Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Combining multiple acquisition modes and computational data annotation for structural characterization in traditional Chinese medicine: Miao Nationality medicine Qijiao Shengbai Capsule as a case study

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Affilication

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Figure Caption

Fig. S1. Molecular networks from QSC in positive (A) and negative (B) ion modes. Nodes with different colors represent various single herbs in the formula (blue was IS; green was AM; orange was ZJ; yellow was EB; gray was EA, ZJ or SF and red was formula).

Fig. S2. MS^E spectra and fragmentation pathway of icariin in QSC under positive ion mode. (A) MS/MS spectra of #82 with parent ion at *m/z* 1375.4617 $[2M+Na]^+$, (B) proposed fragmentation pathway of icariin.

Fig. S3. MS^E spectra and proposed fragmentation pathway of matrine in QSC under positive ion mode. (A) MS/MS spectra of #19 with parent ion at *m/z* 249.1965 $[M+H]^+$, (B) proposed fragmentation pathway of matrine.

Fig. S4 Characterization of isomers with *m/z* 317.2343 and CCS prediction based on ALLCCS : (A) four peaks in extracted ion chromatography (EIC) of *m/z* 317.2343 $[M+Na]^+$, (B) MS/MS spectra of four peaks (peak 175, 176, 177 and 179), (C) chemical structures of 13-oxo-9E,11E-octadecatrienoic acid, 9-oxo-10E,12E-octadecatrienoic acid, 9(10)-epoxy-12Z,15Z-octadecadienoic acid and 13-hydroxy-6Z,9Z,11E-octadecatrienoic acid, (D) the retention time, measured molecular weight, adducts, drift time, measured experimental CCS values and their predicted CCS values from ALLCCS platform of three compounds. Relative error represents the accuracy between measured experimental CCS values and predicted CCS values.

Fig. S5 MS/MS spectra of (A) riligustilide, (B) angelicide and (C) the other 17 isomers with precursor *m/z* 403.1885.

Fig. S1

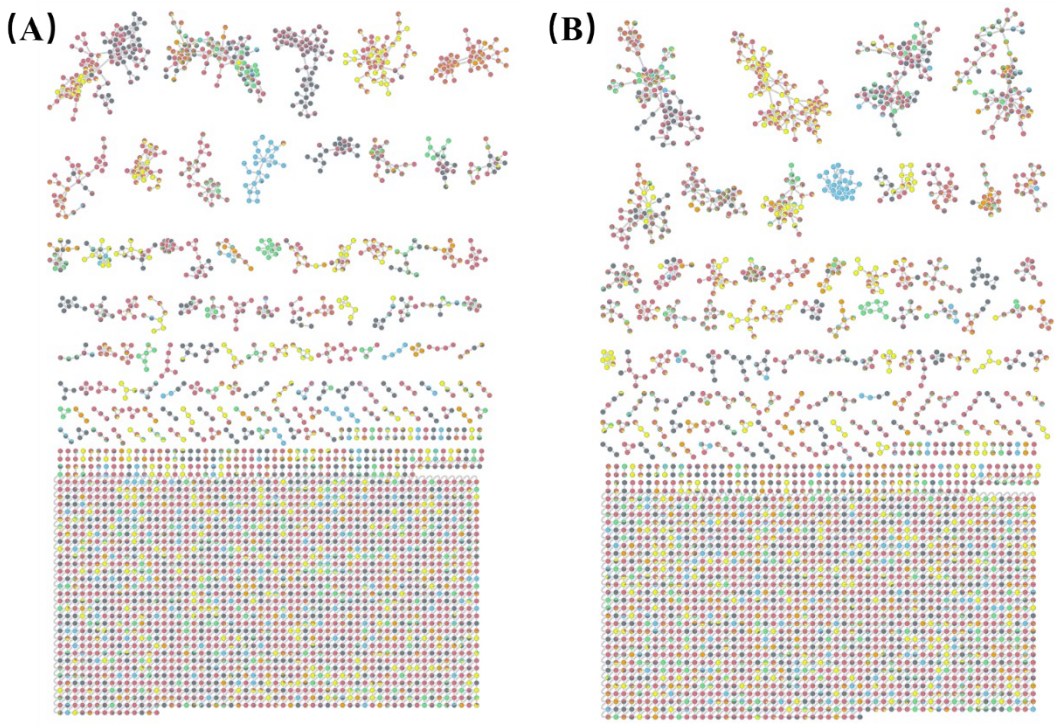

(A)
(B)

Fig. S2

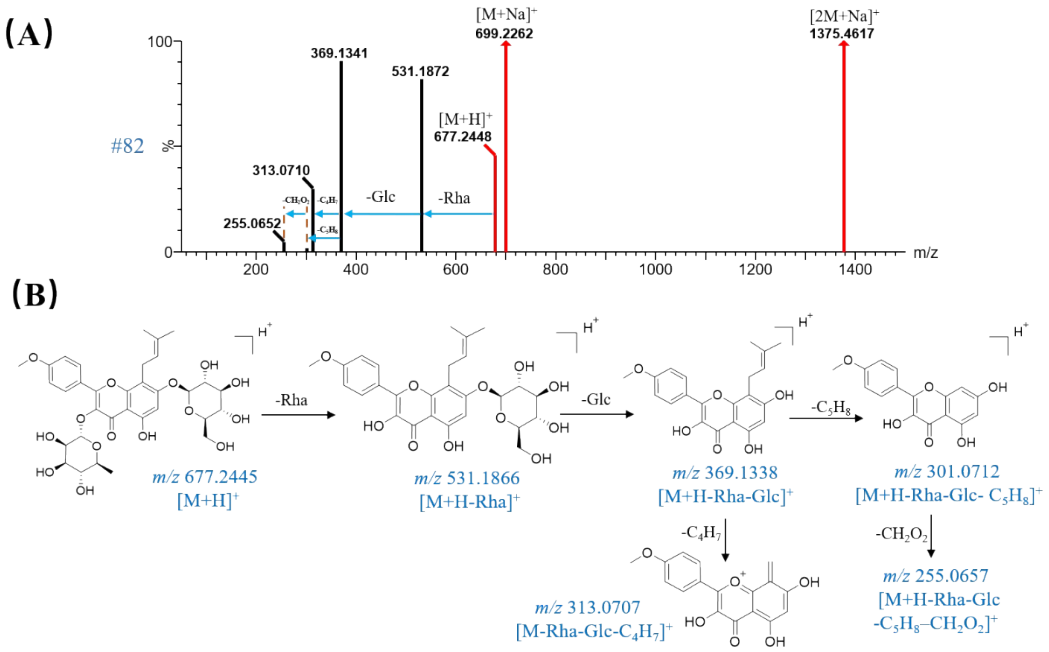

(A)
[M+Na]+
699.2262
[2M+Na]+
1375.4617
369.1341
531.1872
[M+H]+
677.2448
#82
313.0710
255.0652
-Glc
-Rha
100
%
0
200
400
600
800
1000
1200
1400
m/z
(B)
-Rha
-Glc
-C5H8
m/z 677.2445
[M+H]+
m/z 531.1866
[M+H-Rha]+
m/z 369.1338
[M+H-Rha-Glc]+
m/z 301.0712
[M+H-Rha-Glc- C5H8]+
-C4H7
-CH2O2
m/z 313.0707
[M-Rha-Glc-C4H7]+
m/z 255.0657
[M+H-Rha-Glc
-C5H8–CH2O2]+

