Electronic Supplementary Material (ESI) for Analytical Methods.

Table S1 Compounds of MLSTP

NO.	Compound	t_R/min	Molecular formula	Ion mode	Theoretical m/z	Measured m/z	Delat (ppm)	MS/MS fragments	Compound source
1	sucrose	1.14	$C_{12}H_{22}O_{11}$	N	341.10893	341.10846	1.824	341.11,179.06,161.04,143.03,119.03,101.02,89.02,71.01,59.01	a
2	quinic acid	1.19	$C_7H_{12}O_6$	N	191.05611	191.05588	4.530	191.06,127.04,85.03	b
3	gallic acid	1.87	$C_7H_6O_5$	N	169.01425	169.01393	0.780	169.01,125.02,97.03,81.03	a
4	protocatechuic acid*	3.40	$C_7H_6O_4$	N	153.01933	153.01913	0.895	153.02,123.05,109.03,108.02	c
5	hydroxytyrosol*	3.60	$C_8H_{10}O_3$	N	153.05571	153.05545	0.829	153.06,123.05,109.03	d
6	5-o-caffeoylquinic acid	4.07	$C_{16}H_{18}O_9$	P	355.10247	355.10181	-1.545	355.07,163.04,145.03,135.04	b
7	loganin	4.74	$C_{17}H_{26}O_{10}$	N	389.14532	389.14523	2.587	389.15,343.14,181.09,161.04,151.08,136.05,109.06	b
8	3,4-dihydroxybenzaldehyde*	5.59	$C_7H_7O_3$	P	139.03897	139.03900	0.211	139.04,112.05,111.04,93.03	c
9	loganic acid*	6.29	$C_{16}H_{24}O_{10}$	N	375.12967	375.12955	2.604	375.13,213.08,169.09,151.08	b
10	loganic acid_qt	6.43	$C_{10}H_{14}O_5$	P	215.09140	215.09137	-0.140	215.09,197.08,179.07,161.06,151.08,133.06,109.06,81.07	b
11	methyl gallate	6.62	$C_8H_8O_5$	N	183.02989	183.02957	4.208	183.03,168.01,124.02	a
12	osmanthuside	6.80	$C_{19}H_{28}O_{11}$	N	431.15467	431.15579	2.324	431.16,299.11,191.06,149.04,89.	e

	H							02,59.01	
13	oxypaeoniflorin*	7.06	$C_{23}H_{28}O_{12}$	N	495.15079	495.15012	0.843	495.15,333.10,195.07,137.02,93.03	a
14	skimmetin*	7.13	$C_9H_6O_3$	P	163.03908	163.03870	-1.660	163.04,145.03,135.04,117.03,89.04	e
15	chlorogenic acid*	7.13	$C_{16}H_{18}O_9$	N	353.08781	353.08743	0.721	353.09,191.06,179.03,173.05,135.04	b
16	6-O-methylcatalpol	7.39	$C_{16}H_{24}O_{10}$	N	375.12967	375.12964	2.844	375.13,195.07,169.09,151.08,113.02,69.03	d
17	vanillic acid	7.63	$C_8H_8O_4$	N	167.03498	167.03462	0.735	167.03,123.05,95.05	f
18	methyl chlorogenate	7.75	$C_{17}H_{20}O_9$	N	367.10345	367.10315	2.156	367.10,193.05,134.04	b
19	6-hydroxycoumarin	7.80	$C_9H_6O_3$	P	163.03868	163.03870	-1.782	163.04,145.03,135.04,117.03,89.04	e
20	caffeate*	7.81	$C_9H_8O_4$	N	179.03498	179.03467	0.785	179.03,135.05,117.03,107.05	b
21	cryptochlorogenic acid	7.81	$C_{16}H_{18}O_9$	P	355.10247	355.10168	-1.911	355.07,163.04,145.03,135.04	b
22	3-o-feruloylquinic acid	7.84	$C_{17}H_{20}O_9$	P	369.11812	369.11719	-2.218	369.19,177.05,145.03,117.03	b
23	isoscopoletin	7.95	$C_{10}H_8O_4$	P	193.04953	193.04924	-1.530	193.05,179.03,178.03,151.04,137.06,133.03,95.05	c
24	secologanate	8.33	$C_{16}H_{22}O_{10}$	P	375.12857	375.12775	-2.195	375.21,359.06,305.13,285.18,256.18	b
25	secologanic	8.35	$C_{10}H_{12}O_5$	P	213.07575	213.07549	-1.220	213.08,195.07,177.05,151.04,10	b

	acid_qt							7.05,95.05,79.05	
26	paeonin b_qt	8.71	$C_{10}H_{12}O_4$	P	197.08095	197.08047	-1.854	197.08,179.07,151.08,137.06,	a
27	phellodenol A	8.73	$C_{11}H_{10}O_4$	P	207.06518	207.06482	-1.764	207.06,179.07,163.04,151.08	g
28	n-methylhigenamine-7-o-beta-d-glucopyranoside	9.00	$C_{23}H_{29}O_8N$	P	448.19670	448.19632	-0.610	448.20,286.14,255.10,107.05	e
29	8-epiloganin_qt	9.25	$C_{11}H_{16}O_5$	P	229.10705	227.09103	-1.630	229.11,211.10,197.08,179.07,161.06,151.08,137.06,133.06,109.06,105.07,81.07	b
30	isocorypalmine*	9.36	$C_{20}H_{23}NO_4$	N	340.15543	340.15521	2.573	340.16,325.13,310.11,282.11,252.04,224.05	g
31	methyl-p-coumarate*	9.64	$C_{10}H_{10}O_3$	P	179.07027	179.07008	-1.065	179.07,161.06,151.08,147.04,133.06,123.08,109.06,105.07,103.05,79.05	b
32	sweroside*	9.66	$C_{16}H_{22}O_9$	P	359.13366	359.13287	-0.789	359.13,197.08,179.09,151.08,127.04,97.03,85.03	b
33	sweroside aglycone	9.71	$C_{10}H_{12}O_4$	P	197.08083	197.08044	-2.006	197.08,179.07,169.05,161.06,151.08,137.06,127.04,111.08,97.03	b
34	coumarin	9.93	$C_9H_6O_2$	P	147.04405	147.04384	-1.469	147.04,119.05,91.05	
35	methyl salicylate	9.96	$C_8H_8O_3$	P	153.05473	153.05437	-1.638	153.05,125.06,111.04,93.03,65.04	e
36	paeoniflorin*	9.96	$C_{23}H_{28}O_{11}$	P	481.17043	481.16956	-1.825	481.17,319.12,301.11,197.08,179.07,151.08,133.06,105.03	a

