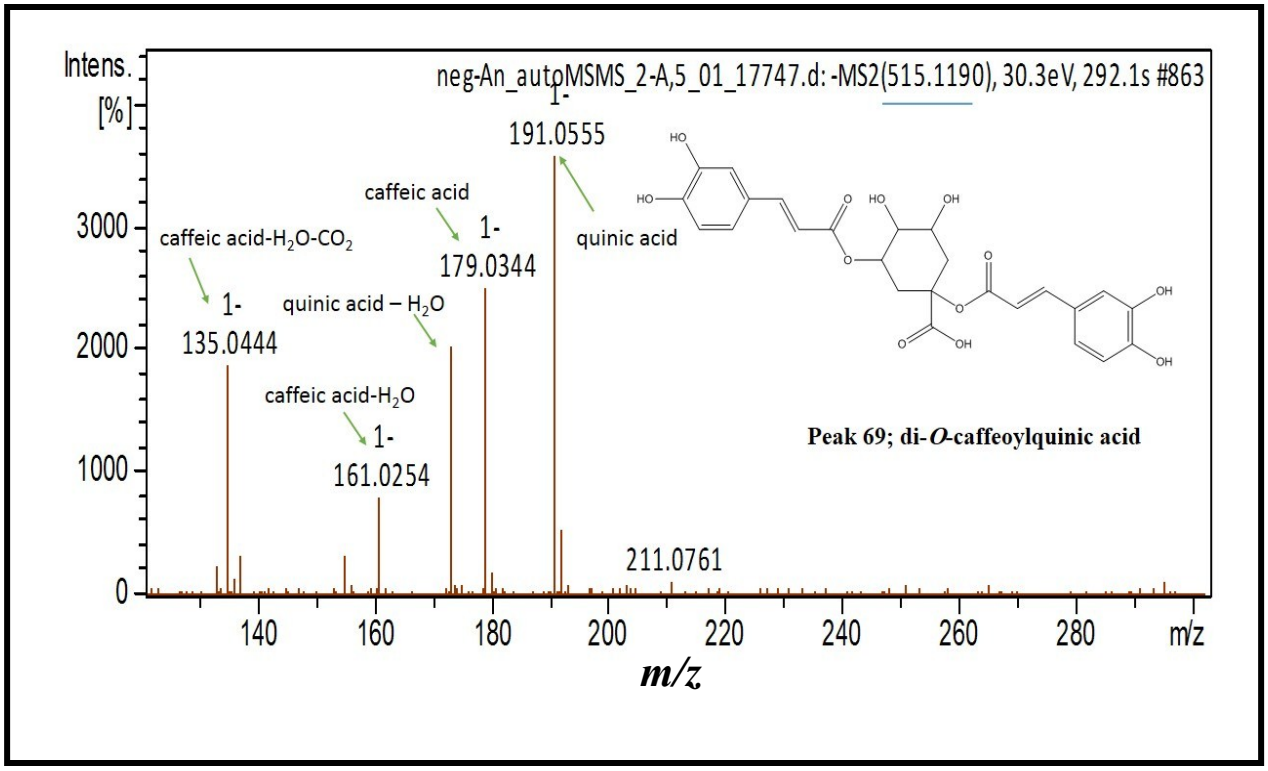

Fig. S5e ESI-MS/MS spectrum of di-*O*-caffeoylquinic acid (peak 69; $C_{25}H_{23}O_{12}^{-}$) in the negative ion mode.

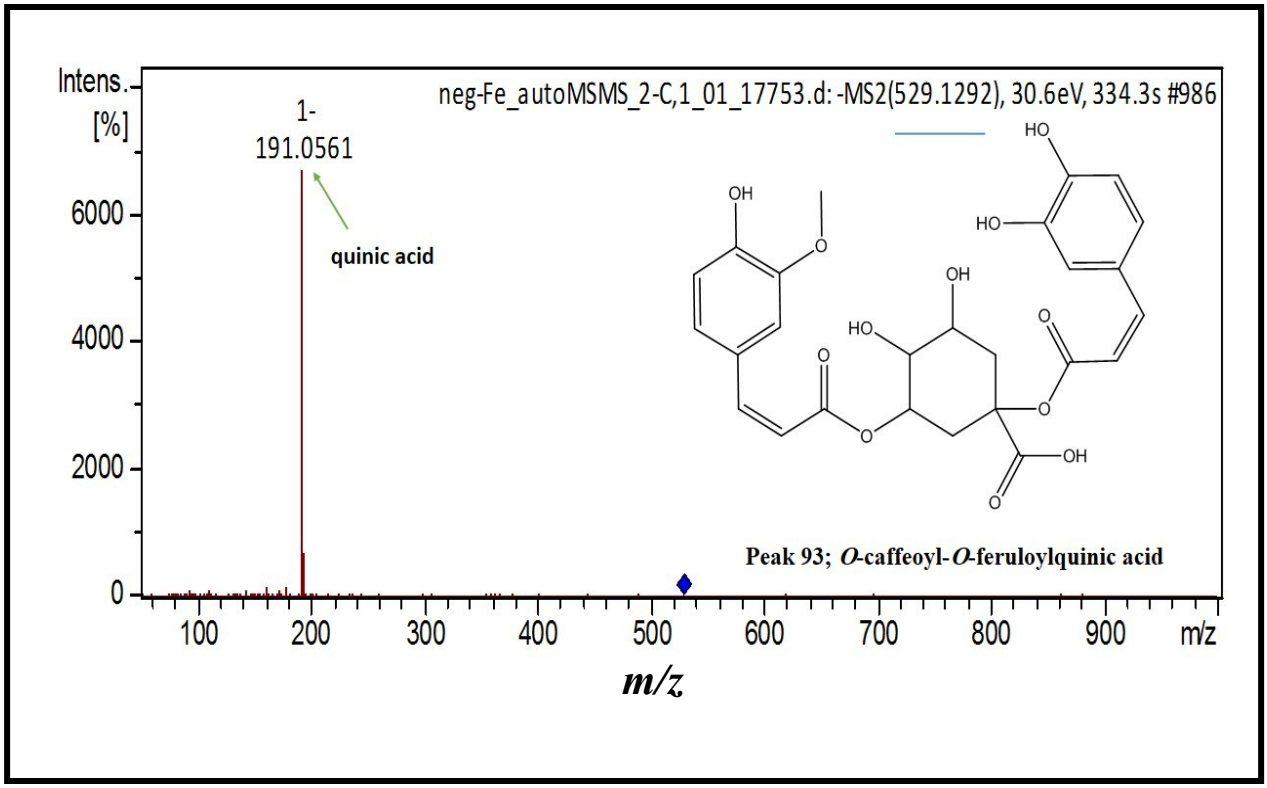

Fig. S5f ESI-MS/MS spectrum of *O*-caffeoyl-*O*-feruloylquinic acid (peak 93; $C_{26}H_{25}O_{12}^{-}$) in the negative ion mode.