Fig. S3

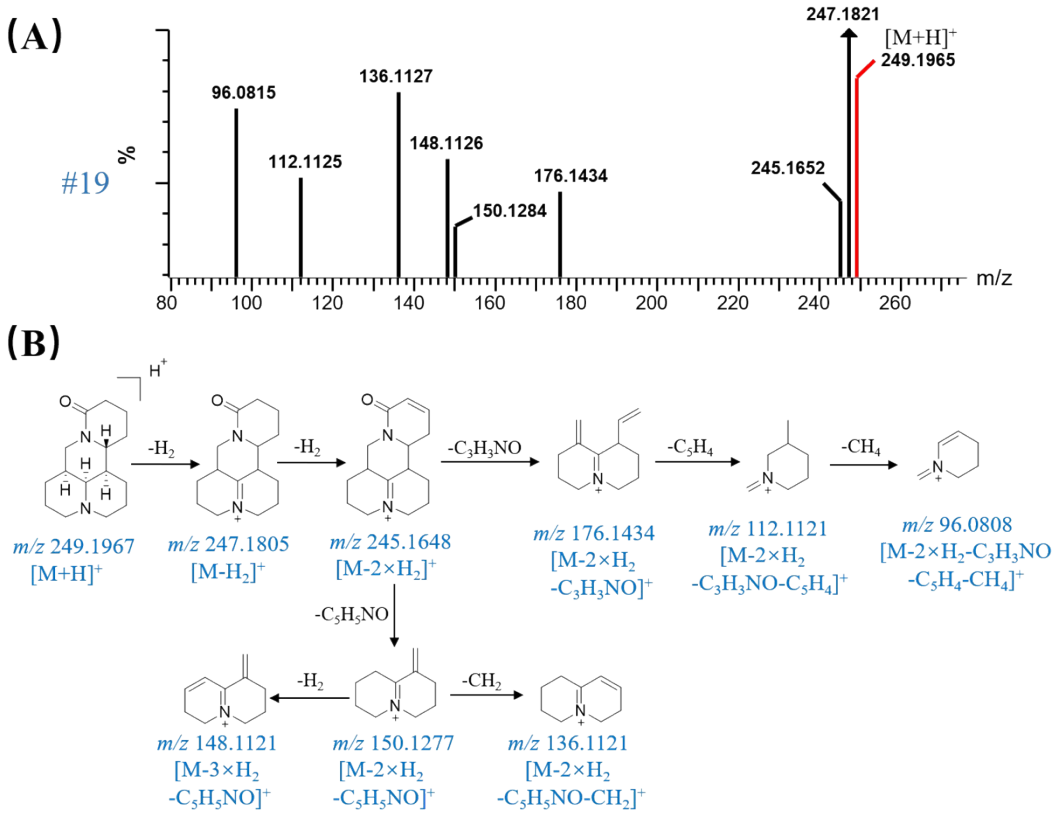
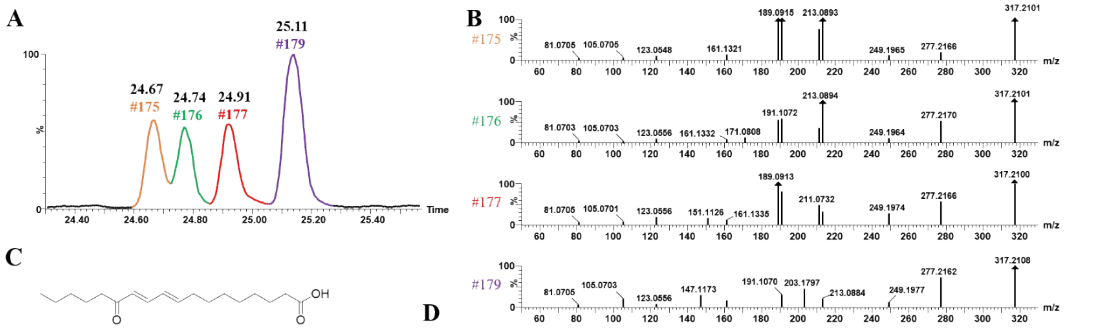
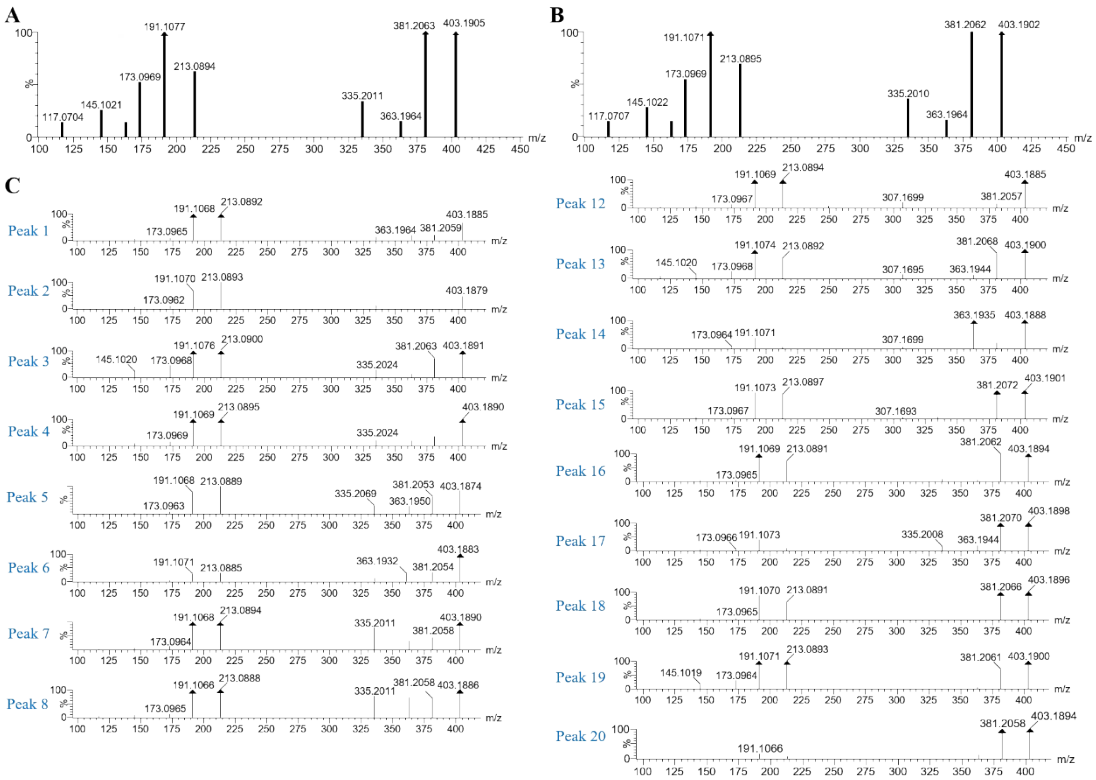


Fig. S4



NO.	RT (min)	*m/z*	Adducts	Drift (ms)	Measured CCS (Å²)	Compound	ALLCCS (Å²)	Relative error
#175	24.67	317.2343	+Na	2.90	188.08	13-oxo-9E,11E-octadecatrienoic acid	188.2512	-0.09%
#176	24.74	317.2349	+Na	2.98	189.96	9-oxo-10E,12E-octadecatrienoic acid	189.6804	0.15%
#177	24.91	317.2341	+Na	3.12	193.77	9(10)-epoxy-12Z,15Z-octadecadienoic acid	190.4587	1.74%
#179	25.11	317.2326	+Na	3.31	198.31	13-hydroxy-6Z,9Z,11E-octadecatrienoic acid	198.7080	-0.20%

Fig. S5


A
B
C
Peak 1
Peak 2
Peak 3
Peak 4
Peak 5
Peak 6
Peak 7
Peak 8
Peak 12
Peak 13
Peak 14
Peak 15
Peak 16
Peak 17
Peak 18
Peak 19
Peak 20
m/z

Tabel. S1 The identification of 202 compounds in QSC sample by using UHPLC-TWIMS-QTOF/MS