37	5-o-feruloylquinic, acid	10.34	$C_{17}H_{20}O_9$	P	369.11812	369.11740	-1.649	369.19,177.05,145.03,117.03	b
38	3-coumaric acid	10.68	$C_9H_8O_3$	P	165.05462	165.05435	-1.640	165.05,137.06,133.03,109.06,95.05	b
39	4-methoxycinnamic acid	10.76	$C_{10}H_{10}O_3$	P	179.07027	179.07007	-1.121	179.07,161.06,147.04,133.06,118.04,109.06,103.05,79.05	d
40	ferulic acid*	10.89	$C_{10}H_{10}O_4$	P	195.06518	193.04927	-1.374	195.06,177.05,163.04,149.06,145.03,134.04,117.03,89.04	e
41	genipin	10.89	$C_{11}H_{14}O_5$	P	227.0914	227.09093	-2.070	227.09,209.08,195.07,177.05,167.07,165.05,151.04,139.04,107.05,95.05	b
42	4-coumaric acid*	10.95	$C_9H_8O_3$	P	165.05462	165.05431	-1.882	165.05,137.06,133.03,109.06,95.05	b
43	dihydrocaffeic acid	10.95	$C_9H_{10}O_4$	P	183.06518	183.06482	-1.996	183.07,165.05,151.04,140.05,123.04,95.05	b
44	scopoletol*	10.95	$C_{10}H_8O_4$	P	193.04953	193.04933	-1.063	193.05,179.03,178.03,151.04,137.06,133.03,95.05	c
45	phellodenol B	10.95	$C_{11}H_{10}O_4$	P	207.06530	207.06474	-2.151	207.06,179.07,163.04,151.08	g
46	secoxyloganin	10.95	$C_{17}H_{24}O_{11}$	P	405.13913	405.13791	-3.031	405.16,243.09,225.08,165.05,151.04,139.04,125.02,95.05,85.03,69.03	b
47	secologanin*	11.18	$C_{17}H_{24}O_{10}$	P	389.14422	389.14374	-1.242	389.17,209.08,195.07,177.05,165.05,151.04,107.05,95.05	b
48	schaftoside	11.24	$C_{26}H_{28}O_{16}$	N	595.13045	595.13019	1.393	595.13,300.03,271.03,255.03	c

49	geniposide	11.47	$C_{17}H_{24}O_{10}$	P	389.14422	389.14389	-0.857	389.14,209.08,177.05,165.05,151.04,107.05,95.05	d
50	isoferulic acid	11.71	$C_{10}H_{10}O_4$	P	195.06518	195.06438	-0.804	195.06,177.05,163.04,149.06,145.03,134.04,117.03,89.04	e
51	kaempferol 3,7-diglucoside	11.74	$C_{27}H_{30}O_{16}$	P	611.16066	611.15979	-1.425	611.20,303.05,285.04,257.04,229.05,201.05,129.05,97.03,85.03	a
52	noricariside_qt	11.80	$C_{20}H_{20}O_8$	P	389.12320	389.12253	-1.449	389.17,353.10,273.08,255.07,177.05,165.05,151.04,107.05,95.05	e
53	tetrahydropalmatine	11.87	$C_{21}H_{25}NO_4$	P	356.18563	356.18539	-0.687	356.19,341.16,192.10,177.08	g
54	rustoside	11.90	$C_{26}H_{28}O_{15}$	N	579.13554	579.13550	1.819	579.13,285.04,255.07,153.02,135.01,119.05	f
55	dihydrodaidzein	11.92	$C_{15}H_{12}O_4$	P	257.08083	257.08047	-1.421	257.08,239.07,211.08,197.06,163.04,147.04,137.02,119.05,53.04	f
56	neoliquiritin	11.94	$C_{21}H_{22}O_9$	N	417.11910	417.11926	3.000	417.12,255.07,153.02,135.01,119.05	c
57	rutin*	11.95	$C_{27}H_{30}O_{16}$	N	609.14610	609.14636	2.214	609.15,300.03,271.03,255.03	f
58	calycosin 7-O-glucoside*	12.03	$C_{22}H_{22}O_{10}$	P	447.12857	447.12781	-1.707	447.13,285.08,270.05,253.05,225.05,197.06,137.02	f
59	ethyl gallate	12.05	$C_9H_{10}O_5$	P	199.06010	199.05981	-1.456	199.06,169.01,125.02	a
60	noroxyhydrastinine	12.07	$C_{10}H_9NO_3$	P	192.06551	192.06531	-1.092	192.07,174.05,164.07,148.08,134.06,118.07,106.07,91.05	g
61	hirsutrin	12.12	$C_{21}H_{20}O_{12}$	N	463.08819	463.08859	3.212	463.09,300.03,271.02,255.07,243.03,179.00,151.00,135.01,119.0	f