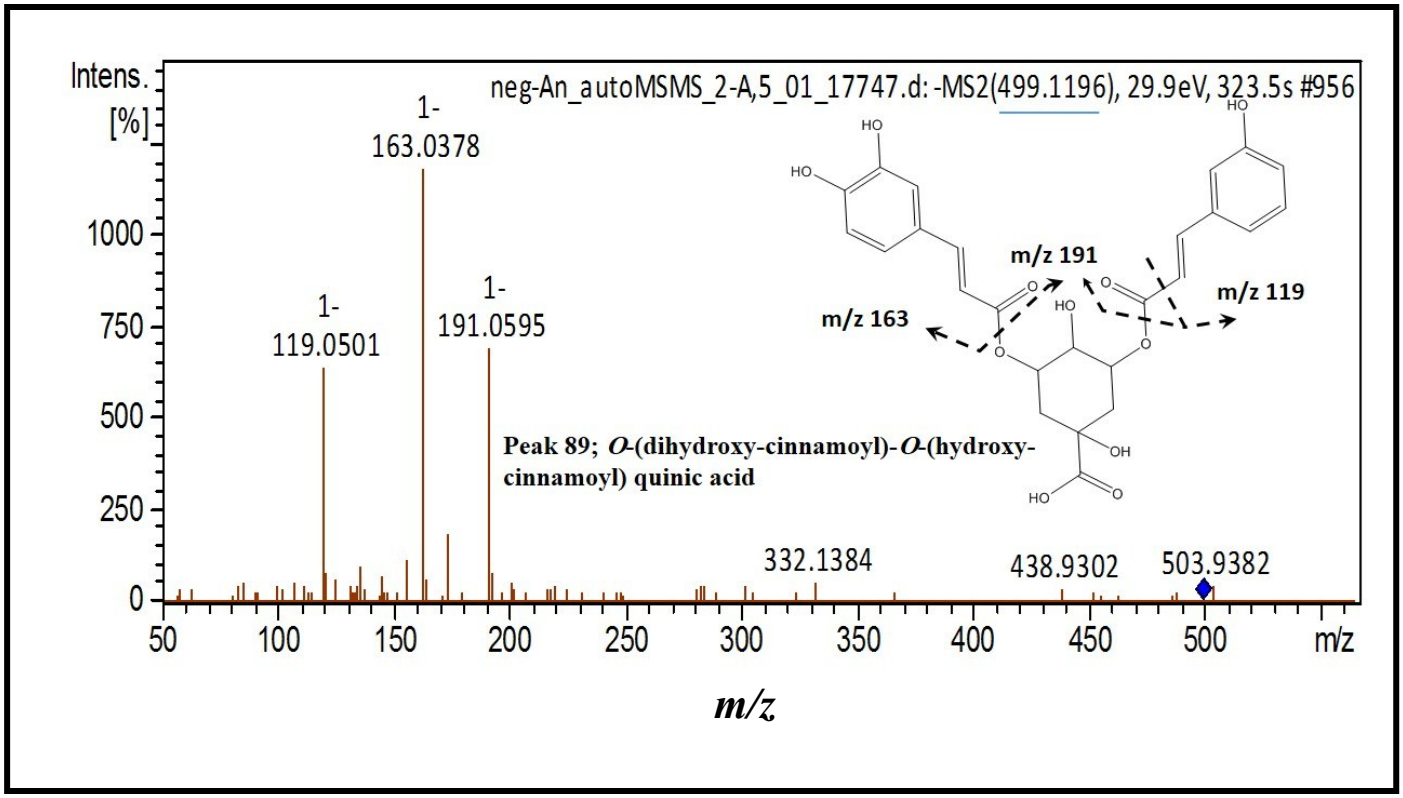

Fig. S5g ESI-MS/MS spectrum of *O*-(dihydroxy-cinnamoyl)-*O*-(hydroxy-cinnamoyl) quinic acid (peak 89; $C_{25}H_{23}O_{11}^{-}$) in the negative ion mode.

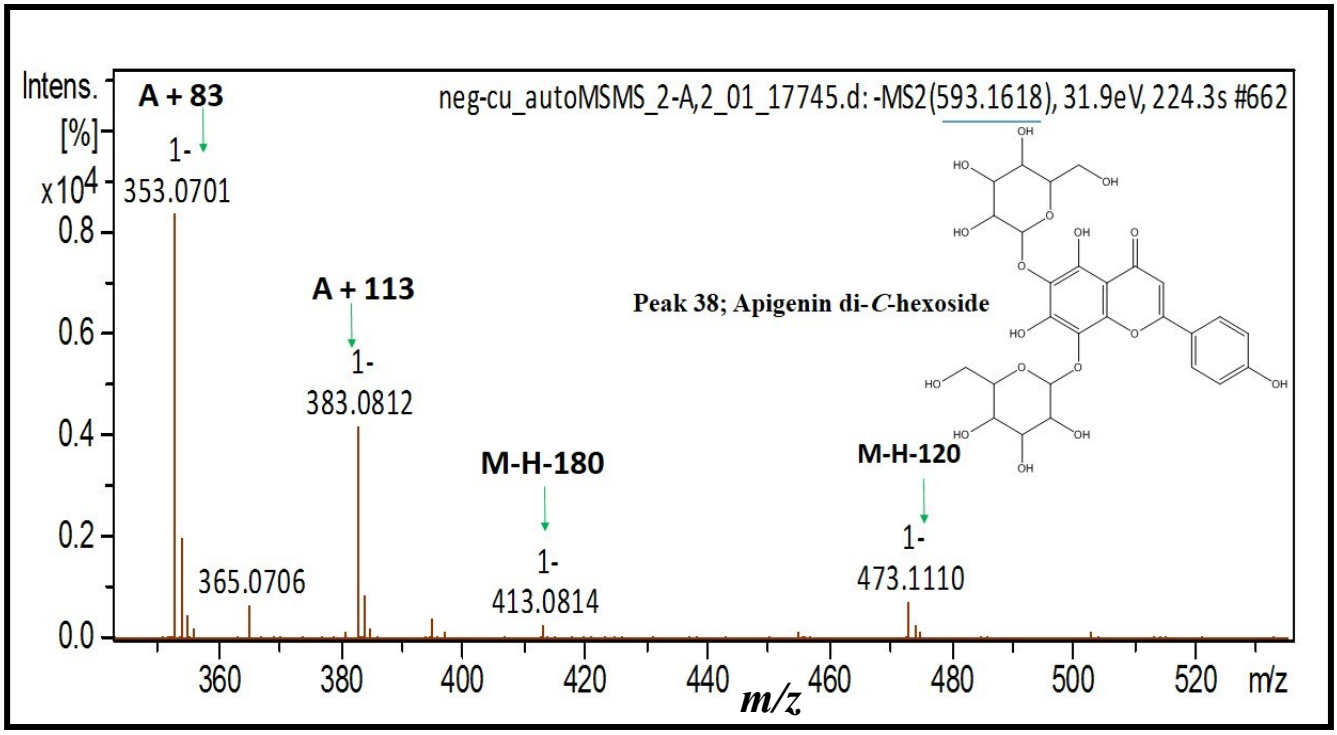

Fig. S6a ESI-MS/MS spectrum of apigenin di-*C*-hexoside (peak 38; $C_{27}H_{29}O_{15}^-$) in the negative ion mode.

