Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

An integrated approach for structural characterization of Gui Ling Ji by traveling wave ion mobility mass spectrometry and molecular network

Yuhao Zhang [a ‡], Huibo Lei [b ‡], Jianfei Tao [bc], Wenlin Yuan [b], Weidong Zhang [ab *], Ji Ye [b *]

Affiliation

[a] *Institute of Interdisciplinary Integrative Medicine Research, Shanghai University of Traditional Chinese Medicine, Shanghai, 201203, China.*
[b] *College of Pharmacy, The Second Military Medical University, Shanghai 200433, China.*
[c] *Pharmacy Department, Shanghai Yang Si Hospital, Shanghai, 200126, China*

Initial annotation of known components

Characterization of flavonoids

Flavonoids, a class of natural products widely existed in plants, often present in free form or in combination with side chains to yield flavonoid derivations. Some herbal medicines of PC, EB, GU and EC in GLJ were rich in flavonoids. Flavonoid derivatives with sugar chains often exhibit high abundance ion response in negative ion mode and could result in the neutral losses of 162.0528 Da (glucose), 146.0579 Da (rhamnose), and 132.0423 Da (xylose) in MS/MS spectra. Non-glycoside flavonoids have exhibited good responses in both of positive and negative ion modes. Their typical fragment ions concerning the neutral losses of 27.9949 Da (CO), 43.9898 Da (CO_2), 18.0106 Da (H_2O) and 15.0235 Da (CH_3) in positive ion mode were selected for structural characterization. Besides, the C ring of flavonoids is also prone to experience Retro-Diels-Alder (RDA) fragmentation to form characteristic fragment ions at *m/z* 149.0239, 137.0233, 121.0284 and 119.0491. Due to these characteristic fragment ions, glycoside and non-glycoside flavonoids were gathered and classified clearly by molecular network based on the MS/MS spectra of GLJ and its each single herbal medicine. Targeted compounds identification for glycoside and non-glycoside flavonoids in **Fig. S5A** was used as examples. By observing the composition of different colors in each node, it is deduced that each flavonoid might be originated from various source of medicinal plants. The nodes in **Fig. S5A** are commonly seen flavonoids in natural plants, thus, almost all the corresponding compounds can be easily matched by the UNIFI software and online GNPS database.

According to the online GNPS database, peak 34, 43, 45, 53, 55, 63, 67, 83, 90 and 121 were initially identified as daidzoside quercetin-3-*O*-arabinoglucoside, rutin, hyperoside, kaempferitrin, isoquercitrin, astragalin, quercetin-3-*O*-glucose-6''-acetate, kaempferin, α-rhamnoisorobin-3-*O*-(3-*O*-acetyl-α-L-rhamnopyranoside), rhamnazin-3-*O*-β-D-glucoside, respectively. The cosine scores were greater than 0.8, indicating the results are reliable. The structural identification of peak 83 was taken (#431) as an example. It showed a $[M-H]^-$ ion at *m/z* 431.0966, estimated molecular formula $C_{21}H_{20}O_{10}$ with mass error of -2.78 ppm. As is shown in **Fig. S5B**, the fragment ion at *m/z* 285.0392 corresponded to the neutral loss of rhamnose, following by successively losses of CH_2O, CO, Oxygen and CO to produce fragment ions at *m/z* 255.0291, 227.0340, 211.0390, and 183.0453, respectively. The fragmentation behavior is therefore all consistent with that of kaempferin (**Fig. S5C**), and thus peak 83 was finally confirmed. Finally, 11 flavonoid glycosides were identified in **Fig. S5A**, including 10 flavonols and 1 isoflavone.

Five clusters related to flavonoids were summarized in molecular network by the MS/MS spectra of GLJ and herbal medicine of PC, EB, GU and EC. After searching the UNIFI database and the online databases, a total of 75

flavonoids were tentatively identified in GLJ (**Table S1**), including 35 flavonoid glycosides and 40 non-glycoside flavonoids. Of these, 18 flavonoids were unambiguously confirmed by comparing their accurate mass measurements of MS^2 spectra and retention times with reference compounds. Discussion on isomers and potential new compounds in flavonoid network were described in detail in corresponding sections below.

Characterization of lyso-GPCs

Lyso-GPCs are a class of endogenous constituents derived from animals, containing glycerophosphocholine skeleton and a free glycerol hydroxyl group at *sn*-1 or *sn*-2. Due to the presence of the glycerophosphocholine skeleton, the fragmentation behavior of this class of constituents is also typical and representative. In positive ion mode, lyso-GPCs are likely to generate the base peak at *m/z* 184.0733$[(P\text{-}Ch)]^+$ and diagnostic fragment ions at *m/z* 166.0610$[(P\text{-}Ch)\text{-}H_2O]^+$, 104.1091$[(P\text{-}Ch)\text{-}HPO_3]^+$ and 86.0979$[(P\text{-}Ch)\text{-}HPO_3\text{-}H_2O]^+$. The MS/MS spectra in positive ion mode of GLJ, and its each single animal-orient medicines of HK, CN, MP were grouped to generate molecular network for the assignment of the lyso-GPCs compounds. Owing to the difference functional group substituted at *sn1* or *sn2* sites, typical fragment ions of lyso-GPCs were varied in negative ion mode, which could be useful for distinguishing their structures.

Fig. S6 shows the molecular network of lyso-GPCs, MS/MS spectra and possible fragmentation patterns of node #482 and #496. In high-energy channel, characteristic daughter ions at *m/z* 184.0733, 166.0610, 104.1091 and 86.0979 in positive ion mode were observed, which were generated from the unstable long-chain fatty acids in lyso-GPCs. However, previous reports demonstrated that lyso-GPCs would produce precursor ions $[M+HCOO]^-$ and $[M\text{-}CH_3]^-$ at low-energy channel in negative ion mode, following by a typical neutral loss of 60.0211 Da (CH_3COOH). Thus, the MS/MS spectra of lyso-GPCs in negative ion mode was collected for differentiating functional group substituted at *sn1* or *sn2* sites. Lysophosphatidylcholines (lysoPCs) and lysoplatelet activating factors (lyso-PAFs), two representative Lyso-GPCs, have exhibited the structural differences on long-chain fatty acyl groups and long-chain fatty ether at *sn*-1 or *sn*-2 position. They can also produce different characteristic fragment ions or neutral losses. For example, peak 232 ($C_{24}H_{50}NO_7P$, $[M+H]^+$, *m/z* 496.3314, mass error of 0.81ppm) exhibited high abundance product ion at *m/z* 255.2324$[(M\text{-}CH_3)\text{-}C_7H_6NO_5P]^-$), which is typical for lysoPCs (a neutral loss of 225.0750 Da, **Fig. S**6). Moreover, several main product ions at *m/z* 224.0682 $[M\text{-}H\text{-}C_{17}H_{33}O_2]^-$, 168.0438 $[P\text{-}Ch\text{-}CH_3]^-$ and 78.9572 $[PO_3]^-$ showed the presence of phosphatidylcholine group (polar headgroups esterified to the *sn-3* position). Thus, peak 232 was identified as 1-hexadecanoyl-sn-glycerol-3-phosphocholine from a search of literature. Similarly, peak 216, 222, 227, 231, 238, 243 and 250 were categorized as lysoPCs and identified by previous publications. In contrary, peak 236 (#482) have displayed the different fragmentation behaviors. It has

shown molecular formula of $C_{24}H_{52}NO_6P$ ($[M+H]^+$) with mass error of -1.45 ppm. A series of product ions at *m/z* 466.3290 $[M-CH_3]^-$, 377.2469 $[M-CH_3-C_4H_9N-H_2O]^-$, 168.0414 $[P-Ch-CH_3]^-$ and 78.9582 $[PO_3]^-$ have been detected, suggesting that this compound belongs to lyso-PAFs. Thus, we definitively assigned it as 1-O-hexadecyl-sn-glycerol-3-phosphocholine. Eventually, by matching with the GNPS database, summarizing the fragmentation rules and consulting the literature, a total of 15 lyso-GPCs were summarized from **Fig. S6**, including 12 lysoPCs and 3 lyso-PAFs.

Characterization of others

The other 68 compounds were tentatively identified from GLJ (as shown in Tab. S1). Stachyose (1), glucose (4), D (+)-sucrose (5), betaine (6), D (-)-fructose(7), adenosine (9), maltol-3-O-β-glucoside (11), 5-hydroxymethylfurfural (12), mesaconine (15), songorine (20), chlorogenic acid (21), fuziline (26), neoline (28), (25S)-inokosterone (58), benzoylmesaconine (77), benzoylaconine (92), benzoylhypacoitine (106), benzoyldeoxyaconine (113), psoralen (132), isopsoralen (139), psoralidin (221), (-)-asarinin (224), bakuchiol (251) and ursolic acid (252) were unambiguously identified and further confirmed by comparison their accurate mass measurements of MS^2 spectra and retention times with reference standards. The other 53 compounds were all presumed by matching MS/MS fragment ions with previously reported literatures.