62	quercetin*	12.13	$C_{15}H_{10}O_7$	P	303.04993	303.04974	-0.624	5 303.05,285.04,257.04,229.05,201.05,153.02,137.02	b,f
63	liquiritin*	12.18	$C_{21}H_{22}O_9$	N	417.11910	417.11917	2.784	417.12,255.07,135.01,119.05	c
64	liquiritigenin*	12.19	$C_{15}H_{12}O_4$	P	257.08083	257.08054	-1.149	257.08,239.07,211.08,197.06,163.04,147.04,137.02,119.05	c
65	licuraside	12.23	$C_{26}H_{30}O_{13}$	P	551.17591	551.17511	-1.465	551.17,419.13,257.08,239.07,211.08,147.04,137.02	c
66	hyperin*	12.25	$C_{21}H_{20}O_{12}$	N	463.08819	463.08850	3.018	463.09,301.04,271.03,255.03,227.04,151.00,121.03	b,f
67	lonicerin	12.29	$C_{27}H_{30}O_{15}$	P	595.16574	595.16449	-2.111	595.16,449.11,287.05,153.02,135.04	b
68	isoquercitrin*	12.36	$C_{21}H_{20}O_{12}$	P	465.10275	465.10260	-0.328	465.10,303.05,285.04,257.04,229.05,137.02,85.03	b,f
69	paeoniflorgenone	12.46	$C_{17}H_{18}O_6$	P	319.11761	319.11734	-0.861	319.12,301.11,197.08,105.03	a
70	gancaonin V	12.56	$C_{19}H_{20}O_4$	P	313.14344	331.15341	-1.783	313.14, 281.12,249.09,189.09,151.08,137.06,119.05,91.05	c
71	baicalin*	12.60	$C_{21}H_{18}O_{11}$	P	447.09230	447.09143	-1.695	447.09,446.21,271.06,169.01	a
72	cynaroside*	12.60	$C_{21}H_{20}O_{11}$	P	449.10783	449.10703	-1.799	449.10,287.05,269.04,241.05,153.02,135.04,85.03	b
73	galloylpaeoniflorin*	12.74	$C_{30}H_{32}O_{15}$	P	633.18139	633.17969	-2.695	633.14,315.07,197.08,171.03,153.02,105.03	a
74	vicenin-2	12.75	$C_{27}H_{30}O_{15}$	P	595.16574	595.16473	-1.708	595.16,449.11,287.05,153.02,135.04	c

75	phenylalanine	12.82	$C_9H_{11}NO_2$	P	166.08625	166.08626	0.029	166.08,120.08,108.04,80.05	h/k/l
76	amurensin	12.92	$C_{26}H_{30}O_{12}$	N	533.16644	533.16644	2.039	534.16,283.06,268.04	g
77	magnoflorine*	12.94	$C_{20}H_{24}NO_4+$	P	342.16998	342.16916	-2.410	342.17,297.11,192.10,177.08,149.08	g
78	nicotiflorin	13.15	$C_{27}H_{30}O_{15}$	P	595.16574	595.16473	-1.708	595.16,449.11,287.05,153.02,135.04	c
79	tetrahydroxydihydrochalcone	13.30	$C_{15}H_{14}O_5$	N	273.07684	273.07690	4.211	273.08,211.08,199.08,183.08,169.06,157.07,147.05,117.07,85.03	c
80	narcissoside	13.42	$C_{28}H_{32}O_{16}$	N	623.16175	623.16119	0.849	623.16,315.05,299.02,271.05,255.03	c
81	cynarin	13.43	$C_{25}H_{24}O_{12}$	P	517.13405	517.13287	-2.287	517.13,499.12,337.09,319.08,163.04,135.04,117.03	b
82	prunetin	13.52	$C_{16}H_{12}O_5$	N	283.06119	283.061	3.180	283.06,268.04,239.04,211.04	c
83	astragalin*	13.57	$C_{21}H_{20}O_{11}$	P	449.10783	449.10663	-2.689	449.10,287.05,269.04,241.05,153.02,135.04,85.03	b
84	listrocol	13.62	$C_{25}H_{24}O_{12}$	P	517.13405	517.13306	-1.919	517.13,499.12,337.09,319.08,163.04,135.04,117.03	b
85	cavidine	13.68	$C_{21}H_{23}NO_4$	P	354.16998	354.16937	-1.736	354.17,338.10,190.09,149.06	g
86	4-O-galloylalbiflorin	13.92	$C_{30}H_{32}O_{15}$	P	633.18151	633.18042	-1.542	633.18,315.07,197.08,171.03,153.02,105.03	a
87	rhoifolin*	13.96	$C_{27}H_{30}O_{14}$	P	579.17083	579.16992	-1.575	579.17,539.12,433.11,271.06,225.05,153.02,119.05	b
88	acteoside*	13.96	$C_{29}H_{36}O_{15}$	N	623.19814	623.16138	1.154	623.20,461.17,161.02	d
89	naringenin	14.00	$C_{15}H_{12}O_5$	P	273.07575	273.07516	-2.161	273.08,255.06,171.03,153.02,147.04,119.05	c