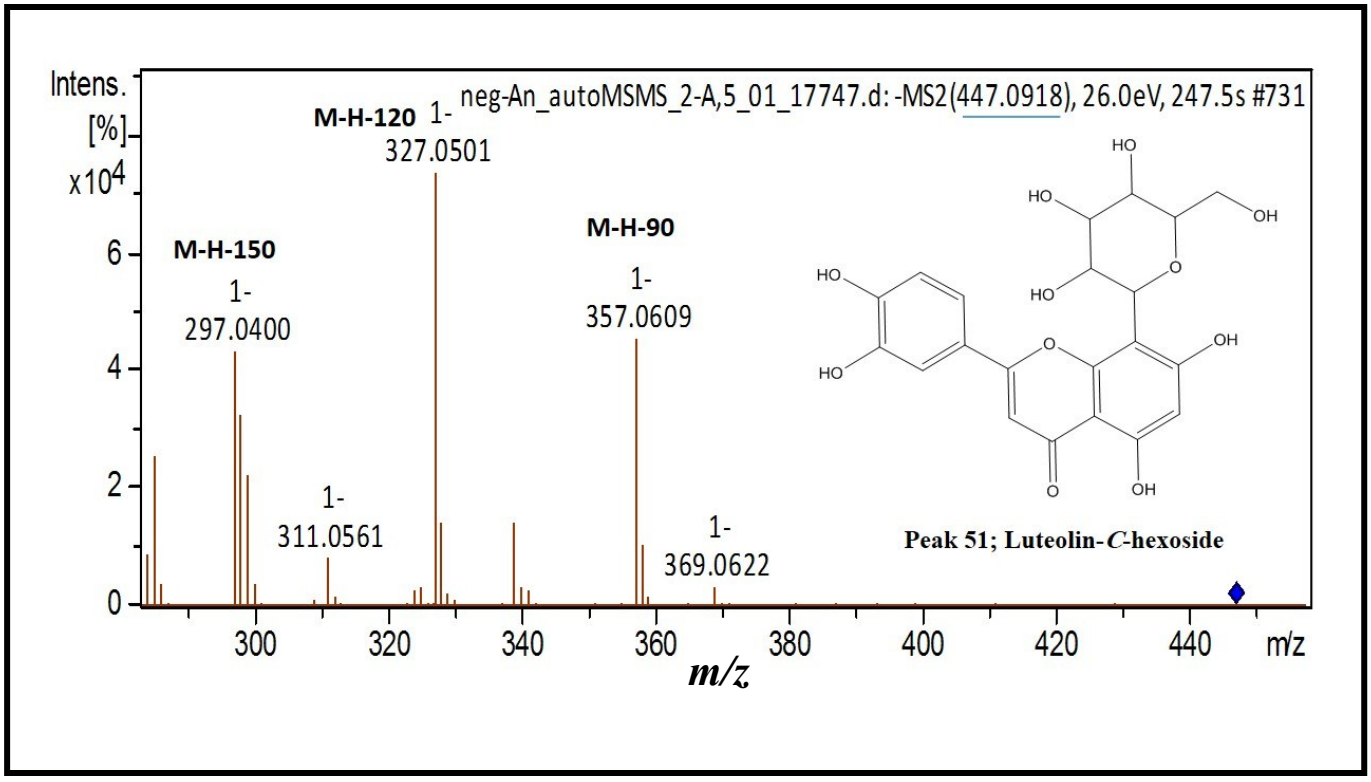

Fig. S6b ESI-MS/MS spectrum of luteolin-*C*-hexoside (peak 51; $C_{21}H_{19}O_{11}^-$) in the negative ion mode.

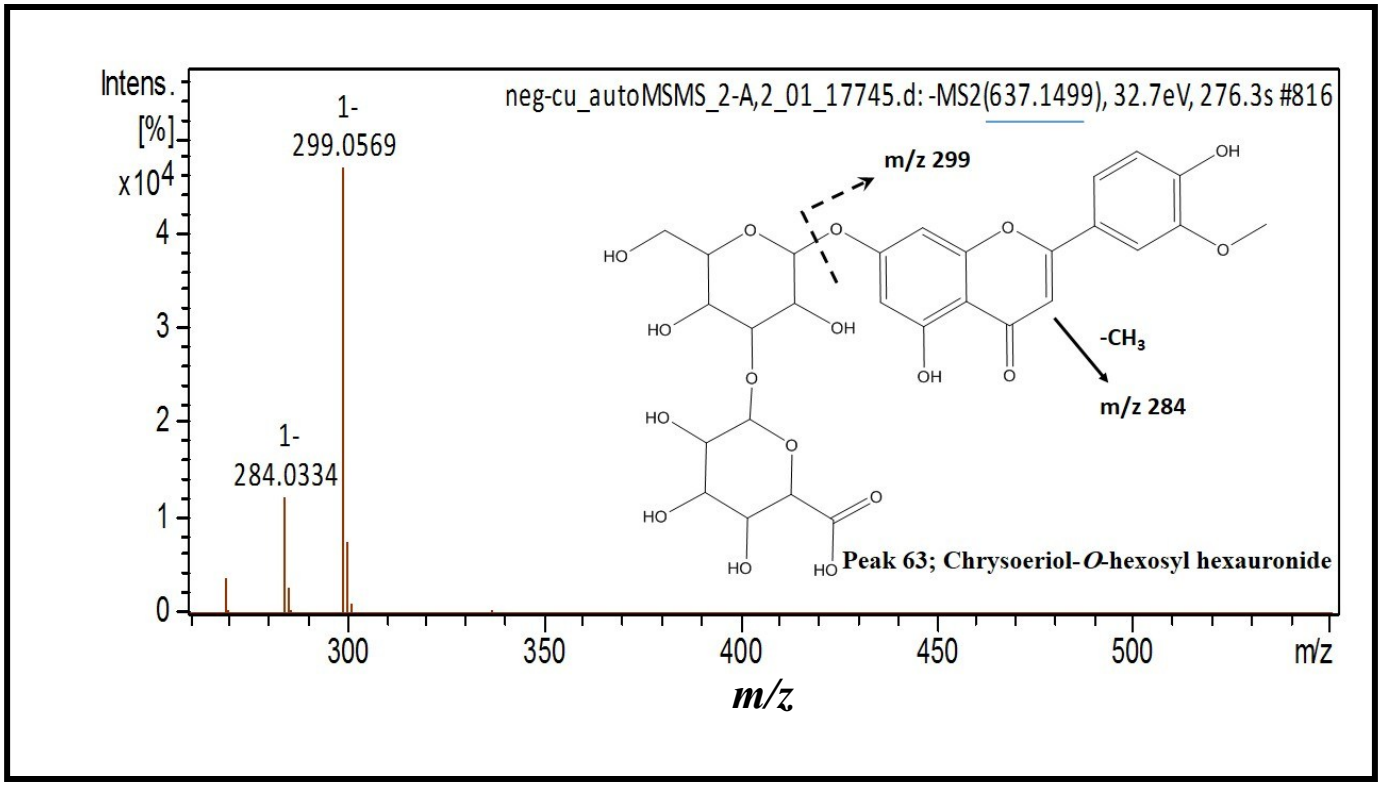

Fig. S7a ESI-MS/MS spectrum of chrysoeriol-*O*-hexosyl hexauronide (peak 63; $C_{28}H_{29}O_{17}^{-}$) in the negative ion mode.