Distinction by diagnostic product ions

It has been estimated that chalcone and flavanone types of flavonoids often existed as isomers in natural plants due to the opened or closed states of C-ring. Compared with flavanone, chalcone could yield much higher abundance of characteristic ions at *m/z* 147.0437 and 119.0491, and these ions can be used as the diagnostic fragment ions. Take the structural characterization procedure of isomers of #323 as an example. By extracting ion chromatography from the original MS data, the same quasi-molecular ions at *m/z* 323.1284 ($C_{20}H_{18}O_4$, $[M+H]^+$) have been displayed in three corresponding chromatographic peaks with different retention times at 35.68min (peak 206), 39.17min (peak 219) and 46.85min (peak 242), respectively. As shown in **Fig. S7**, For isopentenyl flavonoids, in order to form a stable benzyl moiety, isopentenyl cleavage was happened, yielding to the presence of high-abundance diagnostic fragment ion at *m/z* 267.0650 $[M+H-C_4H_7]^+$. Fragment ions at *m/z* 255.0657 and 239.0702 were corresponded to the successive losses of C_5H_9 moiety and water, with error within 2.48 ppm. After searching

the database in UNIFI platform and analyzing its MS/MS fragment ions, peak 206 was consistent with the fragmentation behavior presented by neobavaisoflavone, and was further confirmed by the standard substance. The other two compounds have showed common product ions at *m/z* 203.0700, 175.0401 and 147.0439. Peak 242 had a much higher abundance at *m/z* 203.0705 than that of compound 219 (Fig. S7C), indicating the RDA cleavage of flavonoid was more likely to be produced to form a stable conjugate structure of this compound. The diagnostic product ion at *m/z* 175.0401, which was corresponded to the loss of $C_9H_7O_2$, was resulted from the unstable breakage of chalcone. Compared with peak 242, peak 219 has showed much more abundant of this diagnostic fragment ion (Fig. S7C), suggesting that it belonged to chalcone. Since peak 219 and 242 were a pair of typical flavanone and chalcone isomers, they were tentatively assigned as bavachromene and chromenoflavanone, respectively, and were further confirmed by publication.

Figure Caption

Fig. S1 MS/MS spectra of glycyrrhizic acid and its proposed fragmentation behavior.

Fig. S2 Construction of the molecular network of flavonoids from GLJ and EP for interpreting the novel compound in GLJ (A), MS/MS spectra and possible fragmentation patterns of #513 (peak 199) and #657 (peak 202) from EP (B).

Fig. S3 Extracted ion chromatography of *m/z* 845.4905 $[M+HCOO]^-$ and the MS/MS spectra of three peaks at 22.54 min (peak 88), 26.82 min (peak 129) and 26.93min (peak 131).

Fig. S4 Characterization of isomers with node at #793: (A) EIC of *m/z* 793.4358 $[M-H]^-$ at 30.91 min (peak 65) and 35.87 min (peak 87), (B) MS/MS spectra of peak 65 and peak 87, (C) overlapping mobility profiles of peak 179 (bule trace) and peak 207 (orange trace), (D) predicted CCS value of chikusetsusaponin IVa and zingibroside R1 by CCSbase platform.

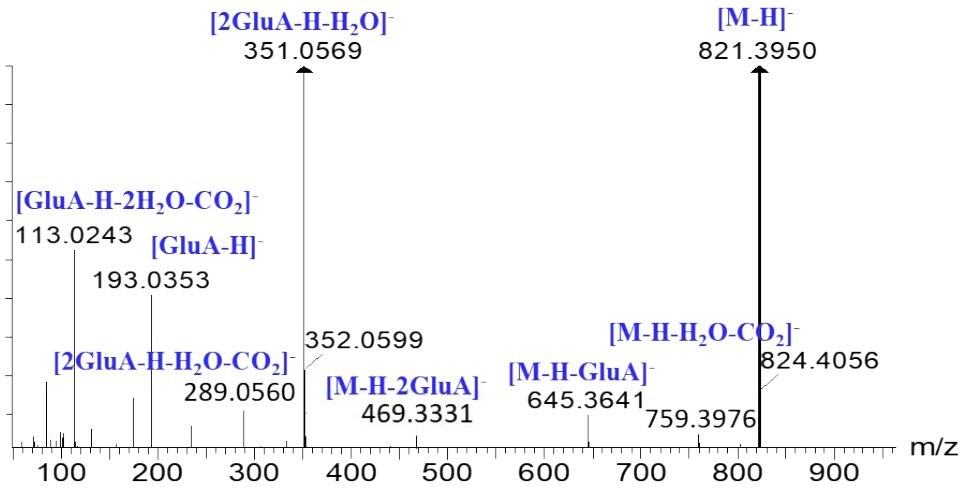
Fig. S5 The molecular network of flavonoids from GLJ, PC, EC, GU, EB(A), MS/MS spectra of #431 (peak 83) (B), possible fragmentation patterns of kaempferin(C).

Fig. S6 The molecular network of lyso-GPCs from GLJ, HK, CN, MP and CE, MS/MS spectra and possible fragmentation patterns of node #482 (peak 236) and #496 (peak 232) in negative ion mode.

Fig. S7 Characterization of isomers with #323: (A) molecular network in which #323 is located (B) extracted ion chromatography (EIC) of *m/z* 323.1278 $[M+H]^+$, including three peaks at 35.68 min (peak 206), 39.17 min (peak 219) and 46.85 min (peak 242), (C) MS/MS spectra of three peaks and Diagnostic ion formation pathways of neobavaisoflavone, bavachromene and chromenoflavanone.

Fig. S1

MS/MS of *m/z* 821.3948



glycyrrhizic acid

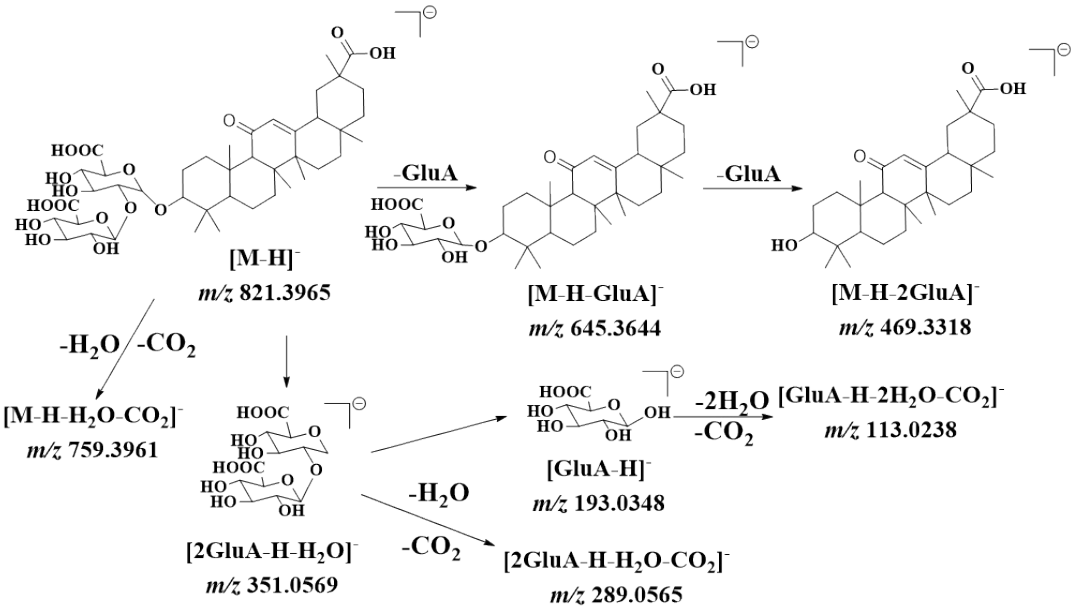


Fig. S2

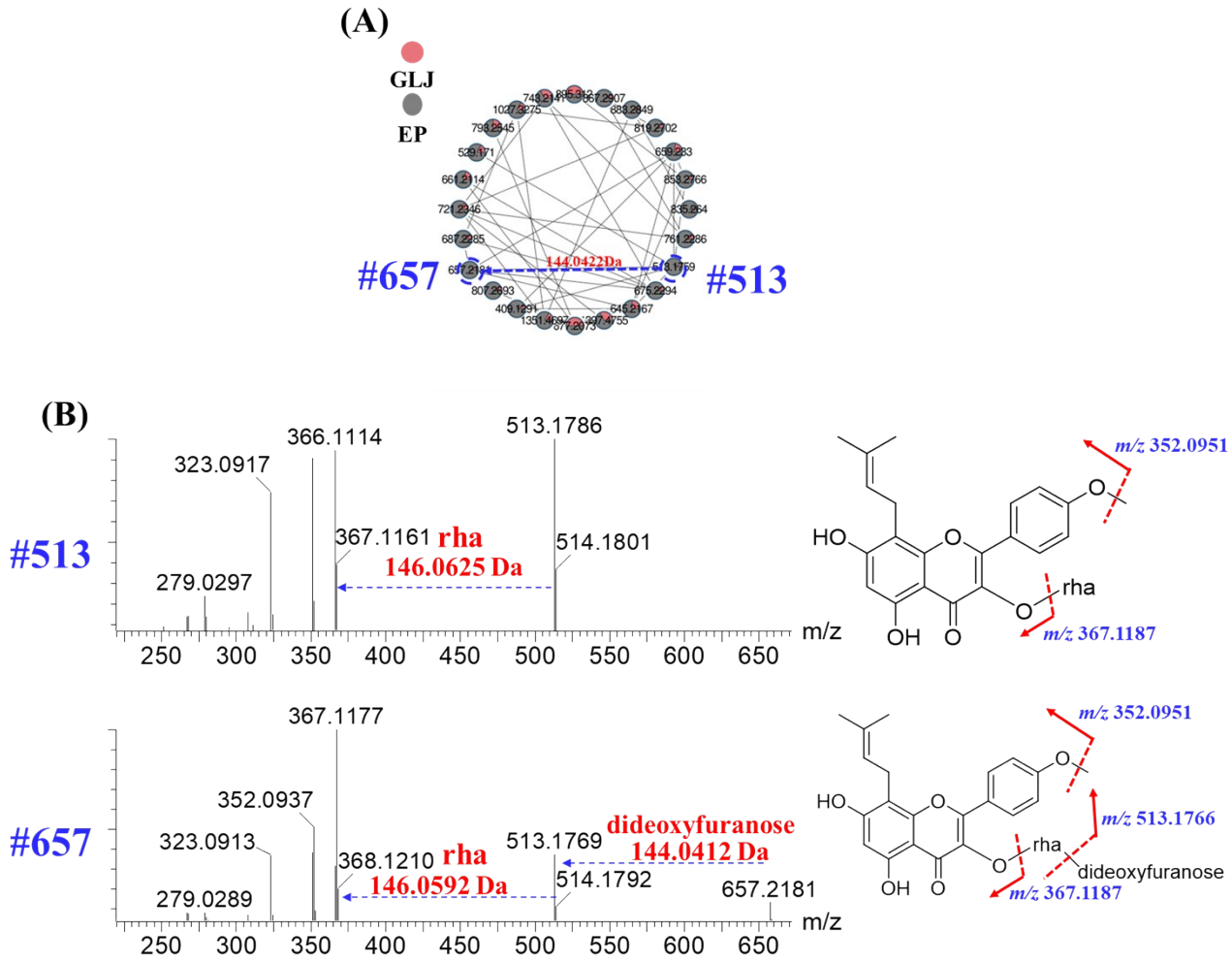

(A)
GLJ
EP
#657
144.0422Da
#513
(B)
#513
366.1114
513.1786
323.0917
367.1161 rha
146.0625 Da
514.1801
279.0297
m/z
250 300 350 400 450 500 550 600 650
m/z 352.0951
HO
O
rha
OH
m/z 367.1187
#657
367.1177
352.0937
323.0913
368.1210 rha
146.0592 Da
513.1769
dideoxyfuranose
144.0412 Da
514.1792
279.0289
657.2181
m/z
250 300 350 400 450 500 550 600 650
m/z 352.0951
m/z 513.1766
rha
dideoxyfuranose
m/z 367.1187