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
1	1.32	$C_7H_{12}O_6$	-	-	-	-	-H	191.0558	1.05	133.0146,115.0029, 87.0088	AM/EB	Quinic acid isomer	Organic acids
2*	1.40	$C_5H_9NO_3$	-	-	-	-	-H	130.0505	0.77	128.0346,112.0400, 84.0446	EA	L-Hydroxyproline	Amino acids
3*	1.45	$C_5H_9NO_2$	-	-	-	-	-H	114.0555	0.00	101.0236,71.0128,6 1.9870	EB/EA	L-Proline	Amino acids
4*	1.50	$C_{15}H_{24}N_2O$	+H	249.1968	0.40	232.1561,218.1410, 176.0506,152.1382, 150.1285,148.1136, 136.1136,112.0773	-	-	-	-	SF	Sophoridine	Alkaloids
5*	1.53	$C_{15}H_{24}N_2O_2$	+H	265.1916	0.00	247.1926,245.1722, 205.1397,148.1139, 136.1132,112.0772	-	-	-	-	SF	Ammothamnine	Alkaloids
6	1.75	$C_6H_{12}O_7$	-	-	-	-	-H	195.0508	1.54	161.0456,129.0189, 111.0096	AM/AS	Galactonic acid	Organic acids
7*	1.77	$C_7H_{12}O_6$	-	-	-	-	-H	191.0552	-2.09	161.0441,133.0115, 111.0089	IS	Quinic acid	Organic acids
8	1.94	$C_4H_6O_5$	-	-	-	-	-H	133.0137	0.00	115.0030,111.0082, 71.0125	ZJ	Malic acid	Organic acids
9	2.00	$C_6H_8O_7$	-	-	-	-	-H	191.0194	1.05	173.0086,128.0347, 111.0085	AM/AS/I S	Citric acid	Organic acids
10*	2.04	$C_6H_{13}NO_2$	-	-	-	-	-H	130.0865	-2.31	128.0350,117.0189,	AM/AS/	Leucine	Amino acids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
										111.0089	EB		
11	2.05	$C_{15}H_{24}N_2O_2$	+H	265.1918	0.75	205.1351,150.1284, 148.1126,136.1124, 112.0766	-	-	-	-	SF	12α-hydroxymatrine	Alkaloids
12	2.34	$C_{13}H_{16}O_9$	-	-	-	-	-H	315.0725	2.86	271.0461,153.0671, 135.0444,101.0603	EB	Protocatechuic acid -3-*O*- glucose	Organic acids
13	2.50	$C_{15}H_{22}N_2O$	+H	247.1819	3.64	150.1286,148.1129, 112.0758,84.0796	-	-	-	-	SF	5,6-dehydrolupanine	Alkaloids
14	2.68	-	-	-	-	-	-	255.0583	-	193.0500,191.0555, 165.0556	SF	Unknown	Unknown
15	3.18	$C_{11}H_{12}O_7$	-	-	-	-	-H	255.0507	0.78	239.0561,175.0608, 153.0193,109.0289	SF	Piscidic acid or isomer	Organic acids
16*	3.24	$C_7H_6O_4$	-	-	-	-	-H	153.0193	3.27	137.0239,109.0289, 85.0644,75.0070	IS/EB	Gentisic acid	Organic acids
17*	3.40	$C_7H_6O_4$	-	-	-	-	-H	153.0194	3.92	137.0247,109.0290, 85.0648,75.0086	IS	Protocatechuic acid	Organic acids
18	3.50	$C_{11}H_{12}O_7$	-	-	-	-	-H	255.0510	1.96	239.0560,175.0611, 153.0193,109.0288	SF	Piscidic acid or isomer	Organic acids
19*	3.60	$C_{15}H_{24}N_2O$	+H	249.1965	-0.80	247.1821,245.1652, 176.1434,150.1284, 148.1126,136.1127, 112.1125,96.0815	-	-	-	-	SF	Matrine	Alkaloids
20	3.99	$C_{15}H_{24}N_2O_2$	+H	265.1914	-0.75	150.0928,136.1136,	-	-	-	-	SF	14β-	Alkaloids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
						111.0451						hydroxymatrine	
21	4.45	$C_{19}H_{28}O_{11}$	+Na	455.1542	2.86	265.1891,107.0584, 91.0544,70.0635	-H	431.1547	-1.39	255.0611,239.0561, 153.0189	EB	Zizybeoside Ⅰ	Flavonoids
22*	4.72	$C_{16}H_{18}O_9$	-	-	-	-	-H	353.0869	-1.13	307.0872,191.0557, 129.0555,115.0762	EB	Chlorogenic acid	Organic acids
23	4.82	$C_{18}H_{26}O_{10}$	-	-	-	-	+HCOO	447.1503	0.00	269.0715,123.0448, 71.0125	EB	Icariside F2	Flavonoids
24	5.48	$C_{16}H_{16}O_6$	+H	305.1028	0.98	265.1913,218.0830, 111.0449	-	-	-	-	AS	Oxypeucedanin hydrate	Others
25	5.73	$C_{10}H_{10}O_4$	-	-	-	-	-H	193.0510	4.66	179.0351,149.0606, 135.0444	SF	Ferulic Acid isomer	Organic acids
26*	6.44	$C_{20}H_{24}NO_4$	-e	342.1692	-3.80	297.1126,265.0860, 237.0899,222.0663	-	-	-	-	EB	Magnoflorine	Alkaloids
27	6.60	$C_{19}H_{28}O_{11}$	-	-	-	-	-H	431.1552	-0.23	341.1168,287.0669, 137.0248,121.0297, 94.0298,71.0139	ZJ	Zizybeoside I isomer	Flavonoids
28	7.23	$C_{16}H_{18}O_8$	-	-	-	-	-H	337.0926	0.89	191.0559,167.0352, 123.0466	AS	5-p-Coumaroylquinic acid	Organic acids
29	7.31	$C_{18}H_{26}O_{10}$	+Na	425.1415	-2.12	261.1592,187.1205, 111.0430,70.0760	-H	401.1444	-1.00	387.1638,269.0999, 161.0467,71.0136	EB/AS	Icariside F2	Flavonoids
30	7.37	$C_{21}H_{20}O_9$	-	-	-	-	-H	415.1028	-0.24	267.0658,223.0614, 163.0400,137.0247	SF	5,7,4′-trihydroxyflavone-	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
31	7.49	$C_{27}H_{30}O_{15}$	-	-	-	-	-H	593.1499	-1.18	433.1343,353.0672, 223.0606,195.0658, 137.0242	EB	7-*O*-α-L-rhamaoside kaempferol-3-*O*-α-L-rhamnopyranosyl (4-1)-β-D-glucopyranoside	Flavonoids
32	8.21	$C_{22}H_{22}O_{11}$	+Na	485.1050	-2.06	365.2071,301.0712, 211.1438,111.0447	-H	461.1096	2.60	299.0565,247.1222, 161.0249,117.0194	AM	Swertiajaponin	Flavonoids
33	8.30	$C_{10}H_{18}O_4$	-	-	-	-	+HCOO	247.1185	0.40	173.0815,163.0397, 119.0501,111.0810	SF	Sebacic acid	Organic acids
34*	8.35	$C_9H_8O_3$	+H	165.0559	4.24	136.0684,111.0444, 81.0336	-H	163.0401	3.68	134.0274,119.0502, 111.0811	EB	P-hydroxycinnamate	Organic acids
35	8.36	$C_{34}H_{46}O_{18}$	+Na	765.2589	0.91	342.1698,285.1286, 189.1201,	+HCOO	787.2648	-1.65	666.3094,417.1692, 375.1434,337.0560, 247.1181,173.0815, 119.0502	SF	Eleutheroside E	Others
36	8.44	$C_{22}H_{22}O_7$	+H	399.1438	-1.50	313.1506,265.1912, 232.0922,137.0599, 111.0447,91.0529	-	-	-	-	EB	Baohuosu	Flavonoids
37	8.80	$C_{28}H_{32}O_{16}$	-	-	-	-	-H	623.1607	-0.80	577.1563,413.1466, 283.0612,163.0397, 149.0243	SF	Complanatuside	Flavonoids
38	9.04	$C_{27}H_{30}O_{14}$	-	-	-	-	-H	577.1552	-0.87	461.1949,283.0614, 268.0372,175.0977,	SF	Chrysoeriol-*O*-pentosylrhamnosid	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
39*	9.08	$C_{10}H_{10}O_4$	-	-	-	-	-H	193.0504	1.55	134.0378 178.0271,149.0609, 134.0370	AS/AM	e Ferulic Acid	Organic acids
40	9.27	$C_{27}H_{30}O_{16}$	-	-	-	-	-H	609.1451	-0.82	463.1339,283.0611, 163.0763,135.0446	ZJ/AS	Quercetin 3-*O*-rutinoside	Flavonoids
41*	9.36	$C_{22}H_{22}O_{10}$	+H	447.1293	-	285.0770,213.0541, 111.0446	+HCOO	491.1190	0.00	283.0611,269.0448, 151.0399,136.0164	AM	Calycosin-7-*O*-β-D-glucoside	Flavonoids
42	9.50	-	+Na	265.1038	-	195.0926,162.0923, 120.0816,111.0449	-H	241.1082	-	197.1185,179.0342, 141.0917	AS	Unknown	Unknown
43*	9.62	$C_{27}H_{30}O_{14}$	-	-	-	-	-H	577.1552	-0.87	431.1823,285.0666, 245.1013,193.0340, 179.0548	AM	Kaempferitrin	Flavonoids
44*	9.62	$C_{21}H_{20}O_{12}$	+Na	487.0841	-2.26	303.0495,287.0519, 271.1139,189.0949	-H	463.0875	-0.43	301.0380,245.1013, 193.0505	EB	Hyperoside	Flavonoids
45	9.67	$C_{26}H_{28}O_{14}$	-	-	-	-	-H	563.1399	-0.36	417.1186,269.0451, 245.0928,193.0576	SF	Kaempferol-7-*O*-rha-xyl	Flavonoids
46*	9.71	$C_{21}H_{20}O_{12}$	-	-	-	-	-H	463.0867	-2.16	301.0335,271.0287, 243.0275,177.0184, 161.0275	EB	Isoquercitrin	Flavonoids
47	9.76	$C_{25}H_{32}O_{10}$	+Na	515.1888	-0.97	443.1675,399.1412, 299.1740,249.1124, 176.0609,111.0446	-H	491.1916	-0.20	447.0936,359.1552, 289.0761,139.0169	IS	Schizandriside	Flavonoids
48	9.80	$C_{10}H_{10}O_4$	-	-	-	-	-H	193.0500	-0.52	165.0187,139.0759,	AS	Dimethyl phthalate	Others