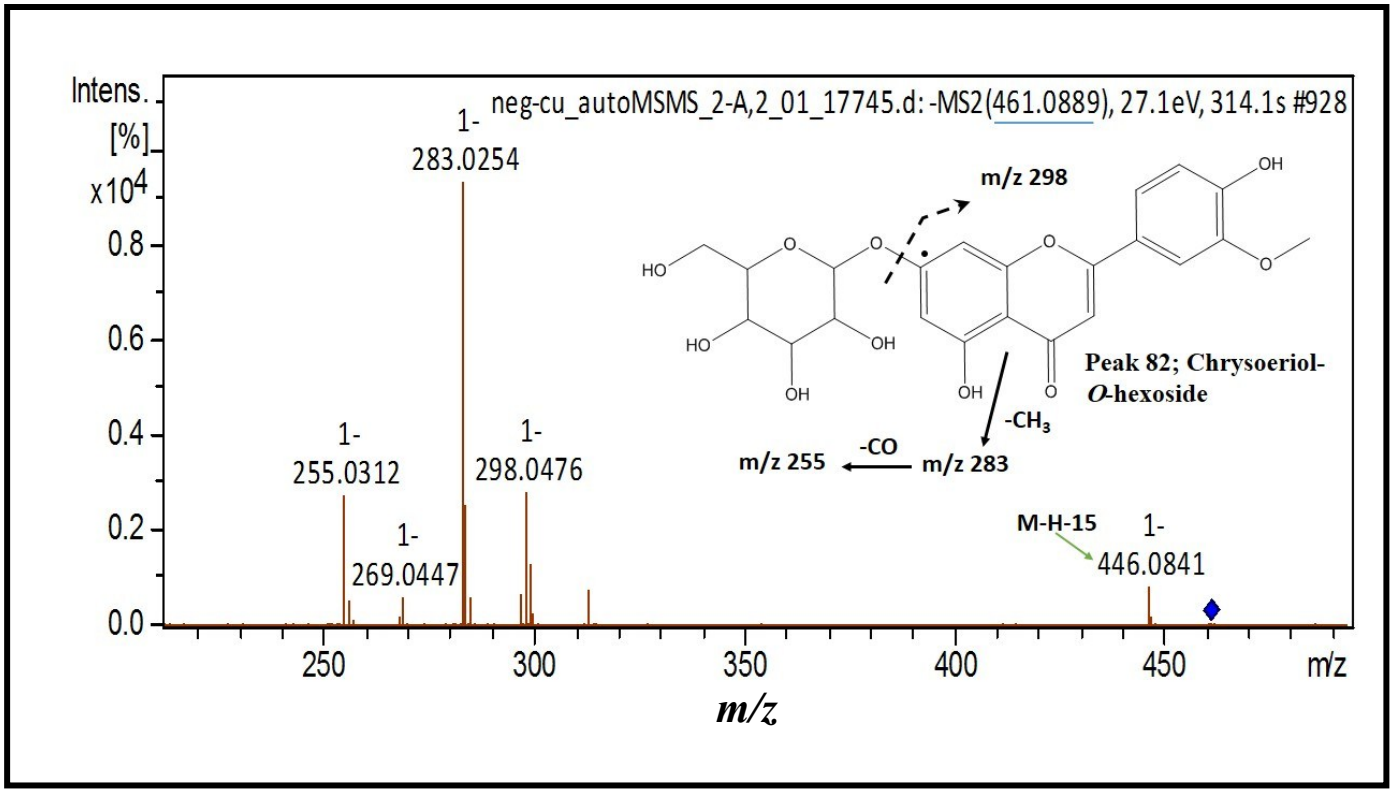

Fig. S7b ESI-MS/MS spectrum of chryseriol-*O*-hexoside (peak82; $C_{22}H_{21}O_{11}^-$) in the negative ion mode.

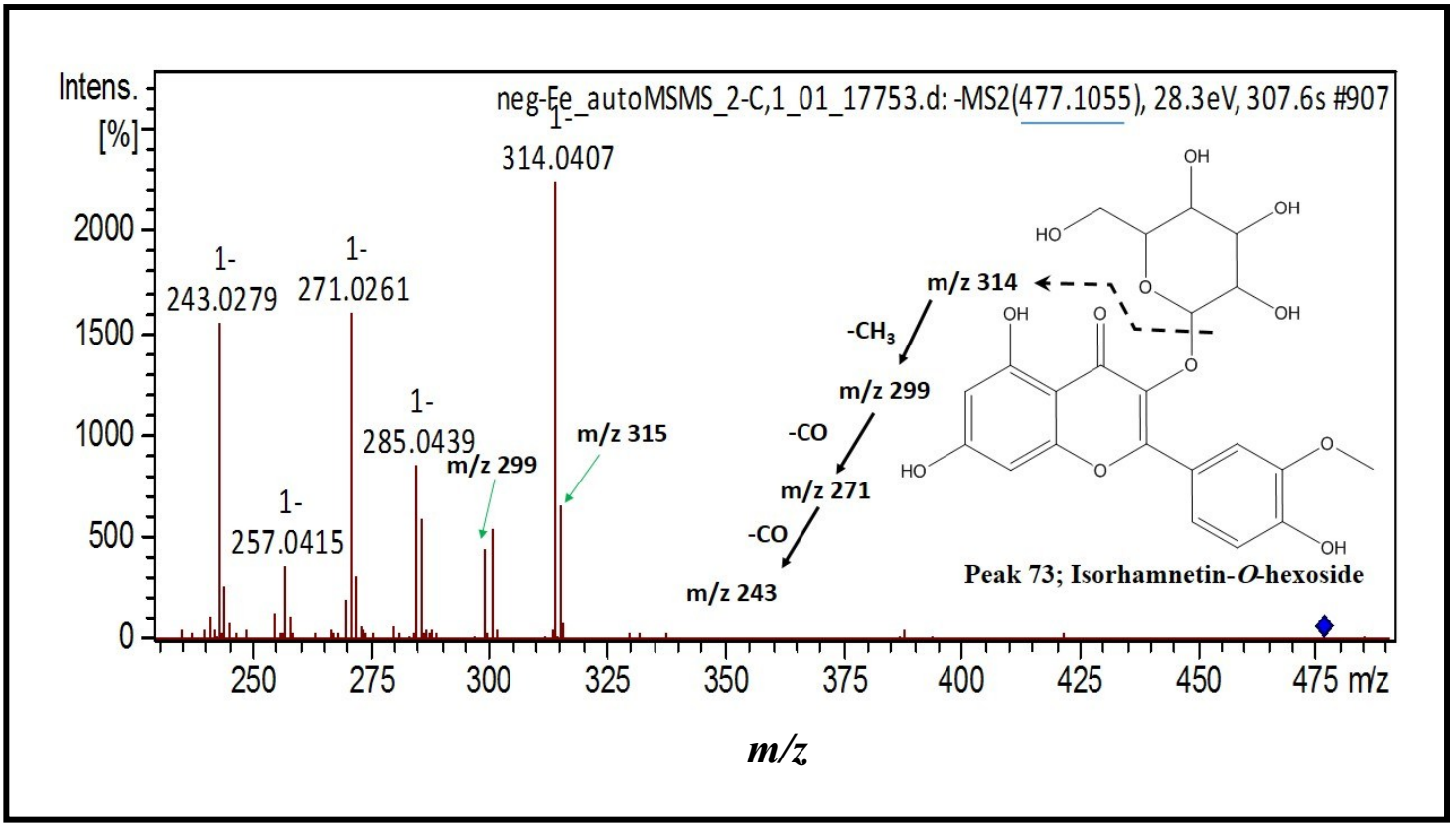

Fig. S8a ESI-MS/MS spectrum of isorhamnetin-*O*-hexoside (peak 73; $C_{22}H_{21}O_{12}^-$) in the negative ion mode.