Fig. S3

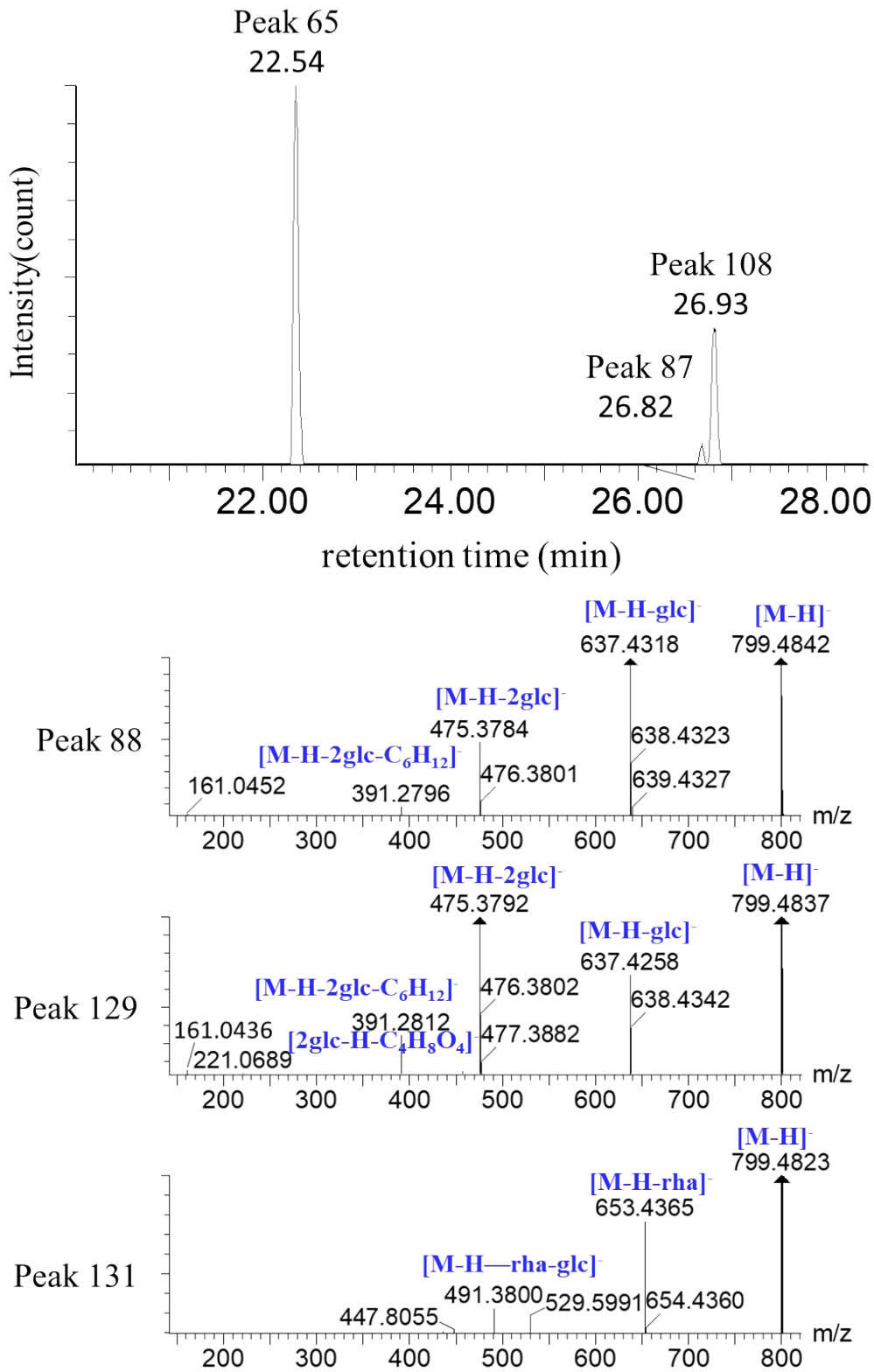
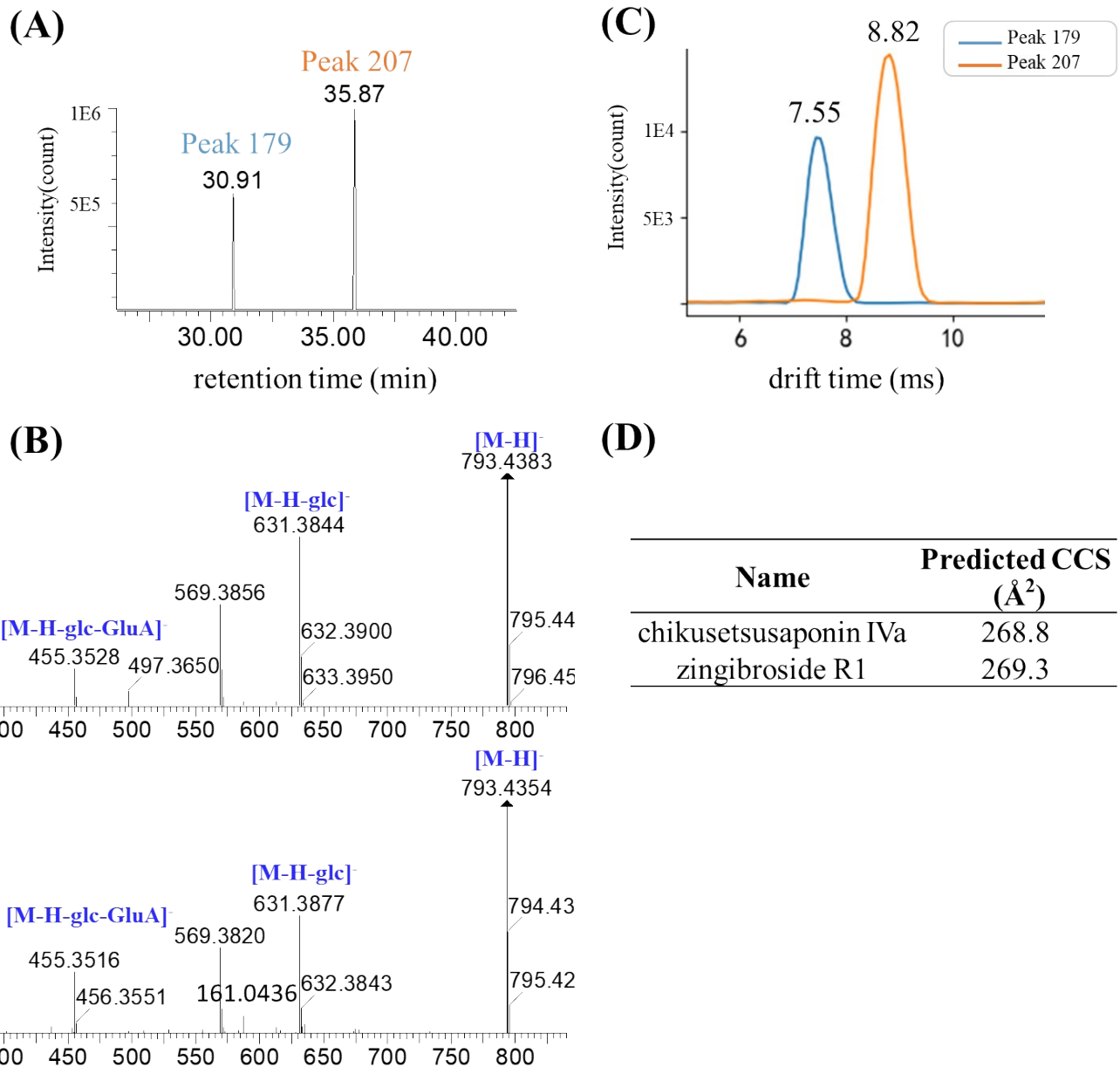

Peak 65
22.54
Peak 108
26.93
Peak 87
26.82
Intensity(count)
22.00
24.00
26.00
28.00
retention time (min)
Peak 88
[M-H-glc]-
637.4318
[M-H]-
799.4842
[M-H-2glc]-
475.3784
638.4323
[M-H-2glc-C6H12]-
476.3801
639.4327
161.0452
391.2796
m/z
200
300
400
500
600
700
800
Peak 129
[M-H-2glc]-
475.3792
[M-H]-
799.4837
[M-H-glc]-
637.4258
[M-H-2glc-C6H12]-
476.3802
638.4342
391.2812
161.0436
[2glc-H-C4H8O4]-
477.3882
221.0689
m/z
200
300
400
500
600
700
800
Peak 131
[M-H]-
799.4823
[M-H-rha]-
653.4365
[M-H—rha-glc]-
491.3800
529.5991
654.4360
447.8055
m/z
200
300
400
500
600
700
800