90	vitexin	14.03	$C_{21}H_{20}O_{10}$	N	431.09837	431.09796	1.593	431.10,268.04,239.04,211.04,121.03	c
91	cosmetin*	14.04	$C_{21}H_{20}O_{10}$	P	433.11292	433.11139	-3.540	433.11,271.06,225.05,153.02,119.05,85.03	b
92	menisporphine	14.36	$C_{19}H_{15}NO_4$	P	322.10738	322.10706	-1.007	322.11,307.08,292.06,279.09,251.09	f
93	isochlorogenic acid B	14.43	$C_{25}H_{24}O_{12}$	P	517.13405	517.13300	-2.035	517.13,499.12,337.09,319.08,163.04,135.04,117.03	b
94	hesperidin*	14.45	$C_{28}H_{34}O_{15}$	P	611.19705	611.19550	-2.531	611.20,449.14,413.12,303.09,263.05,195.03,177.05,153.02,135.04,85.03	f
95	nonanedioic acid	14.46	$C_9H_{16}O_4$	N	187.09758	187.09737	4.728	187.10,169.09,125.10	e
96	rhamnocitrin-3-O-glucoside	14.47	$C_{22}H_{22}O_{11}$	N	461.10893	461.10864	1.740	461.11,299.06-,284.03,271.06,255.03,165.02,133.03	f
97	canadine	14.53	$C_{20}H_{21}NO_4$	N	338.13978	338.13971	3.032	338.14,323.12,308.09,293.07	g
98	albiflorin*	14.72	$C_{23}H_{28}O_{11}$	P	481.17043	481.16907	-2.843	481.17,319.12,301.11,197.08,179.07,151.08,133.06,105.03	a
99	isochlorogenic acid A	14.80	$C_{25}H_{24}O_{12}$	P	517.13405	517.13220	-3.582	517.13,499.12,337.09,319.08,163.04,135.04,117.03	b
100	corydaline	14.88	$C_{22}H_{27}O_4N$	P	370.20139	370.20062	-1.796	370.20,206.12,190.09	g
101	neohesperidin	14.90	$C_{28}H_{34}O_{15}$	P	611.19705	611.19598	-1.745	611.20,449.14,413.12,303.09,263.05,195.03,177.05,153.02,135.04,85.03	f
102	albiflorin	15.00	$C_{23}H_{28}O_{11}$	P	481.17043	481.17004	-0.827	481.17,319.12,301.11,197.08,17	a

	isomer							9.07,151.08,133.06,105.03	
103	pinocembrin	15.20	$C_{15}H_{12}O_4$	P	257.08083	257.08051	-1.266	257.08,239.07,211.08,197.06,163.04,147.04,137.02,119.05	c
104	liquiritin apioside	15.23	$C_{26}H_{30}O_{13}$	P	551.17591	551.17548	-0.793	551.17,419.13,257.08,239.07,211.08,147.04,137.02	c
105	paeonin c	15.42	$C_{17}H_{24}O_9$	N	371.13354	371.13452	2.321	371.14,191.07,69.03,59.01	a
106	7,4'-dihydroxyflavone	15.44	$C_{15}H_{10}O_4$	P	255.06518	255.06444	-2.922	255.06,237.05,227.07,199.07,	c
107	2-valerylbenzoic acid	15.46	$C_{12}H_{14}O_3$	P	207.10157	207.10109	-2.322	207.10,189.09,179.11,171.08,161.10,147.08,133.06,123.04,105.07,91.05	e
108	3,4-di-O-caffeoylquinic acid methyl ester	15.46	$C_{26}H_{26}O_{12}$	P	531.14970	531.14758	-3.996	513.14,163.04,145.03	b
109	glycyroside	15.55	$C_{27}H_{30}O_{13}$	P	563.17591	563.17474	-2.091	563.06,269.08,213.09,163.04	c
110	camphoric acid	15.83	$C_{10}H_{16}O_4$	N	199.09758	199.09743	4.744	199.10,183.02,155.11	e
111	isoformononetin	15.99	$C_{16}H_{12}O_4$	N	267.06628	267.06561	1.590	267.07,252.04,195.05,132.02	c,f
112	ononin*	15.99	$C_{22}H_{22}O_9$	P	431.13365	431.13199	-3.870	431.13,269.08,254.06,213.09,197.06,154.03,107.05	c,f
113	daidzein*	16.09	$C_{15}H_{10}O_4$	P	255.06518	255.06561	1.665	255.06,237.05,227.07,199.07	f
114	wogonin*	16.12	$C_{16}H_{12}O_5$	N	283.06119	283.06082	2.544	283.06,268.04,239.04,211.04	i
115	licochalcone B*	16.13	$C_{16}H_{14}O_5$	P	287.09140	287.09052	-3.065	287.09,269.08,255.10,245.08,193.05,147.04,139.04,121.03	c

116	kaempferol	16.25	$C_{15}H_{10}O_6$	P	287.05501	287.05429	-2.524	287.05,269.04,241.05,151.04,121.03,107.05	b
117	lactinolide	16.32	$C_{10}H_{16}O_4$	N	199.09758	199.09744	4.794	199.10,155.11,137.10	a
118	3,5-di-O-caffeoylquinic acid methyl ester	16.33	$C_{26}H_{26}O_{12}$	N	529.13515	529.13489	1.583	529.13,434.04,367.10,353.09,191.06,179.03,173.05,161.02,135.05,93.03	b
119	isoliquiritigenin	16.38	$C_{15}H_{12}O_4$	P	257.08083	257.08066	-0.682	257.08,239.07,211.08,197.06,163.04,147.04,137.02,119.05,53.05	c
120	gancaonin C	16.74	$C_{20}H_{18}O_6$	N	353.10306	353.10294	2.762	353.10,338.08,323.06,279.07,251.07,191.06	c
121	luteolin*	17.03	$C_{15}H_{10}O_6$	P	287.05501	287.05438	-2.210	287.05,269.04,229.12,153.02,137.02,81.03	b
122	phellopterin	17.03	$C_{17}H_{16}O_5$	P	301.10705	301.10648	-1.893	301.11,286.08,269.08,241.09,167.07,152.05	g
123	calycosin*	17.19	$C_{16}H_{12}O_5$	N	283.06119	283.06097	3.074	283.06,268.04,239.04,211.04	c
124	sebacic acid	17.22	$C_{10}H_{18}O_4$	N	201.11323	201.11299	4.249	201.11,183.10,139.11,116.93	e
125	cistanoside D	17.22	$C_{31}H_{40}O_{15}$	N	651.22944	651.22858	0.358	651.23,193.05,175.04,160.02	d
126	1-O-beta-d-glucopyranosyl-8-O-benzoylpaeoniflorin	17.63	$C_{23}H_{28}O_{10}$	P	465.17563	465.17462	-1.942	465.17,167.07,123.04	a
127	butyl benzoate	17.93	$C_{11}H_{14}O_2$	N	177.09210	177.091810	0.804	177.09,133.03,121.03,101.06,93.03	c
128	senkyunolide	17.93	$C_{12}H_{14}O_4$	N	221.08193	221.08173	4.047	221.08,177.09,159.08,95.03	e