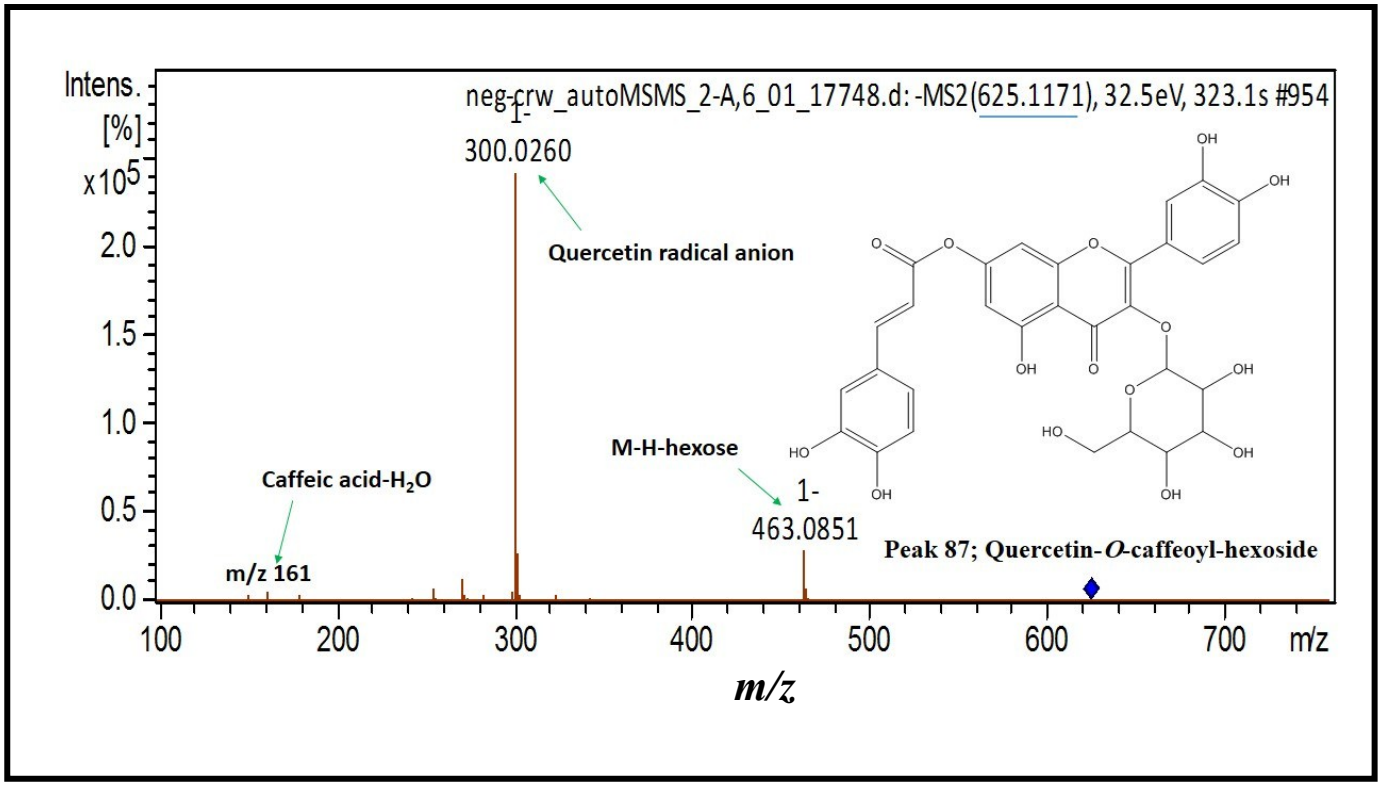

Fig. S8b ESI-MS/MS spectrum of quercetin-*O*-caffeoyl-hexoside (peak 87; $C_{30}H_{25}O_{15}^-$) in the negative ion mode.

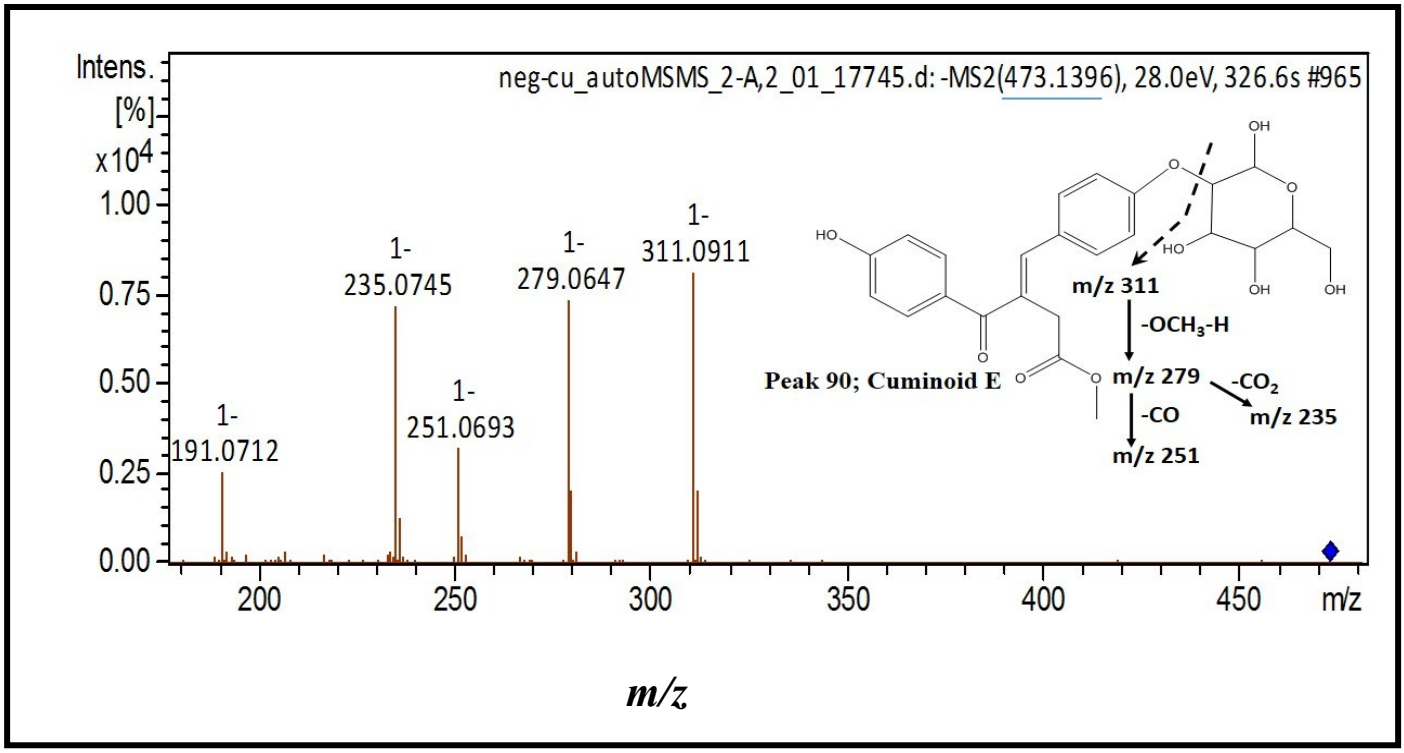

Fig. S9 ESI-MS/MS spectrum of cuminoid E (peak 90; $C_{24}H_{25}O_{10}^-$) in the negative ion mode.