Fig. S4



(D)

Name	Predicted CCS ($Å^2$)
chikusetsusaponin IVa	268.8
zingibroside R1	269.3

Fig. S5

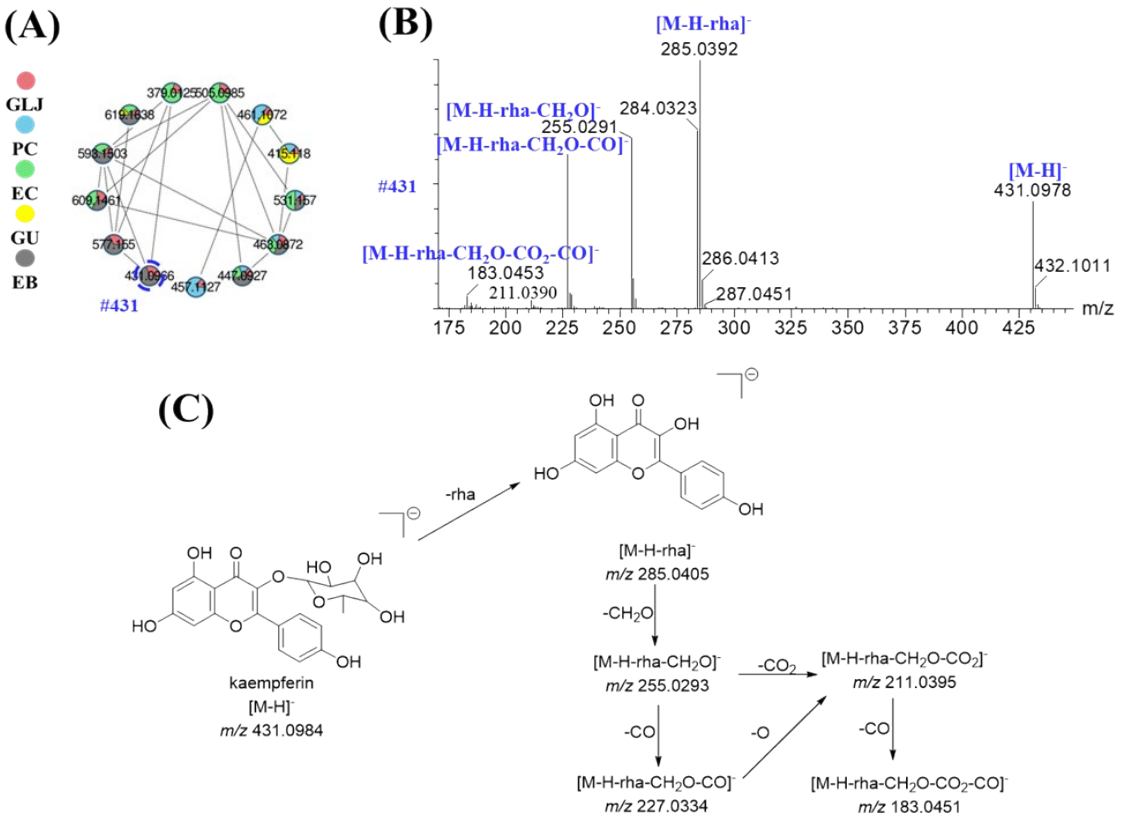

(A)
GLJ
PC
EC
GU
EB
#431
(B)
[M-H-rha]-
285.0392
[M-H-rha-CH2O]-
284.0323
255.0291
[M-H-rha-CH2O-CO]-
#431
[M-H]-
431.0978
[M-H-rha-CH2O-CO2-CO]-
183.0453
211.0390
286.0413
287.0451
432.1011
m/z
(C)
-rha
kaempferin
[M-H]-
m/z 431.0984
[M-H-rha]-
m/z 285.0405
-CH2O
[M-H-rha-CH2O]-
m/z 255.0293
-CO2
[M-H-rha-CH2O-CO2]-
m/z 211.0395
-CO
-O
-CO
[M-H-rha-CH2O-CO]-
m/z 227.0334
[M-H-rha-CH2O-CO2-CO]-
m/z 183.0451

Fig. S6

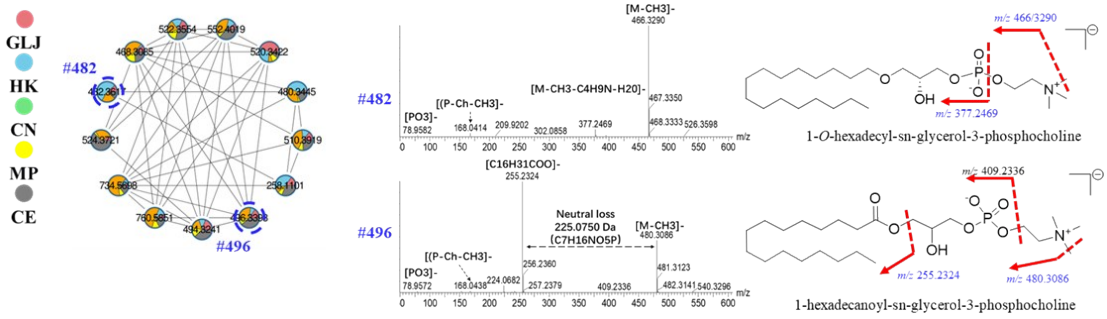

GLJ
HK
CN
MP
CE
#482
#496
#482
[M-CH3]-
466.3290
[(P-Ch-CH3]-
[PO3]-
78.9582
168.0414
[M-CH3-C4H9N-H20]-
467.3350
468.3333
526.3598
[C16H31COO]-
255.2324
m/z 466/3290
m/z 377.2469
1-O-hexadecyl-sn-glycerol-3-phosphocholine
#496
Neutral loss
225.0750 Da
(C7H16NO5P)
[M-CH3]-
480.3086
[(P-Ch-CH3]-
[PO3]-
78.9572
168.0438
224.0682
256.2360
257.2379
409.2336
481.3123
482.3141
540.3296
m/z 409.2336
m/z 255.2324
m/z 480.3086
1-hexadecanoyl-sn-glycerol-3-phosphocholine

Fig. S7

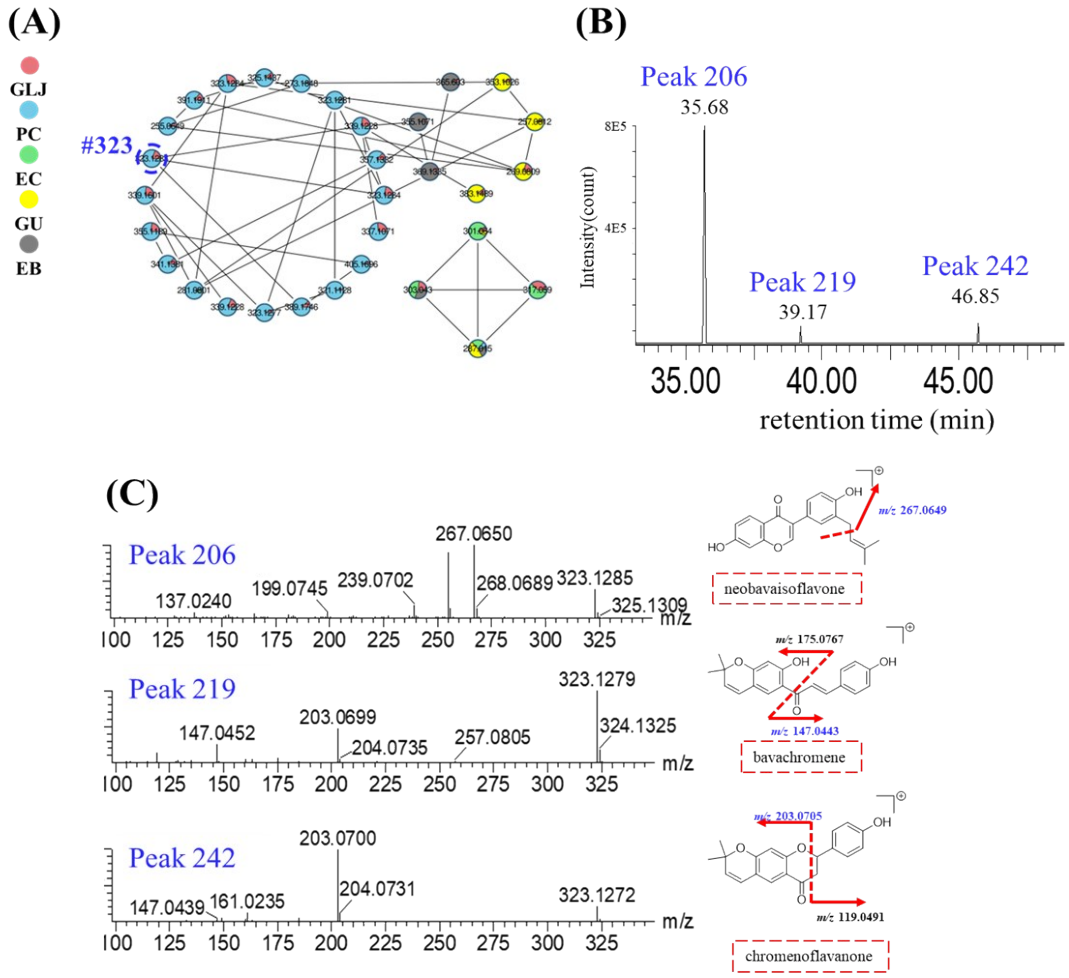

(A)
GLJ
PC
EC
GU
EB
#323
(B)
Peak 206
35.68
Peak 219
39.17
Peak 242
46.85
8E5
4E5
Intensity(count)
35.00
40.00
45.00
retention time (min)
(C)
Peak 206
267.0650
137.0240
199.0745
239.0702
268.0689
323.1285
325.1309
m/z
Peak 219
323.1279
147.0452
203.0699
204.0735
257.0805
324.1325
m/z
Peak 242
203.0700
147.0439
161.0235
204.0731
323.1272
m/z
100 125 150 175 200 225 250 275 300 325
m/z 267.0649
neobavaisoflavone
m/z 175.0767
m/z 147.0443
bavachromene
m/z 203.0705
m/z 119.0491
chromenoflavanone

Table. S1 Characterization of 257 constituents from GLJ by LC-QTOF/MS.