	D								
129	ethyl caffeate*	18.00	$C_{11}H_{12}O_4$	N	207.06628	207.06587	3.307	207.07,179.03,161.02,135.04,133.03	b,e
130	cinnamic acid*	18.02	$C_9H_8O_2$	P	149.05970	149.05942	-1.919	149.06,131.05,121.06,103.05,95.05,93.07,91.05,77.04	d
131	paeonol	18.02	$C_9H_{10}O_3$	P	167.07027	167.06989	-2.279	167.07,149.06,121.06,93.07,91.05	a
132	aucubin*	18.03	$C_{15}H_{22}O_9$	N	345.11910	345.11877	2.206	345.12,183.07,165.06,121.06,101.02,89.02,71.01,59.01	d
133	harpagoside*	18.03	$C_{24}H_{30}O_{11}$	N	493.17153	493.17111	1.362	493.17,447.22,165.06,147.04	d
134	wogonoside	18.74	$C_{22}H_{20}O_{11}$	P	461.10783	461.10696	-1.904	461.10,285.08,270.05,257.08,239.07,186.02,168.00	i
135	apigenin*	18.93	$C_{15}H_{10}O_5$	P	271.06010	271.05954	-2.066	271.06,254.19,226.15,180.07,161.02,137.02	b
136	senkyunolide*	19.06	$C_{12}H_{16}O_2$	P	193.12230	193.12224	-0.343	193.12,175.11,147.12,137.06,	e
137	ammidin	19.09	$C_{16}H_{14}O_4$	P	271.09660	271.09604	-1.643	271.10,137.06,121.03,107.05	e
138	baicalein*	19.11	$C_{15}H_{10}O_5$	P	271.06010	271.05954	-2.066	271.06,243.07,153.02,121.03,107.05	a
139	astraisoflavan glucoside	19.18	$C_{23}H_{24}O_{11}$	P	477.13913	477.13837	-1.609	477.14,315.09,300.06,272.06	f
140	skimmianin*	19.41	$C_{14}H_{13}NO_4$	P	260.09173	260.09146	-1.055	260.09,245.07,230.04,227.06,216.07,199.06,184.04	g
141	chryseriol	19.54	$C_{16}H_{12}O_6$	N	299.05611	299.05569	2.259	299.06,284.03,256.04	b
142	9(11)-dehydroglycyrrhetic acid	19.49	$C_{30}H_{46}O_3$	P	455.35208	455.35117	-1.761	455.35,437.34,419.33,297.22,143.11	c

143	prosapogenin	19.52	$C_{36}H_{58}O_8$	P	619.42044	619.41901	-2.317	619.42,455.35,437.34,409.34,203.18,201.16,189.16,85.03,71.05	c
144	helixin	19.54	$C_{41}H_{66}O_{12}$	P	751.46270	751.46075	-2.600	751.46,455.35,437.34,409.35,279.11,85.03,71.05	c
145	isoflavanone	19.55	$C_{17}H_{16}O_6$	N	315.08741	315.08713	2.588	315.09,285.04,178.03,109.03	f
146	benzoyl paeoniflorin*	19.63	$C_{30}H_{32}O_{12}$	P	585.19676	585.19562	-1.765	585.20,319.12,105.03	a
147	hederagenol	19.88	$C_{30}H_{48}O_4$	P	473.36253	473.36139	-2.422	473.36,437.34,419.33,297.22,143.11,123.12,	c
148	cauloside A	19.88	$C_{35}H_{56}O_8$	P	605.40479	605.40338	-2.337	605.40,587.39,473.36,455.35,437.34,419.33,	c
149	N_1	19.90	$C_{47}H_{76}O_{17}$	P	913.51553	913.51361	-2.099	913.51,455.35,437.34,409.35,391.34,309.12,279.11	c
150	isorhamnetin*	19.97	$C_{16}H_{12}O_7$	N	315.05102	315.05023	0.955	315.05,300.03,109.03	f
151	fagarine	19.99	$C_{13}H_{11}NO_3$	P	230.08116	230.08092	-1.086	230.08,215.06,200.03,186.05,172.04	g
152	rhamnocitrin	20.00	$C_{16}H_{12}O_6$	N	299.05611	299.05600	3.295	299.06,284.03,256.04	f
153	N_2	20.09	$C_{48}H_{72}O_{21}$	P	985.46389	985.46173	-2.187	985.46,615.39,471.35,453.34,435.32,407.33	c
154	dictamine	21.47	$C_{12}H_9NO_2$	P	200.07060	200.07034	-1.325	200.07,185.05,129.05,73.04	g
155	ethyl ferulate*	21.57	$C_{12}H_{14}O_5$	P	223.09648	223.09615	-1.504	223.10,177.05,149.06,145.03,117.03	e
156	sedanolide	21.61	$C_{12}H_{18}O_2$	P	195.13795	195.13773	-1.160	195.14,177.13,149.13,123.12,107.09,93.07,81.07,69.07,67.05,55.05	e
157	butylidenephth	21.73	$C_{12}H_{12}O_2$	P	189.09100	189.09067	-1.778	189.09,171.08,161.10,147.04,14	e