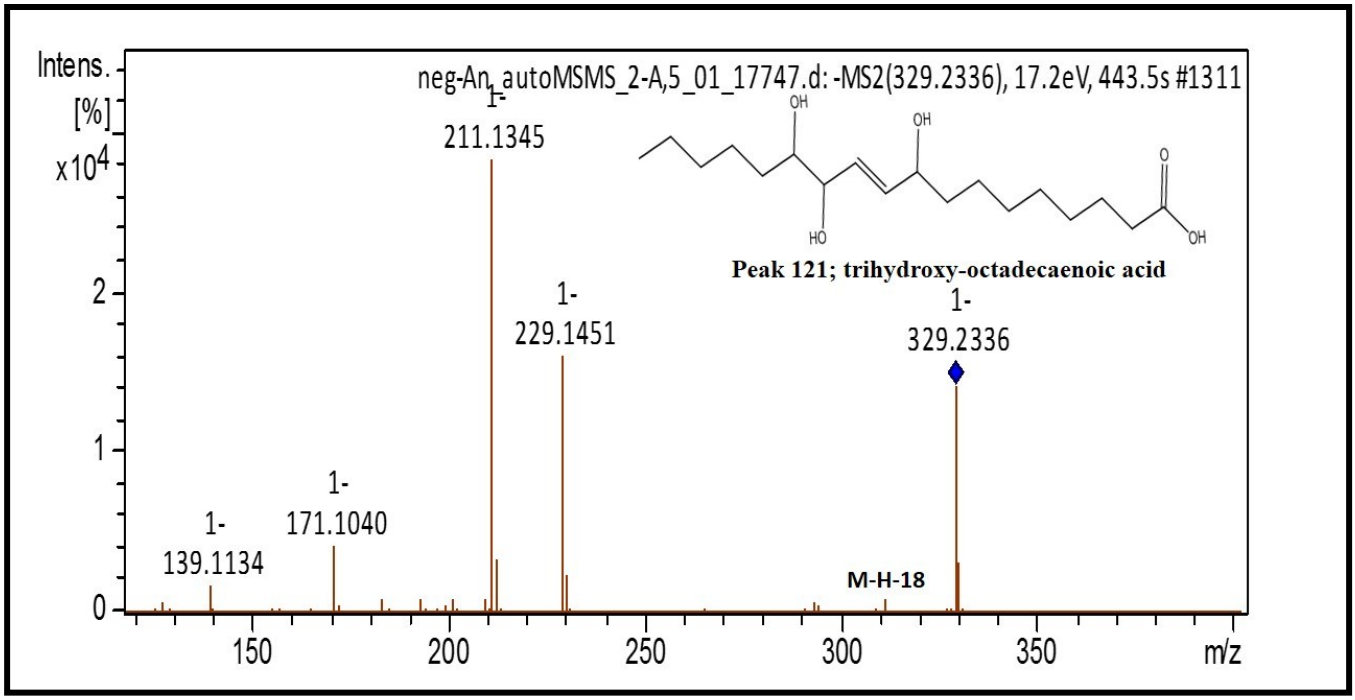

Fig. S10 ESI-MS/MS spectrum of trihydroxy-octadecaenoic acid (peak 121; $C_{18}H_{33}O_5^-$) in the negative ion mode.

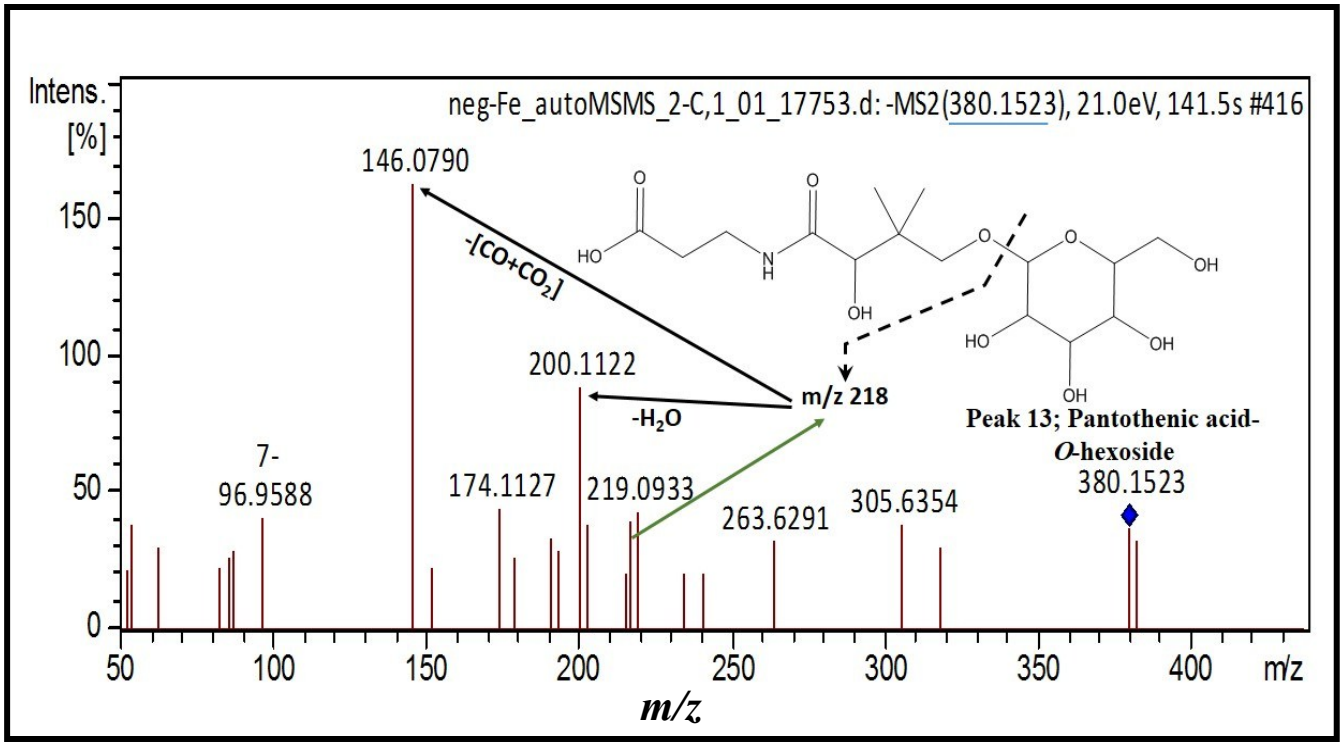

Fig. S11 ESI-MS/MS spectrum of pantothenic acid-*O*-hexoside (peak 13; $C_{15}H_{26}NO_{10}^{-}$) in the negative ion mode.