PEAK (NO)	RT (min)	Formalu	Adduct	Observed (*m/z*)	Mass error (ppm)	Fragment	Identification	origin	type
1	1.070	$C_{24}H_{42}O_{21}$	+Cl	701.1899	-2.00	[M-H]665.2140 [M-H-glc]485.1478 [M-$C_{10}H_{19}O_9$]383.1190 [M-2glc]341.1109 [M-$C_{16}H_{29}O_{14}$]221.0653	stachyose	LB	others
2	1.077	$C_5H_{13}NO$	+H	104.1074	3.84	NF	D-Valinol	CN	others
3	1.100	$C_5H_{11}NO_2$	+H	118.0864	0.85	NF	valine	AC/HK CN/CN	others
4	1.100	$C_6H_{12}O_6$	-H	179.0565	2.23	NF	glucose	LB	others
5	1.123	$C_{12}H_{22}O_{11}$	+Cl	377.0850	-1.59	[M-H]341.1070 [M-H-Fru]179.0563	D(+)-sucrose	LB	others
6	1.146	$C_5H_{11}NO_2$	+H	118.0868	4.23	NF	betaine*	AB/LB	others
7	1.272	$C_6H_{12}O_6$	-H	179.0555	-3.35	NF	D(-)-fructose	LB	others
8	1.713	$C_5H_7NO_3$	+H	130.0506	1.54	NF	pyroglutamic acid	HK/CN CN	others
9	2.021	$C_{10}H_{13}N_5O_4$	+H	268.1046	1.86	[M+H-rib]136.0618	adenosine*	CS	others
10	2.891	$C_{10}H_{13}NO_2$	+H	180.1024	2.78	[M+H-H_2O]162.0891 [M+H-H_2O-CH_3]147.0700 [M+H-2H_2O]144.0827 [M+H-H_2O-CO]134.0975	salsolinol	ACD	others

11	3.645	$C_{12}H_{16}O_8$	-H	287.0761	-3.83	[M-H-glc]125.0230	maltol-3-*O*-β-glucoside*	EU	others
12	6.257	$C_6H_6O_3$	+H	127.0394	3.15	[M-OH]109.0290 [M-CHO]97.0290 [M+H-OH-CHO]81.0345	5-hydroxymethylfurfural*	AC/EC	others
13	6.684	$C_{16}H_{22}O_{10}$	-H	373.1148	2.14	[M-H-glc]211.0616 [M-H-glc-COOH-OH]149.0614 [M-H-glc-2COO]123.0451	geniposidic acid	EU	others
14	8.863	$C_{16}H_{24}O_{10}$	-H	375.1287	-2.67	[M-H-glc]213.0769 [M-H-glc-COO]169.0892 [M-H-glc-COO-H_2O]151.0757 [M-H-glc-$C_3H_4O_3$]125.0630 [M-H-glc-$C_3H_4O_3$-H_2O]107.0480	mussaenoside acid adoxosidic acid 8-epiloganic acid	CT	others
15	9.302	$C_{24}H_{39}NO_9$	+H	486.2704	1.23	[M+H-H_2O]468.2531 [M+H-CH_3OH]454.2531 [M+H-CH_3OH-H_2O]436.2316 [M+H-2CH_3OH]422.2273 [M+H-2CH_3OH-H_2O]404.2013 [M+H-3CH_3OH-H_2O]378.1837	mesaconine*	ACD	others
16	9.470	$C_{16}H_{24}O_{10}$	-H	375.1295	-0.53	[M-glc]213.0754 [M-glc-COO]169.0905 [M-glc-COO-H_2O]151.0749 [M-glc-$C_3H_4O_3$-H_2O]107.0488	mussaenoside acid adoxosidic acid 8-epiloganic acid	CT	others
17	9.904	$C_{21}H_{28}O_{13}$	-H	487.1441	3.28	[M-H-rha-glc]179.0343 [M-H-rha-glc-H_2O]161.0242 [M-rha-glc-CO_2]135.0431 [M-rha-glc-HCOOH]133.0268	cistanoside F	CT	others
18	10.305	$C_{28}H_{42}N_4O_6$	+H	531.3179	0.38	[M-$C_{12}H_{17}N_2O_3$]293.1865 [M-$C_{16}H_{22}N_3O_3$]222.1125 [M-$C_{19}H_{34}N_4O_3$]165.0546 [M-$C_{21}H_{35}N_4O_4$]123.0445	kukoamine A kukoamine B	LB	others

19	10.965	$C_8H_{20}NO_6P$	+H	258.1101	1.94	[P-Ch]184.0738 [P-Ch-H_2O]166.0610 [P-Ch-C_3H_9N]125.0000 [P-Ch-HPO_3]104.1091 [P-Ch-HPO_3-H_2O]86.0979	*sn*-glycerol-3-phosphocholine	CE/HK CN/QN	lyso-GPCs
20	10.997	$C_{22}H_{31}NO_3$	+H	358.2371	-1.67	[M+H-H_2O]340.2263 [M+H-2H_2O]322.2161	songorine*	ACD	others
21	11.089	$C_{16}H_{18}O_9$	-H	353.0878	0.00	[M-H-$C_4H_8O_4$]233.0446 [M-H-$C_5H_8O_5$]205.0499 [M-H-glc]191.0335 [M-H-glc-CO]163.0384	chlorogenic acid*	EU/CC/PG	others
22	11.650	$C_{37}H_{53}N_3O_{16}$	+H	796.3489	-1.26	[M-hex]634.2836 [M-2hex]472.2578 [M-2hex-$C_9H_7O_3$]310.2133 [M-2hex-$C_{13}H_{20}N_2O_3$]220.0965 [M-hex-$C_{16}H_{26}N_3O_3$]163.0396	N-caffeoyl, N'-dihydrocaffeoyl spermidine dihexose	LB	others
23	11.747	$C_{31}H_{43}N_3O_{11}$	+H	634.2956	-3.15	[M-hex]472.2495 [M-hex-$C_9H_7O_3$]310.2101 [M-hex-$C_{13}H_{20}N_2O_3$]220.0966 [M-hex-$C_{16}H_{26}N_3O_3$]163.0382	N_1-dihydrocaffeoyl, N_{10}-caffeoyl spermidine hexose	LB	others
24	11.781	$C_{16}H_{18}O_9$	-H	353.0868	-2.83	[M-H-$C_4H_8O_4$]233.0436 [M-H-$C_5H_8O_5$]205.0495 [M-glc]191.0345 [M-glc-CH_2O]161.0600	cryptochlorogenic acid	EU/PG	others
25	11.801	$C_{34}H_{41}N_3O_9$	+H	636.3134	1.10	[M-hex]474.2641 [M-hex-$C_{12}H_{17}N_2O_3$]236.1305 [M-hex-$C_{13}H_{20}N_2O_3$]222.1127 [M-hex-$C_{16}H_{26}N_3O_3$]165.0541 [M-hex-$C_{18}H_{28}N_3O_4$]123.0471	N_1, N_{10}-dihydrocaffeoyl spermidine hexose	LB	others

26	12.385	$C_{24}H_{39}NO_7$	+H	454.2812	2.64	[M+H-H_2O]436.2698 [M+H-CH_3OH]422.2535 [M+H-2H_2O]418.2586 [M+H-CH_3OH-H_2O]404.2430 [M+H-2H_2O-CH_3OH]386.2318 [M+H-2H_2O-2CH_3OH]354.2055	fuziline*	ACD	others
27	13.092	$C_{31}H_{45}N_3O_{11}$	+H	634.2951	-3.94	[M-hex]472.2495 [M-hex-$C_9H_7O_3$]310.2101 [M-hex-$C_{12}H_{15}N_2O_3$]236.1276 [M-hex-$C_{13}H_{20}N_2O_3$]220.0966 [M-hex-$C_{16}H_{26}N_3O_3$]163.0382	N_1-dihydrocaffeoyl, N_{10}-caffeoyl spermidine hexose	LB	others
28	13.286	$C_{24}H_{39}NO_6$	+H	438.2854	0.91	[M+H-H_2O]420.2746 [M+H-H_2O-CH_3OH]388.2484 [M+H-2CH_3OH-H_2O]356.2231	neoline*	ACD	others
29	13.520	$C_{25}H_{36}N_3O_6$	+H	474.2598	-0.21	[M-$C_{13}H_{20}N_2O_3$]222.1114 [M-$C_{16}H_{26}N_3O_3$]165.0561 [M-$C_{18}H_{28}N_3O_4$]123.0423	N_1, N_{10}-bis-(dihydrocaffeoyl) spermidine	LB	others
30	13.808	$C_{35}H_{48}O_{21}$	-H	801.2443	1.97	[M-H-H_2O]783.2332 [M-H-H_2O-claffeoy]621.2010 [claffeoyl+H_2O]179.0349 [claffeoyl]161.0241 [M-H-caffeoyl-2glc-rha]135.0451 [claffeoyl-CO]133.0286	cistantubuloside C1	CT	others
31	14.825	$C_{25}H_{33}N_3O_6$	+H	472.2452	2.12	[M+H-$C_9H_7O_3$]310.2143 [M-$C_{13}H_{20}N_2O_3$]220.0975 [M-$C_{16}H_{26}N_3O_3$]163.0383 [M-$C_{17}H_{26}N_3O_4$]135.0452	N_1-dihydrocaffeoyl, N_{10}-caffeoyl spermidine	LB	others