	alide*							3.09,133.03,105.03,95.05	
158	formononetin*	21.77	$C_{16}H12O_4$	P	269.08083	269.08038	-1.692	269.08,254.06,237.05,213.09,197.06	g
159	apigenin 7,4'-dimethyl ether	22.26	$C_{17}H_{14}O_5$	P	299.09140	299.09100	-1.338	299.09,284.07,267.07,256.07,184.04	b
160	ilekudinoside D	22.39	$C_{41}H_{66}O_{14}$	P	783.45253	783.45105	-1.893	783.45,603.08,585.38,453.34,435.33,245.15,201.16	c
161	amurensin_qt	22.60	$C_{20}H_{20}O_7$	P	373.12817	373.12747	-1.901	373.16,355.12,299.05,165.02	g
162	saikogenin F	22.61	$C_{30}H_{48}O_4$	P	473.36253	473.36145	-2.295	473.36,437.34,419.33,297.22,143.11,123.12	b
163	astragaloside A*	22.61	$C_{41}H_{68}O_{14}$	P	785.46818	785.46637	-2.308	785.47,473.36,455.35,437.34,143.11,125.10,71.05	f
164	O-glucopyranosyl epiederagenin	22.61	$C_{36}H_{58}O_9$	P	635.41536	635.41382	-2.423	635.41,455.35,437.34,419.33,297.22,143.11,107.09,71.05	c
165	N_3	22.61	$C_{41}H_{66}O_{13}$	P	767.45762	767.45563	-2.591	767.46,587.39,569.38,473.36,455.35,437.34,419.33,143.11,125.10	f
166	glypallidifloric acid	22.93	$C_{30}H_{46}O_3$	P	455.35208	455.35120	-1.695	455.35,437.34,419.33,297.22,143.11	c
167	castanin	23.59	$C_{17}H_{14}O_5$	P	299.09140	299.09079	-2.040	299.09,283.06,266.06,255.07,238.06,210.07,196.05,147.04,134.04	c
168	licoricesaponin G2	23.81	$C_{42}H_{62}O_{17}$	P	839.40598	839.40436	-1.926	839.41,487.34,469.33,451.32,	c
169	isoimperatorin	23.94	$C_{16}H_{14}O_4$	P	271.09660	271.09616	-1.200	271.10,147.04,137.06,123.04,10	e

170	astragaloside II*	24.18	$C_{43}H_{70}O_{15}$	P	827.47874	827.47699	-2.124	9.06 827.47,629.41,473.36,437.34,297.22,175.06,143.11,125.10	f
171	senkyunolide B	24.20	$C_{12}H_{12}O_3$	N	203.07136	203.07120	4.576	203.07,174.03,160.02	b
172	lucyoside Q	24.23	$C_{36}H_{58}O_9$	P	635.41536	635.41388	-2.329	635.41,455.35,437.34,419.33,315.23,297.22,143.11,125.10,107.09,71.05	c
173	isoastragaloside II	24.36	$C_{43}H_{70}O_{15}$	P	827.47875	827.47723	-1.834	827.47,455.35,437.34,419.33,175.06,157.05,143.11,125.10,115.04,97.03,85.03	f
174	glycyrrhizic acid*	25.14	$C_{42}H_{62}O_{16}$	P	823.41106	823.40961	-1.764	823.41,647.38,471.35,453.34,435.32	c
175	soyasaponin I	25.19	$C_{48}H_{78}O_{18}$	P	943.52609	943.52362	-2.620	943.52,599.39,441.37,405.35,305.09,229.19,203.18,141.02,85.03	c
176	saikogenin A	25.24	$C_{30}H_{48}O_4$	P	473.36253	473.36176	-1.640	473.36,437.34,419.33,297.22,143.11,123.12	b
177	3-butylidene-7-hydroxy-2-benzofuran-1-one	25.35	$C_{12}H_{12}O_3$	N	203.07136	203.07124	4.773	203.07,174.03,160.02	e
178	glepidotin A	25.46	$C_{20}H_{18}O_5$	N	337.10814	337.10788	2.462	337.11,293.05,282.05,253.05	c
179	3-(3,4-dihydroxyphenyl)-5,7-dihydroxy-8-	25.79	$C_{20}H_{18}O_6$	N	353.10306	353.10284	2.479	353.10,175.04,133.03	c

180	(3-methylbut-2-enyl)-chromone licoflavonol*	26.15	$C_{20}H_{18}O_6$	N	353.10306	351.08694	1.781	353.10,149.02,136.02,133.03	c
181	licoarylcoumarin	26.19	$C_{21}H_{20}O_6$	N	367.11871	367.11832	1.921	367.12,352.09,337.07-,309.04,	c
182	mimugenone	26.19	$C_{30}H_{46}O_3$	P	455.35208	455.35104	-2.046	455.35,437.34,419.33,297.22,143.11	c
183	calenduloside E methyl ester	26.19	$C_{37}H_{58}O_9$	P	647.41536	647.41370	-2.564	647.41,455.35,453.33,437.34,419.33,297.22,279.21,143.11,141.13,123.12,115.04,97.03,85.03	c
184	N_4	26.21	$C_{43}H_{68}O_{14}$	P	809.46818	809.46613	-2.536	809.47,599.39,455.35,439.36,437.34,419.33,143.11,125.10	f
185	atractylenolide III*	26.39	$C_{15}H_{20}O_3$	P	249.14852	249.14813	-1.569	249.15,231.14,213.13,207.10,189.09,119.09,105.07	i
186	glepidotin B	26.48	$C_{20}H_{20}O_5$	N	339.12379	339.12344	2.182	339.12,167.03,109.03	c
187	butylphthalide*	26.65	$C_{12}H_{14}O_2$	P	191.10665	191.10645	-1.079	191.11,173.10,163.11,149.06,145.10,117.07,91.05	e
188	6-prenylluteolin	26.66	$C_{20}H_{18}O_6$	N	353.10306	353.10269	2.054	353.10,219.07,179.03,133.07	c
189	isolicoflavonol	27.04	$C_{20}H_{18}O_6$	N	353.10306	353.10257	1.714	353.10,297.04,269.04,191.06	c
190	licoisoflavone	27.71	$C_{20}H_{18}O_6$	N	353.10306	353.10275	2.224	353.10,284.03,177.09,125.02	c
191	2-linoleoylglycerol	27.95	$C_{21}H_{38}O_4$	P	355.28440	355.28336	-2.607	355.28,337.27,263.24,245.23,121.10,95.09,81.07,67.05	j
192	luteolin-7,3',4'-	28.32	$C_{18}H_{16}O_6$	P	329.10196	329.10144	-1.594	329.10,313.07,300.06,285.08,25	b