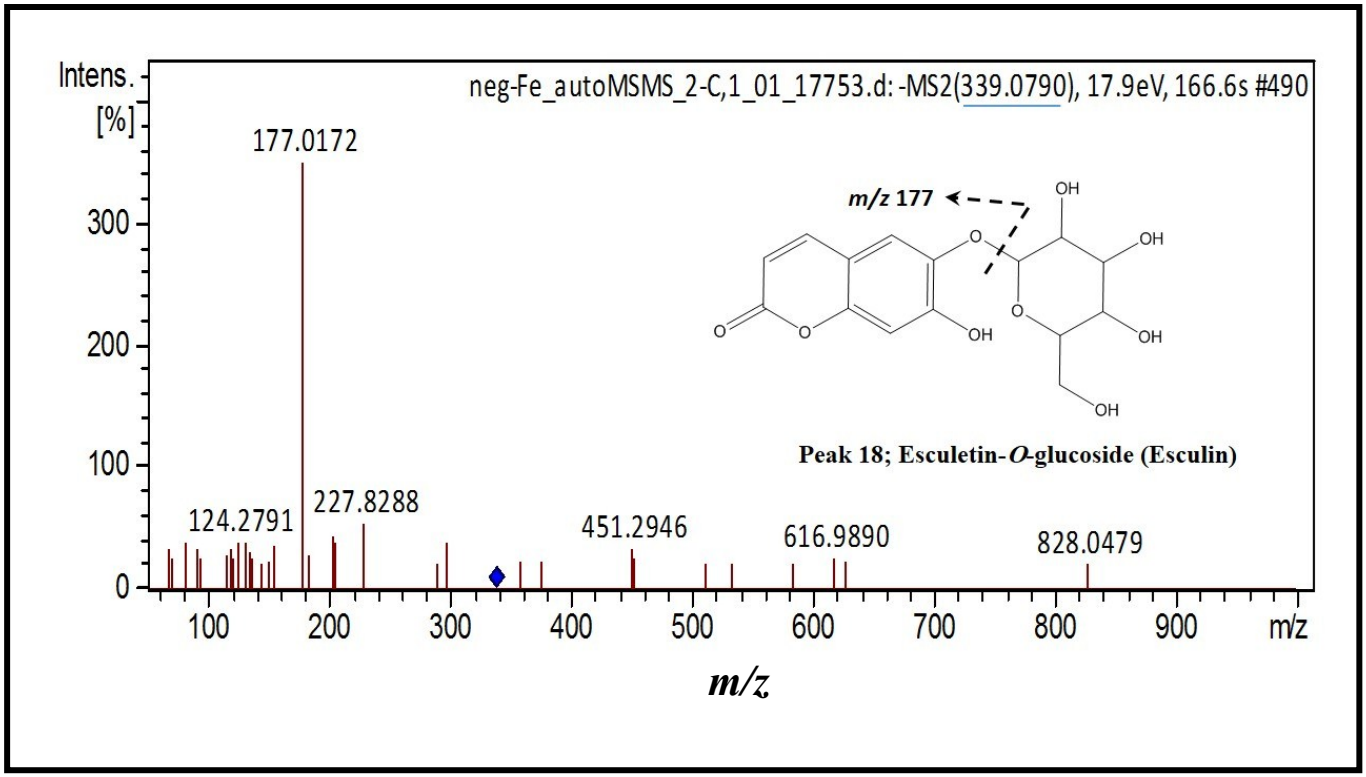

Fig. S12 ESI-MS/MS spectrum of esculin (peak 18; $C_{15}H_{15}O_9^-$) in the negative ion mode.

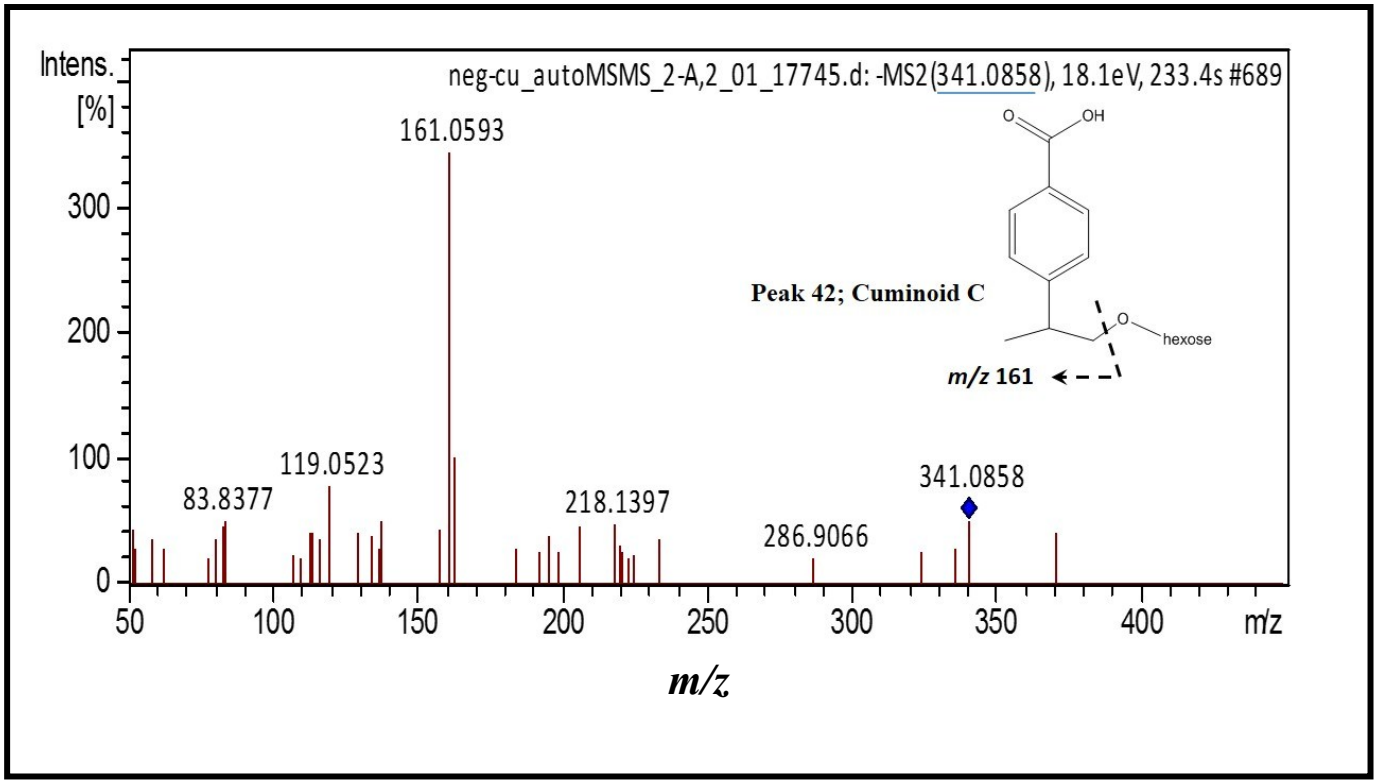

Fig. S13a ESI-MS/MS spectrum of cuminoid C (peak 42; $C_{16}H_{21}O_8^-$) in the negative ion mode.