32	15.791	$C_{29}H_{36}O_{16}$	-H	639.1921	1.5	[M-H-H_2O]621.1826 [M-H-H_2O-claffeoyl]459.1508 [claffeoyl+H_2O]179.0348 [claffeoyl]161.0240 [M-H-caffeoyl-glc-rha]135.0446 [claffeoyl-CO]133.0293	campneoside II	CT	others
33	15.834	$C_{17}H_{18}O_9$	+Na	389.0844	-1.29	[M-glc]187.0397 [M-glc-CO]159.0446 [M-glc-COO]143.0507 [M-glc-2CO]131.0500 [M-glc-CO-COO]115.0538	psoralenoside	PC	others
34	15.985	$C_{21}H_{20}O_9$	-H	415.1031	0.86	[M-H-glc]253.0499 [M-H-glc-H]252.0417 [M-H-glc-2H-CO]223.0398 [M-H-glc-2CO-H]195.0448	daidzoside	PC/GU	flavonoids
35	16.153	$C_{29}H_{36}O_{16}$	-H	639.1924	1.03	[M-H-H_2O]621.1840 [M-H-H_2O-claffeoyl]459.1508 [claffeoyl+H_2O]179.0350 [claffeoyl]161.0242 [M-H-caffeoyl-glc-rha]135.0452 [claffeoyl-CO]133.0290	campneoside II	CT	others
36	16.191	$C_{35}H_{46}O_{20}$	-H	785.2499	1.27	[M-H-caffeoyl]623.2241 [M-H-caffeoyl-rha]477.1564 [M-H-caffeoyl-glc]461.1610 [M-H-caffeoyl-glc-rha]315.1080 [caffeoyl+H_2O]179.0331 [caffeoyl]161.0238 [M-H-caffeoyl-2glc-rha]153.0503 [caffeoyl-CO]133.0275	purpureaside B/C	RG	others

37	16.383	$C_{27}H_{32}O_{14}$	-H	579.1717	0.4	[M-H-glc]417.1143 [M-H-2glc]255.0665 [M-H-2glc-C_8H_7O]135.0091 [M-H-2glc-$C_7H_3O_3$]119.0499 [M-H-2glc-C_8H_7O-C_2H_4]91.0185	glucoliquiritin	GU	flavonoids
38	16.461	$C_{35}H_{46}O_{20}$	-H	785.2505	0.51	[M-H-caffeoyl]623.2140 [M-H-caffeoyl-rha]477.1680 [M-H-caffeoyl-glc]461.1609 [claffeoyl+H_2O]179.0331 [claffeoyl]161.0238 [M-H-caffeoyl-2glc-rha]153.0503 [claffeoyl-CO]133.0275	purpureaside B/C	RG	others
39	16.499	$C_{17}H_{18}O_9$	+Na	389.0849	0.00	[M-glc]187.0400 [M-glc-CO]159.0449 [M-glc-2CO]131.0471	isopsoralenoside	PC	others
40	16.730	$C_{35}H_{46}O_{20}$	-H	785.2488	2.67	[M-H-caffeoyl]623.2179 [M-H-caffeoyl-rha]477.1598 [M-H-caffeoyl-glc]461.1656 [M-H-caffeoyl-glc-rha]315.1076 [claffeoyl]179.0342 [claffeoyl-H_2O]161.0241 [M-H-caffeoyl-2glc-rha]153.0553 [claffeoyl-CO]133.0290	echinacoside*	CT	others
41	17.172	$C_{42}H_{74}O_{15}$	+HCOO	863.4986	2.85	[M-H]817.4957 [M-H-glc]655.4425 [M-H-2glc]493.3903 [glc-H]161.0471	hosenkoside N+2H	IB	saponins
42	17.260	$C_{16}H_{24}O_9$	-H	359.1340	-2.23	[M-H-glc]197.0739 [M-H-glc-COO]153.0888 [M-H-glc-COO-H_2O]135.0783	8-epideoxyloganic acid	CT	others

43	17.549	$C_{26}H_{28}O_{16}$	-H	595.1284	-2.52	[M-H-rha]447.0923 [M-H-rha-H]446.0855 [M-H-2rha]301.0351 [M-H-2rha-2H]299.0185 [M-H-2rha-2H-CO]271.0241	quercetin-3-*O*-arabinoglucoside	EC/EB	flavonoids
44	17.575	$C_{27}H_{32}O_{14}$	-H	579.1714	0.91	[M-H-glc]417.1143 [M-H-2glc]255.0665 [M-H-2glc-C_8H_7O]135.0091 [M-H-2glc-$C_7H_3O_3$]119.0499 [M-H-2glc-C_8H_7O-C_2H_4]91.0185	glucoisoliquiritin	GU	flavonoids
45	17.689	$C_{27}H_{30}O_{16}$	-H	609.1461	0.01	[M-H-glc-rha]300.0270 [M-H-glc-rha-CO]271.0225 [M-H-glc-rha-CO-OH]255.0310 [M-H-glc-rha-2CO]243.0311	rutin*	EU/CS	flavonoids
46	17.891	$C_{35}H_{46}O_{19}$	-H	769.2549	1.43	[M-H-claffeoyl]623.2144 [M-H-claffeoyl-O]607.2243 [M-H-claffeoyl-glc]461.1796 [M-$C_{26}H_{39}O_6$]163.0398 [M-$C_{26}H_{39}O_6$-H_2O]145.0295 [M-$C_{26}H_{39}O_6$-HCOOH]135.0463	poliumoside	CT/RG	others
47	18.261	$C_{38}H_{50}O_{22}$	-H	857.2704	1.98	[M-H-caffeoyl]695.2231 [M-H-caffeoyl-$COCH_2$]653.2276 [claffeoyl+H_2O]179.0344 [claffeoyl]161.0233 [claffeoyl-CO]133.0341	kankanosides K1	CT/RG	others
48	18.501	$C_{26}H_{30}O_{13}$	-H	549.1595	3.28	[M-H-api]417.1268 [M-H-api-glc]255.0649 [M-H-api-glc-C8H7O]135.0092 [M-H-api-glc-C7H3O3]119.0491 [M-H-api-glc-C8H7O-C2H4]91.0176	liquiritin apioside*	GU	flavonoids

49	18.541	$C_{27}H_{44}O_7$	+HCOO	525.3052	-2.28	[M-H]479.3051 [M-$C_8H_{17}O_3$]319.1797 [M-$C_8H_{17}O_3$-H_2O]301.1816 [$C_8H_{15}O_3$]159.1061	β-ecdysterone	AB	others
50	18.595	$C_{21}H_{22}O_9$	-H	417.1188	0.48	[M-H-glc]255.0654 [M-H-glc-C_8H_7O]135.0080 [M-H-glc-$C_7H_3O_3$]119.0494 [M-H-glc-C_8H_7O-C_2H_4]91.0174	liquiritin*	GU	flavonoids
51	18.675	$C_{17}H_{19}NO_4$	+H	302.1390	0.99	[M-$C_{10}H_{12}NO_2$]123.0366 [M-$C_9H_{10}NO_3$]121.0663 [M-$C_{10}H_{10}NO_3$-H_2O]91.0527	dihydro-N-caffeoyltyramine	LB	others
52	18.679	$C_{49}H_{85}NO_{19}$	+HCOO	1036.5668	3.01	[M-H]990.5601 [M-H-xyl]858.517 [M-H-glc]828.5121 [M-H-glc-xyl]696.469 [M-H-2glc-xyl]534.414 [glc+xyl-H-$C_3H_6O_3$]221.066	C32H55NO4+2glc+xyl	IB	others
53	18.967	$C_{21}H_{20}O_{12}$	-H	463.0875	1.51	[M-H-glc]301.0350 [M-H-glc-H]300.0260 [M-H-glc-CH_2O]271.0229 [M-H-glc-CH_2O-OH]255.0293 [M-H-glc-CH_2O-CO]243.0285 [M-H-glc-CH_2O-OH-CO]227.0320	hyperoside*	EC/EU/CS/CC	flavonoids
54	18.970	$C_{37}H_{48}O_{21}$	-H	827.2607	0.97	[M-H-$COCH_2$]785.2545 [M-H-claffeoyl]665.2277 [M-H-claffeoyl-$COCH_2$]623.2173 [M-H-claffeoyl-$COCH_2$-rha]477.1573 [M-H-claffeoyl-$COCH_2$-glc]461.1683 [claffeoyl+H_2O]179.0339 [claffeoyl]161.0236 [claffeoyl-CO]133.0285	tubuloside A	CT	others

55	19.006	$C_{27}H_{30}O_{14}$	-H	577.155	-1.21	[M-H-rha]431.0935 [M-H-2rha]285.0386 [M-H-2rha-2H]283.0219 [M-H-2rha-2H-H_2O]255.0302	kaempferitrin	EB	flavonoids
56	19.024	$C_{44}H_{77}NO_{15}$	+HCOO	904.5244	3.63	[M-H]858.52 [M-H-glc]696.468 [M-H-2glc]534.414 [2glc-H-$C_4H_8O_4$]221.066	C32H55NO4+2glc	IB	others
57	19.165	$C_{21}H_{20}O_{12}$	-H	463.0872	2.16	[M-H-glc]300.0268 [M-H-glc-CH_2O]271.0232 [M-glc-CH_2O-OH]255.0288 [M-H-glc-CH_2O-CO]243.0302 [M-glc-CH_2O-OH-CO]227.0358	isoquercitrin*	EC/EU	flavonoids
58	19.204	$C_{27}H_{44}O_7$	+HCOO	525.3054	-1.90	[M-H]479.3051 [M-$C_8H_{17}O_3$]319.1813 [M-$C_8H_{17}O_3$-H_2O]301.1803	(25S)-inokosterone*	AB	others
59	19.260	$C_{29}H_{36015}$	-H	623.1973	1.28	[M-H-claffeoyl]461.1660 [M-H-claffeoyl-rha]315.1083 [claffeoyl+H_2O]179.0346 [claffeoyl]161.0244 [claffeoyl-CO]133.0290	acteoside*	CT/RG	others
60	19.514	$C_{43}H_{75}NO_{14}$	+HCOO	874.5146	2.84	[M-H]828.5101 [M-H-xyl]696.468 [M-H-xyl-glc]534.414 [glc+xyl-H-$C_3H_6O_3$]221.066	C32H55NO4+glc+xyl	IB	others
61	19.984	$C_{34}H_{44}O_{19}$	-H	755.2401	0.26	[M-H-claffeoyl]593.2101 [claffeoyl+H_2O]179.0331 [claffeoyl]161.0225 [claffeoyl-CO]133.0291	myricoside	CT	others