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
49	9.93	$C_{11}H_{11}NO_3$	+H	206.0818	0.49	188.0717,178.0866, 160.0766	-H	204.0661	0.00	123.0324 186.0557,174.0558, 161.0243	EB ZJ	5-Methoxy-3-indoleaceate	Organic acids
50	10.01	$C_9H_6O_3$	-	-	-	-	-H	161.0246	4.35	137.0234,133.0352, 116.9288	SF	7-hydroxychromone	Others
51	10.52	$C_{22}H_{22}O_{10}$	+Na	469.1108	-0.64	285.0768,178.0867, 153.0189,111.0451, 81.0337	-H	445.1137	0.45	268.0369,239.0334, 221.0811,187.0971, 179.0351	AM/SF	3'-methoxy-5'-hydroxy-isoflavaone-7-*O*-β-D-glucopyranoside	Flavonoids
52	10.72	$C_{21}H_{20}O_{11}$	-	-	-	-	-H	447.0932	1.12	269.0448,187.1005, 125.0966	EB	Luteolin-7-*O*-β-D-glucoside	Flavonoids
53	10.72	$C_{38}H_{48}O_{20}$	+Na	847.2640	0.35	825.2822,663.2297, 355.1187,299.0556, 249.1111	-H	823.2645	-1.94	661.2119,545.1868, 527.1768,353.1012, 279.0872,261.0762	EB	Rouhuoside	Flavonoids
54	10.85	$C_{19}H_{32}O_7$	+Na	395.2043	-0.76	249.1104,148.0764, 111.0449	+HCOO	417.2116	-2.16	209.0805,179.0350, 164.1080,125.0967	EB	Blumel C glucoside	Others
55	10.95	$C_{37}H_{46}O_{19}$	+Na	817.2544	1.59	663.3488,599.2437, 517.2646,355.1830, 283.1121,225.1025, 111.0449	-H	793.2541	-1.76	631.2017,353.1128, 281.0453,253.0498, 187.0986,1510401	EB	Epimedoside E	Flavonoids
56	11.10	$C_{38}H_{48}O_{19}$	+H	809.2880	1.48	663.2299,517.1717, 355.1189,299.0557, 176.0716,111.0448	-H	807.2708	-0.50	645.2178,463.1242, 317.1602,251.0554, 179.0338	EB	Baohuoside V	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
57	11.12	$C_{32}H_{38}O_{14}$	-	-	-	-	-H	645.2175	-1.24	617.2992,513.1549, 343.2118,323.0921, 311.0600,267.0658, 251.0546,217.0494, 179.0336,109.0300	EB	Sagittatoside B	Flavonoids
58	11.18	$C_{27}H_{30}O_{13}$	+Na	585.1582	-0.34	563.1749,431.1338, 269.0813,197.0954, 176.0709,111.0444	+HCOO	607.1671	1.32	561.1821,267.0758, 252.0516,195.0524, 179.0344	SF	3'-methoxy-isoflavone- 7-*O*-glc-xyl	Flavonoids
59	11.27	$C_9H_{16}O_4$	-	-	-	-	-H	187.0977	3.74	144.0458,125.0974, 111.0079,97.0651	IS/AM/AS/EA/ZJ	Azelaic acid	Organic acids
60	11.29	$C_{32}H_{38}O_{15}$	+H	663.2289	0.00	517.1721,441.2465, 355.1190,299.0563, 228.1026,111.0456	-H	661.2133	0.15	515.1540,353.1018, 343.2114,323.0947, 173.1181	EB	Epimedoside A	Flavonoids
61	11.39	$C_{27}H_{30}O_{13}$	+Na	585.1563	-3.59	563.1771,431.1356, 269.0807,192.0667, 111.0448	+HCOO	607.1659	-0.66	561.1805,267.0659, 237.0771,193.0868	SF	3'-methoxy-isoflavone- 7-*O*-glc-xyl	Flavonoids
62	11.75	$C_{21}H_{20}O_{10}$	-	-	-	-	-H	431.0978	0.00	361.1654,285.0446, 243.1235,225.1135	EB	Kaempferol-3-*O*-rhamnoside	Flavonoids
63	11.95	$C_{26}H_{30}O_{14}$	+Na	589.1523	-1.70	367.2083,255.0635, 147.0108,111.0448, 85.0271	-H	565.1558	0.18	433.1126,271.0607, 253.0499,227.0706, 161.0243,135.0090, 91.0192	SF	4'-hydroxyflavanonol-7-*O*-glu-xyl	Flavonoids
64*	12.10	$C_{12}H_{16}O_4$	+Na	247.0945	-0.40	207.1026,189.0912,	-H	223.0972	0.90	205.0868,179.0340,	AS	Senkyunolide I	Phthalides

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
65	12.13	$C_{22}H_{22}O_9$	+Na	453.1173	2.43	161.0971,119.0865 431.1329,269.0836, 207.1012,161.0971, 111.0447,91.0546	+HCOO	475.1248	1.68	135.0445 267.0664,223.0433, 193.0503,135.0445	AM/SF	Ononin	Flavonoids
66	12.28	$C_{28}H_{32}O_{16}$	-	-	-	-	-H	623.1616	0.64	461.2532,299.1854, 285.0410,237.0758, 221.0807,159.1024, 137.0238,116.9282	SF	Complanatuside	Flavonoids
67	12.28	$C_{27}H_{32}O_{12}$	-	-	-	-	+HCOO	593.1877	1.18	383.1129,299.0927, 283.0601,193.0866, 137.0241	EB	Maohuoside A	Flavonoids
68	12.40	-	+Na	441.2463	-	383.1508,369.1340, 367.2064,285.0770, 255.0657,189.0909	+HCOO	463.2538	-	417.2486,343.2118, 329.1389,283.0604, 253.0502,237.0758, 193.0863	EB	Unknown	Unknown
69	12.42	$C_{39}H_{50}O_{20}$	+Na	861.2788	-0.58	839.2982,677.2439, 601.1535,531.1879, 441.2462,369.1340, 313.0718,255.0657, 151.0765,111.0445	+HCOO	883.2859	-1.47	837.2803,675.2287, 623.1625,517.1704, 417.2486,343.2118, 329.1389,253.0502, 237.0758,191.0559, 163.0400,116.9277	EB	Epimedin A	Flavonoids
70	12.48	$C_{28}H_{32}O_{15}$	+Na	631.1643	0.63	471.2205,441.2459, 367.2090,301.0711,	-H	607.1663	0.00	493.2337,447.2229, 343.2238,237.0770,	AM	Spinosin isomer	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
71*	12.65	$C_{12}H_{16}O_4$	+Na	247.0955	3.64	255.0656,111.0450 207.1016,189.1355, 161.0967,111.0445	-H	223.0962	-3.59	149.0604 205.0864,161.0247, 116.9285	AS	Senkyunolide H	Phthalides
72*	12.70	$C_{39}H_{50}O_{20}$	+H	839.2956	-2.14	677.2496,531.1861, 441.2453,369.1342, 367.2090,267.1129, 207.1004,129.0542, 85.0274	+HCOO	883.2887	1.70	837.2833,675.2276, 463.2552,417.2495, 345.2276,343.2126, 219.0738,205.0934, 161.0289	EB	Epimedin A	Flavonoids
73	12.78	-	+Na	441.2459	-	369.1333,285.0765, 267.1129,193.1054	+HCOO	463.2552	-	417.2495,343.2116, 283.0615,237.0762, 219.0659,193.0860	EB	Unknown	Unknown
74*	12.89	$C_{38}H_{48}O_{19}$	+H	809.2852	-1.98	677.2419,531.1864, 369.1349,313.0749	+HCOO	853.2756	-1.17	645.2177,507.1501, 343.2116,201.1126	EB	Epimedin B	Flavonoids
75	12.93	$C_{23}H_{26}O_{10}$	+H	485.1417	-1.44	463.1615,301.1065, 167.0698,85.0273	+HCOO	507.1507	0.79	299.1025,251.0559, 193.0504	AM	9,10-dimethoxypterocarpan-3-*O*-β-D-glucoside	Flavonoids
76*	13.02	$C_{15}H_{10}O_4$	+H	255.0657	0.00	178.0862,147.0107, 111.0452	-H	253.0507	2.37	237.0770,203.1285, 193.0872,101.0246	AM/IS/SF	Daidzein	Flavonoids
77*	13.10	$C_{39}H_{50}O_{19}$	+Na	845.2823	-2.48	823.3009,677.2435, 531.1873,369.1345, 313.0716,129.0543, 85.0275	+HCOO	867.2913	-1.15	821.2856,659.2338, 366.1113,279.0293, 128.0106	EB	Epmedin C	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
78	13.23	$C_{39}H_{50}O_{19}$	+Na	845.2820	-2.84	823.3002,677.2423, 487.1574,369.1345, 313.0698,167.0694, 135.0427	+HCOO	867.2917	-0.69	821.2866,659.2341, 463.1607,301.0726, 253.0506,149.0243, 121.0299	AM	Epmedin C isomer	Flavonoids
79	13.28	$C_{22}H_{22}O_{10}$	+Na	469.1114	0.64	285.0753,175.0395, 151.0382,123.0434	+HCOO	491.1199	1.83	283.0614,235.0605, 109.0297,89.0243	SF	3'-methoxy-5'-hydroxy-isoflavaone-7-*O*-β-D-glucopyranoside	Flavonoids
80	13.38	$C_{16}H_{12}O_5$	+H	285.0757	-2.10	257.0795,189.0878, 137.0579,81.0323	-H	283.0613	2.47	255.0663,195.0659, 119.0505,91.0192	SF/IS	3,7-dihydroxy-3'-methoxy-flavanonol	Flavonoids
81	13.38	$C_{22}H_{26}O_8$	+Na	441.1522	-0.68	367.2086,323.1275, 187.0768,137.0603	-H	417.1546	-0.72	399.1156,367.1181, 195.0661	EB	Syringaresinol	Others
82*	13.52	$C_{33}H_{40}O_{15}$	2M+Na	1375.4617	-1.09	699.2262,677.2448, 531.1872,369.1341, 313.0710,255.0652	+HCOO	721.2355	1.53	513.1766,409.1289, 367.1187,351.0875, 128.0103,89.0244	EB	Icariin	Flavonoids
83*	13.77	$C_{16}H_{12}O_5$	+Na	307.0581	-0.33	285.0762,253.0468, 225.0550,213.0541, 171.0220,162.0146	-H	283.0614	2.83	268.0378,211.0401, 147.0813	AM/SF/IS	Calycosin	Flavonoids
84	14.14	$C_{17}H_{14}O_6$	+H	315.0860	-2.86	285.0757,249.1093, 196.1331,111.0447	-H	313.0720	2.56	225.1126,213.1125, 169.1230	IS/AM	2’,4'-dihydroxy-5,6-dimethoxyisoflavaone	Flavonoids
85	14.18	$C_{17}H_{18}O_6$	-	-	-	-	-H	317.1019	-1.89	283.0613,268.0368,	AM	5'-hydro-	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
										221.0810,177.0195, 137.0247,119.0506		isomucronulatol	
86	14.42	$C_{26}H_{32}O_8$	+Na	495.2003	1.62	473.2186,455.2077, 413.1587,303.1593, 285.0757,179.0337, 151.0391,123.0437	-H	471.2015	-0.85	453.1917,439.1750, 411.1448,283.0610, 255.0655,177.0197, 149.0240,121.0293	SF	Kushenol K	Flavonoids
87	14.50	$C_{27}H_{32}O_{11}$	+Na	555.1829	-2.34	533.2001,387.1442, 369.1333,313.0709, 279.1952,129.0542	-H	531.1865	-0.19	385.1261,367.0975, 301.0715,213.1122, 169.1238	EB	Icaritin 3-*O*-Rhamnoside	Flavonoids
88	14.80	$C_{41}H_{68}O_{14}$	+Na	807.4497	-1.24	785.4661,351.2143, 269.0813,175.0869	+HCOO	829.4565	-2.53	783.4518,357.1358, 345.2276,327.2163, 283.0596,207.3657	AM	Astragaloside IV isomer	Saponins
89	14.89	$C_{21}H_{22}O_7$	+H	387.1447	0.77	369.1334,313.0706, 285.0742,235.0964, 179.0337	-H	385.1285	-0.52	367.1176,357.1328, 353.1013,299.0546, 283.0602,269.0814, 255.0610,235.0958, 207.1022,177.0189, 161.0244,149.0238, 121.0287	SF	M1(3,2'-di-hydroxy-isoxanthohumol)	Flavonoids
90	14.96	-	+Na	427.2673	-	349.1804,273.0746, 137.0383	+HCOO	449.3661	-	403.3489,347.0562, 271.1158,135.0350	IS	Unknown	Unknown
91	15.18	-	+Na	351.2153	-	279.1932,265.0975, 247.0869,206.0839	-H	327.2169	-	215.1280,197.1175	AM/AS	Unknown	Unknown