	trimethylether*							6.07	
193	astragaloside I*	28.35	$C_{45}H_{72}O_{16}$	P	869.48931	869.48761	-1.958	869.49,653.40,455.35,437.34,401.32,297.22,217.07,143.11	f
194	gonzalitosin I	28.42	$C_{18}H_{16}O_6$	P	329.10196	329.10135	-1.868	329,10,313.07,285.07,270.05,256.07,168.04,167.03	b
195	glycyrrhetyl 30-monoglucuronide	28.49	$C_{36}H_{54}O_{10}$	P	647.37897	647.37823	-1.150	647.38,453.34,435.32,285.22,217.16,107.09,95.09,85.03	c
196	ligustilide*	29.01	$C_{12}H_{14}O_2$	P	191.10665	191.10646	-1.027	191.11,173.10,163.11,149.06,145.10,117.07,91.05	e
197	kanzonols W	29.23	$C_{20}H_{16}O_5$	N	335.09249	335.09241	3.014	335.09,291.10,185.08,127.08	c
198	glabridin*	29.72	$C_{20}H_{20}O_4$	N	323.12888	323.12869	2.799	323.13,201.09,135.04	c
199	3β-hydroxyatractylone	30.01	$C_{15}H_{20}O_2$	P	233.15360	233.15355	-0.242	233.15,215.14,205.16,187.15,159.08,131.09,119.09,105.07	i
200	atractylenolide II*	30.46	$C_{15}H_{20}O_2$	P	233.15360	233.15346	-0.628	233.15,215.14,187.15,177.09,159.08,151.08,131.09,117.07,105.07,95.09	i
201	licoisoflavone B*	30.47	$C_{20}H_{16}O_6$	N	351.08741	351.08725	2.664	351.09,321.04,283.10,265.09,199.07,146.97	c
202	atractylenolide I*	33.30	$C_{15}H_{18}O_2$	P	231.13795	231.13780	-0.677	231.14,213.13,203.14,175.08,163.08,161.06,149.06,135.04,105.07	i
203	linolenic acid	33.83	$C_{18}H_{30}O_2$	P	279.23185	279.23169	-0.597	279.23,261.22,223.17,209.15,137.13,123.12,109.10,95.09,81.07,	j

204	enoxolone*	35.27	$C_{30}H_{46}O_4$	P	471.34688	471.34555	-2.835	67.05 471.35,425.34,407.33,317.21,235.17,217.16,175.15,95.09	c
205	gancaonin U	36.48	$C_{24}H_{28}O_4$	P	381.20603	381.20535	-1.799	381.21,363.19,335.20,297.11,279.14,191.11,173.10,135.04	c
206	linoleic acid	43.73	$C_{18}H_{32}O_2$	N	279.23295	279.23257	2.554	280.24,279.23,96.96	j
207	9,12-octadecadienal	44.35	$C_{18}H_{32}O$	P	265.25270	265.25229	-1.139	265.25,247.24,149.13	j
208	ethyl linolenate	45.33	$C_{20}H_{34}O_2$	N	305.24860	305.24835	2.762	305.25,105.07,95.09,93.07,69.07,67.05	j
209	oleic acid	46.76	$C_{18}H_{34}O_2$	N	281.24860	281.24835	2.998	281.25, 95.09,93.07,69.07,67.05	j
210	mandenol	47.50	$C_{20}H_{36}O_2$	N	307.26425	307.26404	2.874	307.26,225.19,93.07,69.07,67.05	j
211	icos-5-enoic acid	50.56	$C_{20}H_{38}O_2$	N	309.27990	309.27972	2.952	309.28,95.09,81.07,67.05	k

Note: Compounds with " * " were compounds have passed comparison verification with reference standards; N represents Negative Ion Mode, P represents Positive Ion Mode; the calculation formula of the relative deviation value is $Delat(ppm) = \frac{m/z_{Theoretical} - m/z_{Measured}}{m/z_{Theoretical}} \times 10^6$; a represents Paeoniae Radix Alba, b represents Lonicerae Japonicae Flos, c represents Glycyrrhizae Radix Et Rhizoma, d represents Scrophulariae Radix, e represents Angelicae Sinensis Radix, f represents Astragali Radix, g represents Phellodendri Chinrnsis Cortex, h represents Hirudo, i represents Atractylodis Rhizoma, j represents Coicis Semen, k represents Scolopendra, l represents Scorpion.