62	20.110	$C_{29}H_{36015}$	-H	623.1966	2.41	[M-H-claffeoyl]461.1651 [M-H-claffeoyl-rha]315.1106 [claffeoyl+H_2O]179.0338 [claffeoyl]161.0234 [claffeoyl-CO]133.0280	isoacteoside*	CT/RG	others
63	20.204	$C_{21}H_{20}O_{11}$	-H	447.0927	-1.57	[M-H-rha]301.0338 [M-H-rha-H]300.0249 [M-H-rha-CO-H]271.0273 [M-H-rha-CO-OH]255.0295	quercitrin	PC/EC/GU/EB	flavonoids
64	20.304	$C_{42}H_{72}O_{15}$	+HCOO	861.4835	2.67	[M-H]815.4791 [M-H-glc]653.4254 [M-H-2glc]491.3731 [M-H-2glc-CH_3OH]459.3431 [glc-H]161.0441	hosenkoside N	IB	saponins
65	20.348	$C_{48}H_{82}O_{20}$	+HCOO	1023.5361	1.95	[M-H]977.5308 [M-H-glc]815.4777 [M-H-2glc]653.4250 [M-H-3glc]491.3727	hosenkoside B	IB	saponins
66	20.594	$C_{29}H_{36}O_{14}$	-H	607.2019	2.14	[claffeoyl+H_2O]179.0348 [claffeoyl]161.0234 [claffeoyl-CO]133.0287	syringalide a 3‘-α-l -rhamnopyranoside*	CT	others
67	20.671	$C_{23}H_{22}O_{13}$	-H	505.0985	0.59	[M-H-CH_2O-glc]300.0249 [M-H-CH_2O-glc-H]271.0273 [M-H-CH_2O-glc-OH]255.0295	quercetin-3-O- glucose-6"-acetate	EC	flavonoids
68	20.818	$C_{32}H_{38}O_{16}$	-H	677.2073	2.08	[M-H-rha]530.1434 [M-H-rha-glc]369.1008 [M-H-rha-glc-2H]367.0819	anhydroicaritin-3-O- glucoside(1-2)-rhamnose	EB	flavonoids
69	20.850	$C_{47}H_{80}O_{19}$	+HCOO	993.5248	1.31	[M-H-xyl]815.4747 [M-H-xyl-glc]653.4521	hosenkoside F	IB	saponins
70	21.012	$C_9H_{16}O_4$	-H	187.0968	-4.28	[M-C_2H_5O-H_2O]125.0963	epieucommiol	EU-neg	others

							eucommiol		
71	21.025	$C_{21}H_{34}O_9$	-H	429.2123	-1.63	[M-glc]267.1581 [M-glc-H_2O]249.1471	neorehmannioside D	RG	others
72	21.066	$C_{17}H_{17}NO_4$	+H	300.1232	0.33	[M-$C_8H_{10}NO$]163.0400 [M-$C_8H_{10}NO$-CO]135.0444	N-caffeoyltyramine	LB	others
73	21.114	$C_{32}H_{38}O_{16}$	-H	677.2083	0.6	[M-H-glc]515.1533 [M-H-2glc]353.1018 [M-H-2glc-2H]351.0853 [M-H-2glc-2H-CO]323.0918	hexandraside E	EB	flavonoids
74	21.126	$C_{21}H_{22}O_{10}$	-H	433.1132	-0.69	[M-H-glc]271.0585 [M-H-glc-C_8H_8O]151.0005 [M-H-glc-$C_5H_3O_4$]119.0475	prunin	GU	flavonoids
75	21.360	$C_{48}H_{82}O_{19}$	+HCOO	1007.5411	1.59	[M-H-glc]799.4407 [M-H-2glc]637.4231 [M-H-3glc]475.3824 [M-H-3glc-C_6H_{12}]391.2827	20-*O*-gluginsenoside-Rf	PG	saponins
76	21.416	$C_{37}H_{46}O_{19}$	-H	793.2545	1.96	[M-H-glc]631.2026 [M-H-rha-xyl]514.1464 [M-H-rha-xyl-glc-H]351.0872 [M-H-rha-xyl-glc-H-CO]323.0928	epimedoside D	EB	flavonoids
77	21.599	$C_{31}H_{43}NO_{19}$	+H	590.2969	1.52	[M+H-CH_3OH]558.2697 [M+H-CH_3OH-H_2O]540.2601 [M+H-$_2CH_3OH$-H_2O]508.2361	benzoylmesaconine*	ACD	others
78	21.617	$C_{54}H_{92}O_{25}$	+HCOO	1185.5909	0.08	[M-H-glc]977.5336 [M-H-glc-OH]960.5161 [M-H-2glc]815.4745 [M-H-3glc]653.4227 [M-H-4glc]489.3641	hosenkoside K	IB	saponins

79	21.645	$C_{31}H_{38}O_{16}$	-H	665.2080	1.05	[M-H-claffeoyl-COCH2]461.1710 [claffeoyl+H2O]179.0314 [claffeoyl]161.0240 [claffeoyl-CO]133.0285	2'-acetylacteoside	CT	others
80	21.770	$C_{47}H_{80}O_{18}$	+HCOO	977.5306	1.64	[M-H-xyl]799.4407 [M-H-xyl-glc]637.4293 [M-H-xyl-2glc]475.3890 [M-H-xyl-2glc-C_6H_{12}]391.2791	noto-ginsenoside-R1	PG	saponins
81	21.798	$C_{39}H_{50}O_{22}$	-H	869.2704	1.95	[M-H-glc]707.2300 [M-H-glc-$COCH_2$]665.2298 [M-H-glc-2$COCH_2$]623.2203 [claffeoyl]161.0243 [M-H-caffeoyl-2glc-rha-2$COCH_2$]135.0475 [claffeoyl-CO]133.0286	acteoside-2Ac-glc	CT	others
82	21.967	$C_{42}H_{72}O_{15}$	+HCOO	861.4841	2.67	[M-H]815.4747 [M-H-glc]653.4323	hosenkoside J hosenkoside E	IB	saponins
83	22.071	$C_{21}H_{20}O_{10}$	-H	431.0966	-2.78	[M-H-rha] 285.0392 [M-H-rha-H]284.0323 [M-H-rha-H-CH_2O]255.0291 [M-H-rha-CO-CH_2O]227.0340 [M-H-rha-H-2CO-OH-H]211.0390 [M-H-rha-CO-CH_2O-CO_2]183.0453	kaempferin	EB	flavonoids
84	22.174	$C_{32}H_{38}O_{15}$	-H	661.2114	2.72	[M-H-rha]514.1443 [M-H-glc]499.1563 [M-H-glc-rha]353.1031 [M-H-glc-rha-2H]351.0898 [M-H-glc-rha-2H-CO]323.0959	ikarisoside B	EB	flavonoids
85	22.255	$C_{53}H_{90}O_{24}$	+HCOO	1155.5785	1.64	[M-H]1109.5771 [M-H-xyl]977.5362 [M-H-xyl-glc]815.4768 [M-H-xyl-2glc]653.4233	hosenkoside M	IB	saponins

86	22.255	$C_{26}H_{30}O_{13}$	-H	549.1595	3.277726	[M-H-api-glc]255.0645 [M-H-api-glc-C_7H_8O]151.0397 [M-H-api-glc-C_8H_7O]135.0069 [M-H-api-glc-$C_7H_3O_3$]119.0487	licuraside	GU	flavonoids
87	22.382	$C_{48}H_{82}O_{20}$	+HCOO	1023.5337	1.95	[M-H]977.5316 [M-H-glc]815.4786 [M-H-2glc]653.4260 [M-H-3glc]491.3737	hosenkoside C	IB	saponins
88	22.540	$C_{42}H_{72}O_{14}$	+HCOO	845.4875	2.84	[M-H-glc]637.4318 [M-H-2glc]475.3784 [M-H-2glc-C_6H_{12}]391.2796	ginsenoside Rg1	PG	saponins
89	22.540	$C_{48}H_{82}O_{18}$	+HCOO	991.5461	1.71	[M-H-rha]799.4831 [M-H-rha-glc]637.4303 [M-H-rha-2glc]475.3764 [M-H-rha-2glc-C_6H_{12}]391.2911	ginsenoside Re	PG	saponins
90	22.596	$C_{29}H_{32}O_{15}$	-H	619.1638	-4.04	[M-H-rha-CH_2O]431.0956 [M-H-2rha-CH_2O-2H]283.0233 [M-H-2rha-CH_2O-2H-CO]255.0276	α-rhamnoisorobin-3-*O*-(3-*O*-acetyl-α-L-rhamnopyranoside)	EC/GU/EB	flavonoids
91	22.802	$C_{31}H_{38016}$	-H	665.2063	3.61	[M-H-glc]503.1834 [M-H-glc-$COCH_2$]461.1701 [claffeoyl+H_2O]179.0333 [claffeoyl]161.0232 [claffeoyl-CO]133.0298	tubuloside B	CT	others
92	22.806	$C_{32}H_{45}NO_{10}$	+H	604.3115	-0.17	[M+H-H_2O]586.3176 [M+H-CH_3OH]572.2854 [M+H-CH_3OH-H_2O]554.2840 [M+H-$_2CH_3OH$-H_2O]522.2520	benzoylaconine*	ACD	alkaloid