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
92	15.25	$C_{26}H_{32}O_7$	+H	457.2227	0.22	439.2121,421.2006, 321.1701,303.1592, 179.0336,168.0148	-H	455.2077	1.54	437.1955,385.1275, 293.1751,207.1024, 161.0245,116.9282	SF	Kurarinol or isomer	Flavonoids
93	15.30	$C_{32}H_{38}O_{15}$	+Na	685.2094	-2.04	663.2280,607.2144, 457.2220,355.1183, 351.2139,299.0557, 265.0973,189.0914	-H	661.2123	-1.36	455.2064,327.2172, 397.0394,207.0653, 161.0240	EB	Ikarisoside B isomer	Flavonoids
94	15.50	$C_{15}H_{10}O_5$	+H	271.0611	1.84	265.0975,249.1963, 111.0447,91.0526	-H	269.0452	0.74	221.0810,193.0862, 161.0243,116.9276	SF	Baicalein	Flavonoids
95	15.59	$C_{26}H_{28}O_{11}$	-	-	-	-	-H	515.1552	-0.19	457.1856,347.0223, 269.0541,193.0864	EB	Epimedoside C	Flavonoids
96	15.64	$C_{25}H_{30}O_8$	+Na	481.1836	-0.42	459.2007,441.1893, 271.0592,179.0329, 165.0172	-H	457.1863	0.22	429.1902,439.1748, 423.1805,399.1417, 371.1110,355.1895, 295.1549,279.1599, 269.0453,248.9731, 177.0181,161.0243, 128.0095,116.9276	SF	M2	Flavonoids
97	15.92	$C_{31}H_{36}O_{14}$	+Na	655.1989	-2.14	501.2566,355.1179, 297.0761,235.0965, 179.0346	-H	631.2042	2.38	533.1298,363.0175, 283.0605,207.1020, 161.0245	EB	Ikarisoside F	Flavonoids
98	15.97	$C_{32}H_{38}O_{14}$	+Na	669.2157	-0.30	647.2338,355.1186, 299.0558,235.0976,	-H	645.2172	-1.70	631.2017,353.0998, 329.2361,283.0608,	EB	Sagittatoside B	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
99	15.99	$C_{18}H_{34}O_5$	+Na	353.2313	2.55	179.0345 299.0563,265.0968, 235.0965,179.0344, 111.0452	-H	329.2331	0.91	161.0242 283.0610,229.1437, 161.0241	AM/IS/EA/ AS/EB/ZJ	(Z)-5,8,11-trihydroxyoctadec-8-enoic acid or isomer	Organic acids
100	16.09	$C_{18}H_{34}O_5$	+Na	353.2317	3.68	299.0553,297.0762, 235.0967,179.0344	-H	329.2330	0.61	283.0604,229.1437, 161.0241	AM/IS/EA/ AS/EB/ZJ	(Z)-5,8,11-trihydroxyoctadec-9-enoic acid or isomer	Organic acids
101	16.20	$C_{18}H_{34}O_5$	+Na	353.2318	3.96	301.0708,277.2161, 235.0969,179.0348, 111.0446	-H	329.2342	4.25	299.0554,229.1438, 227.1280,177.0914, 161.0237	AM/IS/EA/ AS/EB/ZJ	(Z)-5,8,11-trihydroxyoctadec-10-enoic acid or isomer	Organic acids
102	16.24	$C_{18}H_{34}O_5$	+Na	353.2321	4.81	297.0771,269.0805, 235.0993,179.0346, 111.0445	-H	329.2335	2.13	299.0559,229.1437, 227.1281,177.0920, 161.0244	AM/IS/EA/ AS/EB/ZJ	(Z)-5,8,11-trihydroxyoctadec-11-enoic acid or isomer	Organic acids
103	16.25	$C_{26}H_{32}O_7$	+H	457.2217	-1.97	385.1296,369.1346, 353.2018,301.0712, 179.0345	-H	455.2049	-4.61	371.1141,329.2332, 299.0556,161.0246, 116.9287	SF	Kurarinol or isomer	Flavonoids
104	16.30	$C_{18}H_{34}O_5$	+Na	353.2310	1.70	299.0553,297.0762, 235.0967,179.0344, 111.0452	-H	329.2330	0.61	299.0548,229.1437, 227.1267,177.0917, 161.0241	AM/IS/EA/ AS/EB/Z	(Z)-5,8,11-trihydroxyoctadec-12-enoic acid or	Organic acids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
											J	isomer	
105	16.39	$C_{26}H_{32}O_7$	+Na	479.2043	-0.63	351.2146,331.1884, 207.1013,179.0346	-H	455.2061	-1.98	439.1753,371.1138, 329.2330,299.0555, 205.0864,177.0915, 161.0968	SF	Kurarinol or isomer	Flavonoids
106*	16.62	$C_{41}H_{68}O_{14}$	+Na	807.4495	-1.49	785.4681,605.4042, 587.3950,473.3627, 437.3411,351.2164, 269.0818,245.0489, 143.1059,73.0271	+HCOO	829.4578	-0.96	783.4526,369.1356, 327.2216,287.1019, 207.1024,161.0971	AM	Astragaloside IV	Saponins
107	16.66	$C_{21}H_{22}O_6$	+Na	393.1318	1.02	371.1504,351.2159, 325.1440,285.0762, 209.0463,179.0331, 107.0500	-H	369.1343	1.35	351.1230,341.1383, 337.1073,325.1429, 283.0614,279.1599, 219.0655,207.1022, 191.0573,177.0194, 161.0239,149.0235, 116.9289	SF	2-hydroxy-isoxanthohumol	Flavonoids
108*	16.80	$C_{41}H_{68}O_{14}$	+Na	807.4502	-0.62	491.2390,455.2230, 412.3652,355.1185, 299.0630,269.0811, 143.1072	+HCOO	829.4567	-2.29	783.4517,369.1331, 353.1016,327.2176, 287.2222,213.1491, 161.0970	AM	Astragaloside III	Saponins
109	16.82	$C_{26}H_{28}O_{10}$	+H	501.1761	0.00	355.1179,299.0547, 269.0805,143.1077	-H	499.1607	0.60	353.1019,327.2174, 295.0976,227.0349,	EB	Baohuoside II	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
110*	16.99	$C_{48}H_{78}O_{18}$	+Na	965.5076	-1.04	943.5247,797.4670, 635.4163,617.1045, 599.3950,459.3831, 441.3733,423.3627, 221.1906,191.1072, 177.0559	-H	941.5115	0.53	171.1029,116.9289 371.1133,327.2180, 229.1455,116.9264	AM	Soyasaponin I	Saponins
111	17.17	$C_{27}H_{30}O_{11}$	+Na	553.1697	1.99	455.2255,283.0605, 269.1458,161.0306	-H	529.1709	-0.19	367.1543,339.1597, 281.0455,253.0500, 229.1443,205.0867	EB	Icariside Ⅰ	Flavonoids
112*	17.54	$C_{16}H_{12}O_4$	+H	269.0822	2.97	253.0483,197.0584, 154.0222	-H	267.0661	1.50	252.0425,223.0397, 195.0452	AM/SF/IS	Formononetin	Flavonoids
113	17.54	$C_{18}H_{34}O_5$	+Na	353.2312	2.26	213.0917,207.1094, 177.0566,137.0608	-H	329.2333	1.52	253.0750,219.0685, 116.9296	AS	Pinellice acid	Organic acids
114	17.67	$C_{21}H_{20}O_6$	+H	369.1341	0.81	353.2314,269.0815, 247.0653,191.1071, 149.0610	-H	367.1179	-0.82	329.2440,267.0746, 207.1017,163.1127	EB	Icaritin isomer	Flavonoids
115	17.77	$C_{33}H_{40}O_{15}$	+Na	699.2255	-1.43	369.1337,313.0739, 309.2068,201.0095, 129.0564,85.0297	-H	675.2276	-1.93	367.1179,329.2328, 267.0652,207.1017, 163.1127	EB	Icariin isomer	Flavonoids
116*	17.77	$C_{21}H_{22}O_5$	2M+Na	731.2829	-0.41	377.1375,355.1563, 269.0810,235.0971, 191.1072,179.0348	2M-H	707.2850	-0.85	353.1398,329.2331, 279.1602,233.0816, 189.0915	SF	Isoxanthohumol	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
117	17.88	$C_{26}H_{30}O_7$	+Na	477.1902	2.72	455.2083,437.1967, 377.1371,355.1531, 175.0610,143.1076	-H	453.1902	-2.43	439.1756,353.1400, 279.1594,161.0247	SF	Kushenol N or isomer	Flavonoids
118	18.12	$C_{43}H_{70}O_{15}$	+Na	849.4612	0.00	827.4788,809.4687, 629.4062,455.3529, 437.3426,419.3314, 353.2321,175.0608, 143.1073	+HCOO	871.4675	-1.84	825.4612,535.1955, 329.2325,219.0652, 165.1281	AM	Isoastragaloside II or isomer	Saponins
119	18.32	$C_{12}H_{14}O_3$	-	-	-	-	-H	205.0872	3.41	161.0975,145.0300, 106.0424	AS	6,7-Epoxyligustilide	Phthalides
120	18.44	$C_{32}H_{38}O_{14}$	+Na	669.2136	-3.44	647.2282,515.1919, 369.1333,353.2305, 167.0714	-H	645.2176	-1.08	367.1305,329.2323, 301.1073,205.0862, 161.0970	EB	Sagittatoside B	Flavonoids
121	18.51	$C_{35}H_{58}O_9$	+Na	645.3955	-3.72	531.1868,369.1332, 353.2292,270.0054, 95.0847	+HCOO	667.4053	-0.60	529.1877,367.1301, 329.2433,219.0657	AM	Astramembrannin II	Saponins
122	18.58	$C_{33}H_{40}O_{14}$	+Na	683.2307	-1.32	661.2495,515.1924, 369.1333,353.2305, 313.0731	-H	659.2350	1.52	367.1183,351.0886, 329.2323,219.0660, 116.9275	EB	2''-*O*-rhamnosy Icarside II	Flavonoids
123*	18.70	$C_{16}H_{12}O_5$	+H	285.0766	1.05	283.0605,255.0652, 175.0394,163.0404, 151.0401,147.0451, 123.0455	-H	283.0612	2.12	255.0647,203.0711, 145.0291,116.9279	IS	Maackiain	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
124	18.85	$C_{33}H_{40}O_{14}$	+Na	683.2299	-2.49	661.2491,515.1933, 369.1341,353.2303, 313.0711	-H	659.2344	0.61	441.1905,329.2332, 243.1599,219.0656, 116.9274	EB	3''-*O*-rhamnosy Icarside II	Flavonoids
125	18.91	$C_{25}H_{30}O_7$	+H	443.2073	0.68	425.1945,307.1544, 301.0715,277.1438, 165.0182	-H	441.1903	-2.27	423.1800,385.1266, 363.0168,279.1599, 161.0242,116.9281	SF	Norkurarinol or isomer	Flavonoids
126	19.00	$C_{25}H_{30}O_7$	+H	443.2077	1.58	425.1968,353.2294, 307.1540,301.0702, 283.0599,165.0177	-H	441.1917	0.91	423.1800,385.1275, 369.0991,279.1596, 161.0244,116.9287	SF	Norkurarinol or isomer	Flavonoids
127	19.03	$C_{33}H_{40}O_{14}$	+Na	683.2314	-0.29	661.2515,515.1927, 369.1337,353.2299, 313.0716	-H	659.2339	-0.15	441.1906,371.1493, 329.2325,299.0919, 269.0444,219.0657, 205.0863,116.9276	EB	4''-*O*-rhamnosy Icarside II	Flavonoids
128	19.13	$C_{43}H_{70}O_{15}$	+Na	849.4602	-1.18	827.4777,809.4655, 629.4042,455.3519, 437.3418,419.3308, 353.2300,175.0610, 143.1074	+HCOO	871.4678	-1.49	825.4620,535.1954, 329.2328,311.2218, 219.0661,116.9278	AM	Isoastragaloside II or isomer	Saponins
129	19.27	$C_{26}H_{30}O_7$	+Na	477.1886	-0.63	455.2070,439.1738, 369.1339,349.1989, 179.0347,119.0863	-H	453.1935	4.85	439.1767,435.1813, 425.1970,421.1662, 383.1162,303.1607, 275.1659,177.0198, 149.0246,121.0295	SF	Kushenol N	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
130*	19.38	$C_{16}H_{14}O_4$	+H	271.0976	2.21	161.0607,137.0636, 123.0446	-H	269.0816	0.74	254.0614,239.0349, 225.0549,211.0396, 116.9278	IS	Medicarpin	Flavonoids
131	19.41	$C_{12}H_{12}O_3$	+H	205.0866	0.49	187.0762,169.0658, 159.0813,137.0608, 123.0536,91.0553	-H	203.0714	2.95	173.0238,145.0288, 132.0211,116.9281	AS	3-Butylidene-4-hydroxyphthalide	Phthalides
132	19.82	$C_{43}H_{70}O_{15}$	+Na	849.4615	0.35	827.4786,809.4685, 629.4057,455.3529, 437.3423,419.3315, 247.1521,175.0595	+HCOO	871.4682	-1.03	825.4625,533.1818, 327.2166,311.2216, 219.0670,116.9284	AM	Isoastragaloside II or isomer	Saponins
133*	19.86	$C_{27}H_{30}O_{10}$	2M+Na	1051.3555	-2.00	537.1731,515.1898, 369.1333,313.0701, 249.1960,213.0887, 129.0561,85.0275	2M-H	1027.3601	0.10	513.1766,367.1171, 351.0871,323.0918, 279.0298,251.0350, 116.9280	EB	Baohuoside Ⅰ	Flavonoids
134	19.98	$C_{21}H_{20}O_7$	+H	385.1274	-3.38	369.1337,313.0712, 191.1070,177.0535, 123.0545	-H	383.1121	-2.61	331.2471,287.2227, 203.0698,116.9273	EB	2′-hydroxy-β-anhydroicaritin	Saponins
135	20.00	$C_{20}H_{20}O_6$	+H	357.1333	-1.40	335.2199,297.0767, 191.1071,179.0345	-H	355.1184	0.56	309.2070,255.0661, 248.9724,161.0237, 116.9287	SF	Leachianone G	Flavonoids
136	20.10	$C_{26}H_{30}O_6$	2M+Na	899.3977	-0.56	461.1963,439.2119, 421.2003,303.1700, 297.0767,179.0334,	2M-H	875.3997	-1.14	437.1969,383.1129, 275.1653,217.0862, 161.0249,137.0246,	SF	Kurarinone or isomer	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Add ucts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
137	20.24	$C_{12}H_{12}O_3$	-	-	-	151.0383 -	-H	203.0731	0.00	116.9287 174.0323,161.0240, 159.0816,116.9282	AS	3-Butylidene-4-hydroxyphthalide	Phthalides
138	20.42	$C_{26}H3_2O_7$	+Na	479.2045	-0.21	457.2234,439.2118, 423.1425,351.2142, 333.2035,297.0770, 179.0348	-H	455.2067	-0.66	437.1958,309.2067, 283.0606,241.1805, 161.0245,116.9281	SF	Kurarinol or isomer	Flavonoids
139	20.51	$C_{25}H_{28}O_7$	+H	441.1918	1.13	409.2553,367.1181, 179.0343,165.0187	-H	439.1763	1.37	421.1654,395.1850, 261.1513,177.0194, 161.0237,116.9278	SF	Kushenol L	Flavonoids
140	20.59	$C_{20}H_{20}O_5$	+H	341.1400	3.22	303.1600,285.0766, 179.0355,165.0187	-H	339.1231	-0.29	257.1652,219.0664, 161.0248,116.9289	SF	Desmethylxanthohumol	Flavonoids
141*	20.73	$C_{45}H_{72}O_{16}$	+Na	891.4702	-1.79	861.4083,671.4153, 437.1948,419.1853, 335.2196,217.0708, 143.1073	+HCOO	913.4799	0.22	563.2283,437.1955, 311.2226,245.0812, 179.0347	AM	Astragaloside I	Saponins
142*	20.99	$C_{12}H_{16}O_2$	+H	193.1224	-2.59	175.1126,147.1175, 137.0607,119.0860, 105.0707,91.0545	-H	191.1072	0.00	189.0914,171.1024, 161.0244,116.9279	AS	Senkyunolide A	Phthalides
143	21.05	$C_{20}H_{18}O_6$	+H	355.1186	1.13	335.2192,193.1227, 175.1124,137.0604	-H	353.1024	-0.28	311.2224,293.2107, 269.1642,116.9278	EB	Desmethylanhydroicaritin	Flavonoids
144	21.15	$C_{26}H_{32}O_7$	+H	457.2222	-0.87	398.2415,385.1275, 337.2356,315.0856,	-H	455.2071	0.22	439.1760,425.1963, 383.1130,313.2384,	SF	Kurarinol or isomer	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
145	21.15	$C_{18}H_{34}O_2$	+Na	337.2354	-0.30	165.0169 279.2313,249.1960, 207.1015,191.1071, 123.0539	-H	313.2383	1.28	177.0183,161.0242 265.1468,203.0704, 161.0241,116.9282	AS/AM	Octadecanedioic acid or isomer	Organic acids
146	21.20	$C_{25}H_{30}O_6$	+H	427.2113	-1.87	409.1998,376.2596, 337.2346,297.0750, 179.0349,165.0182	-H	425.1962	-0.47	411.1801,383.1124, 313.2377,279.1599, 177.0194,161.0243, 116.9285	SF	Kushenol T	Flavonoids
147	21.25	$C_{45}H_{72}O_{16}$	+Na	891.4706	-1.35	869.4871,671.4147, 437.3412,367.2092, 335.2191,317.1359, 217.0711,145.1019	+HCOO	913.4793	-0.44	867.4739,467.1701, 311.2219,297.0771, 190.9986,116.9279	AM	Isoastragaloside I	Saponins
148*	21.29	$C_{12}H_{14}O_2$	+H	191.1070	-1.05	173.0970,145.1019, 117.1169	-	-	-	-	AS	Butylphthalide	Phthalides
149	21.39	$C_{18}H_{34}O_4$	+Na	337.2359	1.19	279.2318,249.1960, 207.1014,189.0907, 123.0545	-H	313.2382	0.96	265.1465,205.0866, 161.0241,116.9280	IS/AM/AS	Octadecanedioic acid or isomer	Organic acids
150	21.39	-	+Na	757.3982	-	467.1953,337.2359, 297.1527,179.0344	+HCOO	779.4064	-	455.2070,313.2382	IS	Unknown	Unknown
151	21.53	$C_{27}H_{32}O_6$	+Na	475.2087	-2.10	453.2256,437.1936, 303.1592,179.0339	-H	451.2116	-1.11	435.1451,409.1642, 299.1289,161.0239, 148.0181,116.9289	SF	2'-methoxykurarinone	Flavonoids
152	21.59	$C_{18}H_{34}O_6$	+Na	337.2354	-0.30	279.2320,249.1967,	-H	313.2379	0.00	265.1468,203.0695,	IS/AM/A	Octadecanedioic	Organic