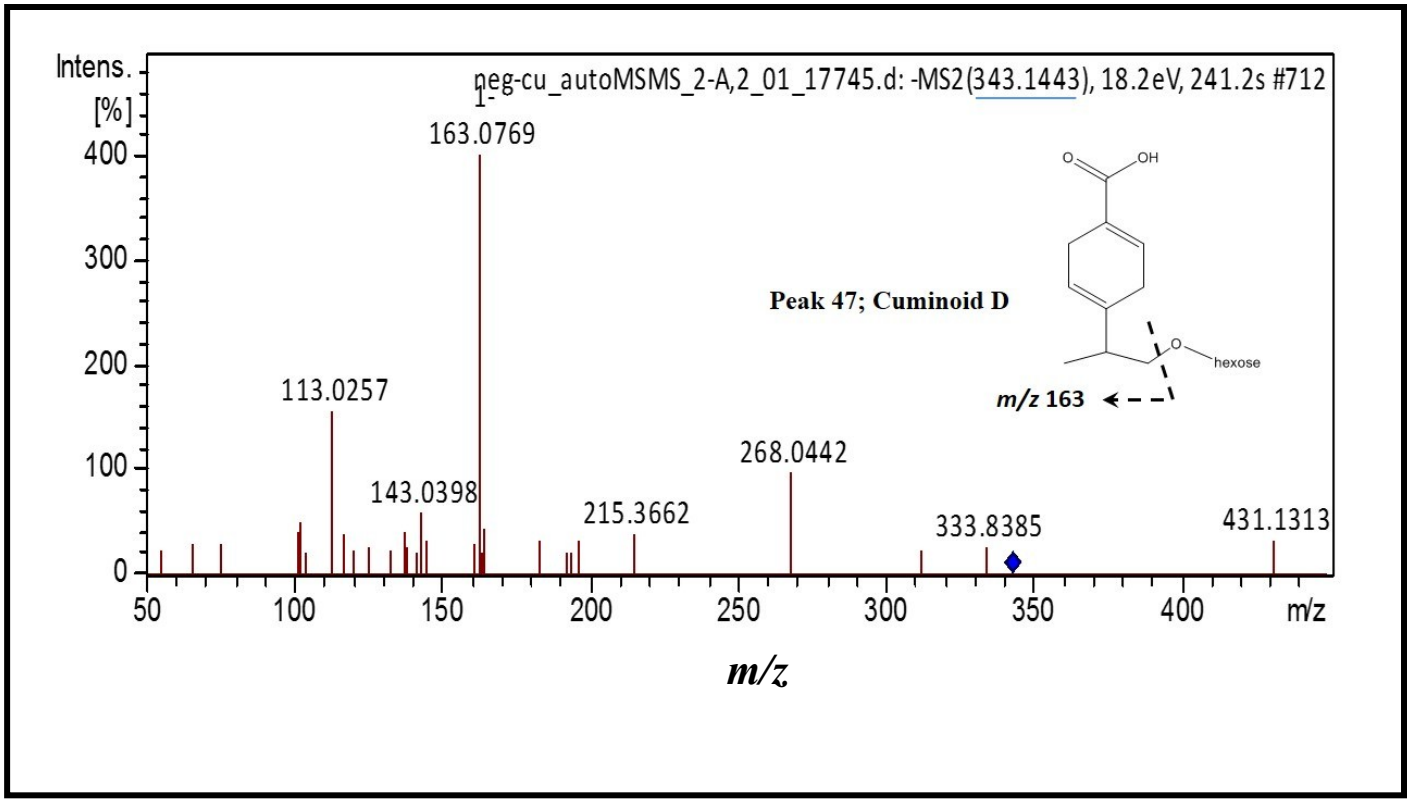

Fig. S13b ESI-MS/MS spectrum of cuminoid D (peak 47; $C_{16}H_{23}O_8^-$) in the negative ion mode.

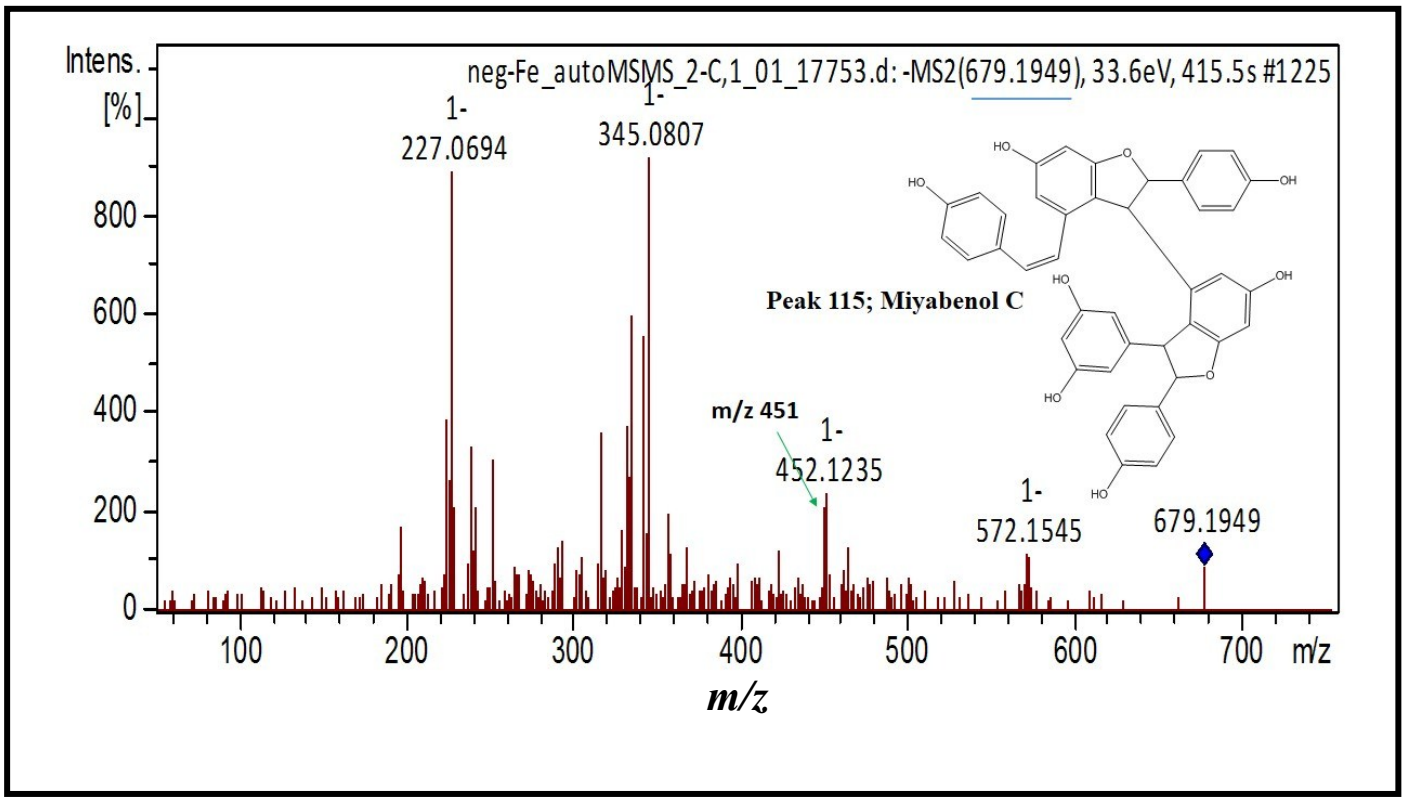

Fig. S14 ESI-MS/MS spectrum of miyabenol C (peak 115; $C_{42}H_{31}O_9)^-$ in the negative ion mode.