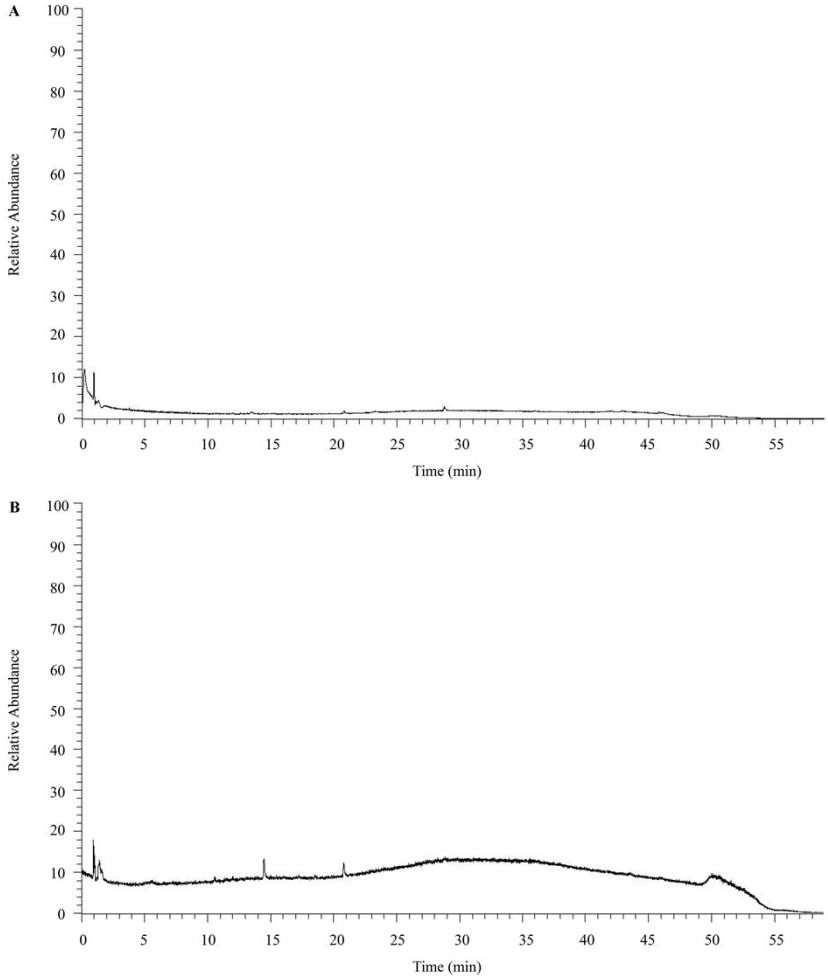

Figure S1 Total ion chromatograms for blank control in positive ion mode (A) and negative mode (B).

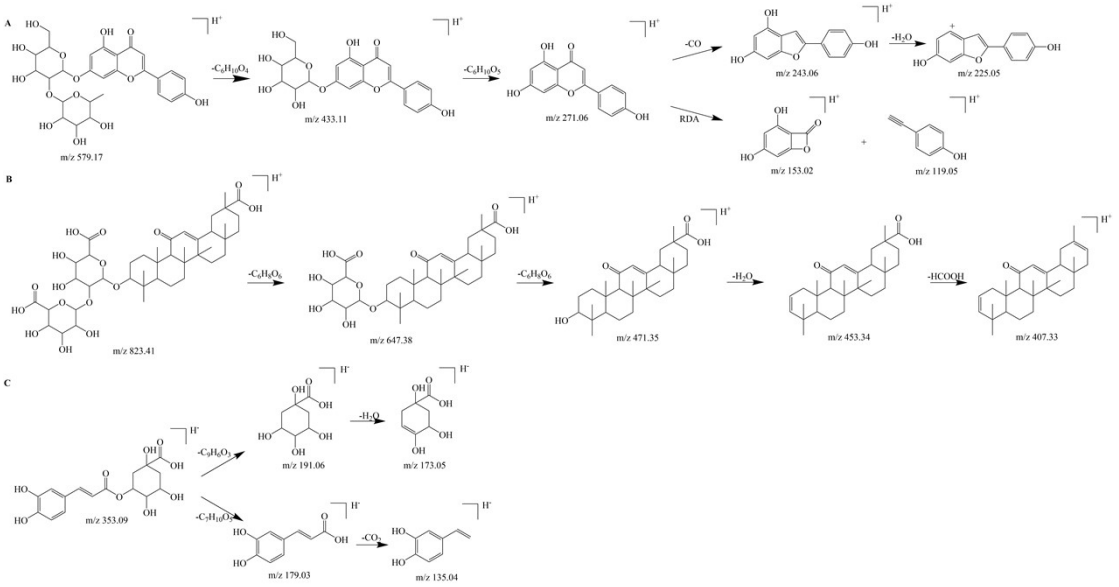

Figure S2 MS fragmentation behaviors of flavonoids (A), triterpenes (B) and

phenolic acids (C)

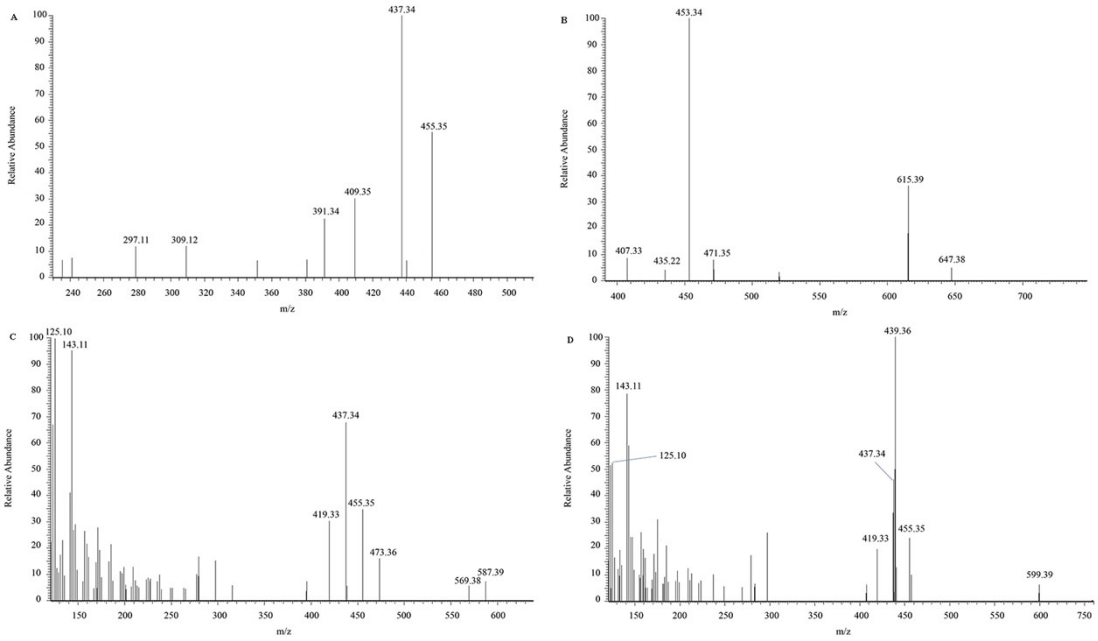

Figure S3 MS/MS spectra of compound N_1 (A), N_2 (B), N_3 (C) and N4 (D)