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
						207.1018,191.1074, 123.0558				161.0242,116.9279	S	acid or isomer	acids
153*	21.63	$C_{30}H_{50}O_5$	+Na	513.3527	-5.65	453.2336,437.2132, 419.2047,333.2881, 189.1362,119.1329	-	-	-	-	AM	Cycloastragenol	Others
154	21.71	$C_{25}H_{28}O_6$	+H	425.1957	-1.65	407.1862,383.1562, 369.1342,289.1440, 165.0190	-H	423.1808	0.00	405.1696,387.1291, 261.1494,191.0553, 161.0244,137.0237, 116.9278	SF	Sophoraflavanone G	Flavonoids
155	21.80	$C_{18}H_{34}O_9$	+Na	337.2356	0.30	279.2322,249.1964, 207.1015,189.0917, 123.0558	-H	313.2382	0.96	265.1464,201.1123, 161.0237,116.9277	IS/AM/AS	Octadecanedioic acid or isomer	Organic acids
156	21.96	$C_{45}H_{72}O_{16}$	+Na	891.4708	-1.12	644.3220,437.3475, 335.2195,305.1314, 191.1108,173.0977, 145.1020,117.0704	+HCOO	913.4803	0.66	439.1753,409.1644, 395.1852,311.2214, 297.1127,219.0657, 116.9279	AM	Isoastragaloside I	Saponins
157	21.99	$C_{12}H_{14}O_2$	+H	191.1069	-1.57	173.0957,145.1011, 117.0698	-	-	-	-	AS	3-butylphthalide	Phthalides
158	22.01	$C_{26}H_{30}O_7$	+Na	477.1891	0.42	455.2080,437.1969, 335.2195,297.0751, 277.1798,179.0337	-H	453.1916	0.66	439.1763,421.1649, 369.1350,339.1233, 275.1652,219.0657, 177.0194,149.0235, 116.9281	SF	Kushenol N or isomer	Flavonoids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
159*	22.05	$C_{15}H_{10}O_5$	-	-	-	-	-H	269.0452	0.74	241.0491,222.5054, 116.9280	AM/AS/IS	Emodin	Others
160	22.35	$C_{26}H_{28}O_6$	+Na	459.1789	1.09	437.1930,421.1994, 339.2498,333.2021, 249.1941,179.0324	-H	435.1810	0.46	395.1839,353.2129, 309.0761,189.0919, 177.0181,161.0235, 116.9279	SF	M3(anhydrokushenol N)	Flavonoids
161*	22.49	$C_{12}H_{14}O_2$	+H	191.1069	-1.57	173.0961,163.1115, 155.0854,145.1012, 117.0697,91.0541	-	-	-	-	AS	Ligustilide	Phthalides
162*	22.63	$C_{12}H_{12}O_2$	+H	189.0917	0.53	173.0971,155.1071, 145.1020,117.0707, 91.0548	-H	187.0762	1.60	163.1123,145.0291, 116.9278	AS	Butylidene phthalide	Phthalides
163	22.91	$C_{21}H_{22}O_5$	+H	355.1546	0.28	299.0924,249.1967, 191.1074,179.0350	-H	353.1395	1.70	293.2116,275.2013, 177.0197,166.0256, 116.9280	SF	Xanthohumol	Flavonoids
164	23.02	$C_{18}H_{30}O_3$	-	-	-	-	-H	293.2122	1.71	275.2018,269.2130, 219.0663,116.9285	IS/AM	9-Hydroxy-10,12,15-octadecatrienoic acid	Organic acids
165	23.51	$C_{25}H_{28}O_6$	+H	425.1971	1.65	407.0827,391.2453, 333.2035,191.1071	-H	423.1808	0.00	405.1676,295.2278, 261.2280,248.9726, 161.0244,116.9281	SF	Kushenol E	Flavonoids
166	23.60	-	+Na	627.3358	-	419.1825,318.2400,	+HCOO	649.3434	-	603.3386,333.1707,	AM/AS/	Unknown	Unknown

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
167	23.82	$C_{26}H_{30}O_6$	+Na	461.1942	0.43	263.2368,191.1077 439.2128,421.1991, 315.0859,297.0769, 179.0349	-H	437.1962	-0.46	265.1481 423.1809,353.2112, 271.2277,161.0244, 116.9279	SF SF	Kurarinone or isomer	Flavonoids
168	24.11	$C_{24}H_{28}O_4$	+Na	403.1885	0.00	381.2059,363.1955, 335.2074,213.0892, 191.1068,173.0965, 145.1020	-H	379.1909	0.00	367.1178,353.2107, 295.2273,189.0917, 116.9283	AS	Riligustilide/Angelicide isomer	Phthalides
169*	24.19	$C_{21}H_{20}O_6$	+H	369.1338	0.00	313.0709,265.0960, 249.1957,135.0441	-H	367.1186	1.09	311.1684,295.2271, 265.1469,203.0707, 116.9279	EB	Icaritin	Flavonoids
170	24.21	$C_{24}H_{28}O_4$	+Na	403.1879	-1.49	335.2005,213.0893, 191.1070,173.0962, 145.1022	-H	379.1919	2.64	367.1191,295.2277, 293.2115,265.1477, 189.0914,116.9284	AS	Riligustilide/Angelicide isomer	Phthalides
171	24.34	$C_{30}H_{36}O_7$	+Na	531.2359	0.00	509.2527,475.2100, 453.2254,421.2013, 279.2305,179.0329	-H	507.2374	-1.77	489.2250,437.1613, 423.1805,355.1907, 329.2119,295.2277, 277.2169,248.9716, 177.0193,161.0251, 128.0108,116.9274	SF	Kushenol M	Flavonoids
172	24.52	$C_{24}H_{28}O_4$	2M+Na	783.3876	0.38	403.1891,381.2063, 363.1961,335.2024, 213.0900,191.1076,	-H	379.1912	0.79	367.1179,297.2426, 293.2106,269.2116, 189.0918,116.9281	AS	Riligustilide/Angelicide isomer	Phthalides

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
173	24.67	$C_{24}H_{28}O_4$	+Na	403.1890	1.24	173.0968,145.1020 381.2035,379.1892, 363.1955,335.2024, 213.0895,191.1069, 173.0969	-H	379.1920	2.90	353.2122,293.2119, 265.1473,189.0921, 116.9278	AS	Riligustilide/Angelicide isomer	Phthalides
174	24.67	$C_{25}H_{28}O_5$	+H	409.2018	0.73	391.1909,335.2037, 317.2087,277.2171, 179.1418	-H	407.1859	0.25	329.1387,293.2118, 261.1495,248.9724, 116.9283	SF	Kushenol A	Flavonoids
175	24.67	$C_{18}H_{30}O_3$	+Na	317.2101	2.52	277.2166,249.1965, 213.0893,211.0738, 191.1069,189.0916, 161.1321,123.0548, 105.0705,81.0705	-H	293.2119	0.68	269.2118,265.1472, 255.2327,203.0705, 189.0916,183.0121, 116.9281	AS/IS/AM/EB	13-oxo-9E,11E-octadecatrienoic acid	Organic acids
176	24.74	$C_{18}H_{30}O_3$	+Na	317.2101	2.52	277.2170,249.1964, 213.0894,211.0735, 191.1072,189.0915, 171.0808,161.1332, 123.0556,105.0703, 81.0703	-H	293.2117	0.00	277.1432,269.2117, 265.1472,255.2324, 189.0910,183.0112, 116.9278	AS/IS/AM/EB	9-oxo-10E,12E-octadecatrienoic acid	Organic acids
177	24.91	$C_{18}H_{30}O_3$	+Na	317.2100	2.21	277.2166,249.1974, 213.0890,211.0732, 191.1070,189.0913, 161.1335,151.1126,	-H	293.2116	-0.34	269.2117,265.1468, 255.2319,203.0710, 183.0106,152.9952, 116.9280	IS/AS/AM/EB	9(10)-epoxy-12Z,15Z-octadecadienoic acid	Organic acids

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
178	25.05	$C_{24}H_{28}O_4$	2M+Na	783.3854	-2.43	123.0556,105.0701, 81.0705 403.1874,381.2053, 363.1950,335.2069, 213.0889,191.1068, 173.0963	-H	379.1906	-0.79	309.1730,297.2426, 189.0917,116.9280	AS	Riligustilide/Angelicide isomer	Phthalides
179	25.11	$C_{18}H_{30}O_3$	+Na	317.2108	4.73	277.2162,249.1977, 213.0884,203.1797, 191.1070,161.1329, 147.1173,123.0556, 105.0703,81.0705	-H	293.2114	-1.02	279.2317,265.1471, 255.2316,183.0112, 152.9950,116.9280	AS/IS/AM/EB	13-hydroxy-6Z,9Z,11E-octadecatrienoic acid	Organic acids
180	25.29	$C_{24}H_{28}O_4$	+Na	403.1883	-0.50	381.2054,363.1932, 335.2032,213.0885, 191.1071,173.0963	-H	379.1914	1.32	361.1659,297.2432, 152.9959,116.9282	AS	Riligustilide/Angelicide isomer	Phthalides
181	25.34	$C_{24}H_{28}O_4$	2M+Na	783.3860	-1.66	403.1890,381.2058, 363.1950,335.2011, 213.0894,191.1068, 173.0964	-H	379.1911	0.53	361.1655,309.1732, 297.2425,293.2109, 189.0914,116.9278	AS	Tokinolide B isomer	Phthalides
182	25.57	$C_{24}H_{28}O_4$	2M+Na	783.3875	0.26	403.1886,381.2058, 363.1956,335.2011, 213.0888,191.1066, 173.0965	-H	379.1903	-1.58	353.2009,295.2280, 293.2102,189.0914, 116.9280	AS	Tokinolide B isomer	Phthalides
183*	25.82	$C_{24}H_{28}O_4$	2M+	783.3873	0.00	403.1896,381.2079,	-H	379.1905	-1.05	353.1996,317.1751,	AS	Tokinolide B	Phthalides

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
			Na			363.1957,335.2013, 307.1692,213.0900, 191.1094,173.0970, 145.1017,117.0707				295.2271,265.1470, 249.1850,189.0912, 116.9278			
184	25.91	$C_{30}H_{36}O_6$	+H	493.2571	-3.85	453.1921,419.1834, 265.1894,249.1947, 179.0335	-H	491.2429	-1.02	451.1714,437.1595, 423.1804,355.1913, 329.2111,295.2275, 279.0064,248.9729, 205.0851,161.0237, 128.0099,116.9278	SF	Kushenol B	Flavonoids
185*	26.10	$C_{24}H_{28}O_4$	2M+Na	783.3861	-1.53	403.1908,381.2062, 363.1954,335.2003, 307.1691,213.0894, 191.1073,173.0969, 145.1018,117.0708	-H	379.1899	-2.64	353.1998,325.1839, 295.2272,265.1470, 189.0918,116.9281	AS	Riligustilide/Angelicide	Phthalides
186*	26.19	$C_{24}H_{28}O_4$	2M+Na	783.3862	-1.40	403.1906,381.2065, 363.1954,353.2004, 307.1690,213.0893, 191.1078,173.0966, 145.1021,117.0703	-H	379.1897	-3.16	353.1993,325.1839, 295.2271,293.1800, 269.2118,265.1471, 189.0911,116.9280	AS	Levistolide A	Phthalides
187	26.31	$C_{18}H_{36}O_3$	-	-	-	-	-H	299.2594	2.67	265.1468,183.0111, 116.9282	EA	Hydroxystearic acid	Organic acids
188	26.51	$C_{24}H_{28}O_4$	2M+	783.3846	-3.45	403.1885,381.2057,	-	-	-	-	AS	Levistolide A isomer	Phthalides

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
189	26.68	$C_{24}H_{28}O_4$	Na 2M+Na	783.3876	0.38	307.1699,213.0894,191.1069,173.0967 403.1900,381.2068,363.1944,307.1695,213.0892,191.1074,173.0968,145.1020	-	-	-	-	AS	Levistolide A isomer	Phthalides
190	26.97	$C_{18}H_{34}O_3$	-	-	-	-	-H	297.2428	-0.67	269.2119,116.9281	EA	Ricinelaidic acid	Organic acids
191	26.92	$C_{24}H_{28}O_4$	+Na	403.1888	0.74	381.2060,363.1935,307.1699,213.0888,191.1071,173.0964,145.1018	-	-	-	-	AS	Levistolide A isomer	Phthalides
192	27.05	$C_{24}H_{28}O_4$	2M+Na	783.3876	0.38	403.1901,381.2072,335.2022,307.1693,213.0897,191.1073,173.0967,145.1025	-	-	-	-	AS	Levistolide A isomer	Phthalides
193	27.15	$C_{24}H_{28}O_4$	2M+Na	783.3861	-1.53	403.1894,381.2062,335.2006,213.0891,191.1069,173.0965,145.1012	-	-	-	-	AS	Levistolide A isomer	Phthalides
194	27.27	$C_{24}H_{28}O_4$	2M+Na	783.3864	-1.15	403.1898,381.2070,363.1944,335.2008,213.0894,191.1073,	-	-	-	-	AS	Levistolide A isomer	Phthalides

NO.	RT (min)	Formula	Positive mode				Negative mode				Origin	Identitfcation	Type
			Adducts	Observed *m/z*	Error (ppm)	MS^n	Adducts	Observed *m/z*	Error (ppm)	MS^n			
195	27.35	$C_{24}H_{28}O_4$	2M+Na	783.3885	1.53	173.0966,145.1019 403.1896,381.2066, 213.0891,191.1070, 173.0965,145.1019	-	-	-	-	AS	Levistolide A isomer	Phthalides
196	27.50	$C_{24}H_{28}O_4$	2M+Na	783.3857	-2.04	403.1900,381.2061, 363.1945,213.0893, 191.1071,173.0964, 145.1019	-	-	-	-	AS	Levistolide A isomer	Phthalides
197	27.70	$C_{24}H_{28}O_4$	2M+Na	783.3873	0.00	403.1894,381.2058, 363.1938,213.0893, 191.1066,145.1017	-	-	-	-	AS	Levistolide A isomer	Phthalides
198*	28.51	$C_{30}H_{48}O_3$	-	-	-	-	-H	455.3519	-1.32	271.2275,248.9726, 116.9282	ZJ/IS	Betulinic acid	Organic acids
199	28.83	$C_{16}H_{30}O_2$	-	-	-	-	-H	253.2175	2.76	237.0761,183.0047, 116.9277	EA/ZJ	ethyl 9Z-tetradecenoate	Others
200*	28.92	$C_{30}H_{48}O_3$	-	-	-	-	-H	455.3522	-0.66	283.0632,253.2159, 116.9276	ZJ	Oleanic acid	Organic acids
201	29.41	$C_{18}H_{32}O_2$	-	-	-	-	-H	279.2332	2.86	265.1465,248.9714, 116.9276	AS	Linoleic acid	Organic acids
202	31.13	$C_{18}H_{37}NO$	+H	284.2958	1.76	230.1398,123.0560, 103.9561,88.0762	-	-	-	-	IS/EB.AS/SF	Hexadecylacetamide	Others

Note: RT: retention time, *: the compound identified by a standard; IS (Xue Renshen): *Indigofera stachyoides* Lindl.; AM (Huang Qi): *Astragalus membranaceus* (Fisch.) Bge.var.*mongholicus* (Bge.) Hsiao; AS (Dang Gui): *Angelica sinensis* (Oliv.) Diels; EA (E Jiao): *Equus asinm* L.; ZJ (Da Zao): *Ziziphus jujuba* Mill.; SF (Ku Shen): *Sophora flavescens* Ait.; EB (Yin Yanghuo): *Epimedium brevicornu* Maxim.