93	22.881	$C_{21}H_{22}O_9$	-H	417.1194	-0.95896	[M-H-glc]255.0655 [M-H-glc-C_7H_8O]151.0449 [M-H-glc-C_8H_7O]135.0089 [M-H-glc-$C_7H_3O_3$]119.0486 [M-H-glc-C_8H_7O-C_2H_4]91.0174	isoliquiritin*	GU	flavonoids
94	22.904	$C_{51}H_{86}O_{23}$	+HCOO	1111.5533	1.88	[M-H-rha]919.4995 [M-H-glc]903.4970 [M-H-rha-glc]757.4514 [M-H-rha-2glc]595.3811 [M-H-rha-3glc]433.3323	C27H4504+3glc+rha	AC	saponins
95	22.923	$C_{20}H_{20}O_6$	+H	357.1332	0.18	[M + H- C_4H_8O]285.0752 [M-C_8H_8O-C_3H_5-H_2O]177.0552 [M-C_8H_8O-C_4H_7O]165.0188 [$C_9H_7O_2$]147.0446 [C_8H_7O]119.0492	tomentosanol D	PC	flavonone
96	22.978	$C_{50}H_{84}O_{23}$	-H	1051.5309	1.52	[M-H-xyl]919.4923 [M-H-glc]889.4857 [M-H-glc-xyl]757.4370 [M-H-2glc-xyl]595.3870 [M-H-3glc-xyl]433.3363	officinalisnin-II	AC	saponins
97	23.021	$C_{51}H_{86}O_{23}$	+HCOO	1111.5327	1.88	[M-H-rha]919.4995 [M-H-glc]903.4970 [M-H-rha-glc]757.4514 [M-H-rha-2glc]595.3811 [M-H-rha-3glc]433.3323	C27H4504+3glc+rha	AC	saponins
98	23.290	$C_{45}H_{76}O_{19}$	+HCOO	965.4932	-2.59	[M-H]919.4894 [M-H-glc]757.4365 [M-H-2glc]595.3864 [M-H-3glc]433.3307	asparagoside E	AC	saponins

99	23.294	$C_{31}H_{40}O_{15}$	-H	651.2326	-4.91	[M-$C_{10}H_9O_3$]475.1769 [$C_{10}H_9O_4$]193.0504 [$C_{10}H_9O_4$-H_2O]175.0390 [$C_{10}H_9O_4$-H_2O-CH_3]160.0172	martyside	RG	others
100	23.317	$C_{47}H_{80}O_{19}$	+HCOO	993.5264	2.92	[M-H-xyl]815.4747 [M-H-xyl-glc]653.4521	hosenkoside G	IB	saponins
101	23.415	$C_{45}H_{76}O_{19}$	+HCOO	965.4931	-2.59	[M-H]919.4877 [M-H-glc]757.4365 [M-H-2glc]595.3839 [M-H-3glc]433.3329	asparagoside E	AC	saponins
102	23.438	$C_{39}H_{48}O_{20}$	-H	835.264	3.13	[M-H-glc]673.2112 [M-H-gluA-rha]515.1519 [M-H-gluA-rha-glc]353.1021	3-[(4-O-Acetyl-6-deoxy-3-O-β-D-xylopyranosyl-α-L-mannopyranosyl)oxy]-7-(β-D-glucopyranosyloxy)-5-hydroxy-2-(4-hydroxyphenyl)-8-(3-methyl-2-buten-1-yl)-4H-1-benzopyran-4-one	EB	flavonoids
103	23.451	$C_{15}H_{10}O_4$	+H	255.0649	1.12	[M+H-CO]227.0699 [M+H-2CO]199.0753 [M+H-2CO-H_2O]181.0645 [M+H-2CO-H_2O-CHO]152.0622 [M+H-C_8H_6O]137.0232	daidzein	PC	flavonoids
104	23.474	$C_{42}H_{72}O_{15}$	+HCOO	861.4830	2.67	[M-H]815.4747 [M-H-glc]653.4323	hosenkoside J hosenkoside E	IB	saponins
105	23.599	$C_{20}H_{18}O_6$	+H	355.1189	-3.36	[M+H-C_3H_6O-H_2O]279.0647 [M+H-C_3H_6O-H_2O-CO]251.0692 [M+H-C_3H_6O-H_2O-$_2$CO]223.0744	3-hydroxy-6-(4-hydroxyphenyl)-2-(2-hydroxypropan-2-yl)-2,3-dihydrofuro[3,2-g]chromen-5-one	PC	flavonoids

106	23.658	$C_{31}H_{43}NO_9$	+H	574.3010	-0.17	[M+H-CH_3OH]542.2744 [M+H-2CH_3OH]510.2497 [M+H-2CH_3OH-H_2O]492.2418 [M+H-3CH_3OH]478.2166 [M+H-3CH_3OH-H_2O]456.1717	benzoylhypacoitine*	ACD	alkaloid
107	24.118	$C_{45}H_{58}O_{24}$	+HCOO	1027.3275	2.55	[M-H-glc]819.2691 [M-H-glc-$C_{12}H_{18}O_8$]529.1697 [M-H-glc-C12H18O8-O]513.1769 [M-H-2glc-$C_{12}H_{18}O_8$]367.1173 [M-H-2glc-$C_{12}H_{18}O_8$-O]351.0883 [M-H-2glc-$C_{12}H_{18}O_8$-CO_2]323.0924	anhydroicaritin-3-O-rhamnodide(1-2)-furan acid-7-O-glucoside+glc	EB	flavonoids
108	24.161	$C_{48}H_{82}O_{20}$	+HCOO	1023.5356	2.44	[M-H]977.5316 [M-H-glc]815.4789 [M-H-2glc]653.4255 [M-H-3glc]491.3709	hosenkoside A	IB	saponins
109	24.336	$C_{41}H_{70}O_{14}$	+HCOO	831.4766	-2.16	[M-H]785.47 [M-H-xyl]653.4212 [M-H-xyl-glc]491.37	hosenkoside H	IB	saponins
110	24.463	$C_{39}H_{50}O_{20}$	+HCOO	883.2849	2.60391	[M-H-glc]675.2272 [M-H-rha-2glc]367.1187 [M-H-rha-2glc]366.1102 [M-H-rha-2glc-CH_3]351.0829 [M-H-rha-2glc-CH_3-CO]323.0910	epimedin A*	EB	flavonoids
111	24.486	$C_{15}H_{12}O_4$	-H	255.0654	3.53	[M-H-C8H7O]135.0074 [M-H-C7H3O3]119.0489 [M-H-C7H3O3-C2H4]91.0177	liquiritigenin	GU/AB	flavonoids
112	24.772	$C_{38}H_{48}O_{19}$	+HCOO	853.2766	0.117195	[M-H-glc]645.2178 [M-H-glc-rha(2-1)xyl]367.1175 [M-H-glc-rha(2-1)xyl-CH_3]351.0874 [M-H-glc-rha(2-1)xyl-CH_3-CO]323.0921	epimedin B*	EB	flavonoids

113	25.007	$C_{32}H_{46}O_9N$	+H	588.3171	0.68	[M+H-CH_3OH]556.2884 [M+H-CH_3OH-H_2O]538.2941 [M+H-2CH_3OH]524.2614 [M+H-2CH_3OH-H_2O]506.2642	benzoyldeoxyaconine*	ACD	alkaloid
114	25.021	$C_{47}H_{80}O_{19}$	+HCOO	993.5247	2.92	[M-H-xyl]815.4747 [M-H-xyl-glc]653.4521	hosenkoside L	IB	saponins
115	25.039	$C_{39}H_{50}O_{19}$	+HCOO	867.2907	1.844822	[M-H-glc]659.2330 [M-H-glc-2rha]367.1168 [M-H-glc-2rha-CH_3]351.0868 [M-H-glc-2rha-CH_3-CO]323.0919	epimedin C	EB	flavonoids
116	25.291	$C_{23}H_{22}O_7$	-H	409.1291	0.43	[M-H-CH_2CO-H]366.1095 [M-H-CH_2CO-H-CH_3]351.0864 [M-H-CH_2CO-H-CH_3-CO]323.0908	icaritin+C2H2O	EB	flavonoids
117	25.438	$C_{15}H_{10}O_7$	-H	301.0351	1.00	[M-H-$_2$CO-OH]228.0448 [M-H-$C_7H_7O_2$]178.9967 [M-H-$C_8H_6O_4$]151.0071 [M-H-$C_7H_4O_4$]149.0313 [M-H-$C_7H_4O_4$-CO]121.0309 [M-H-$C_7H_4O_4$-CO-CH_3]107.0144	quercetin	PC/EC/ GU/EB	flavonoids
118	25.562	$C_{33}H_{40}O_{15}$	+HCOO	721.2346	-1.10921	[M-H-rha]529.1719 [M-H-glc]513.1766 [M-H-glc-rha]367.1186 [M-H-glc-rha-CH_3]351.0874 [M-H-glc-rha-CH_3-CO]323.0911	icariin*	EB	flavonoids
119	25.895	$C_{48}H_{82}O_{19}$	+HCOO	1007.5425	0.69	[M-H-glc]799.4684 [M-H-glc-H2O]781.4883 [M-H-2glc]638.4379 [M-H-3glc]475.3751	hosenkoside O	IB	saponins

120	25.922	$C_{42}H_{72}O_{15}$	+HCOO	861.4836		[M-H]815.4791 [M-H-glc]653.4254 [M-H-2glc]491.3731 [M-H-2glc-CH_3OH]459.3431	hosenkoside D	IB	saponins
121	25.935	$C_{23}H_{24}O_{12}$	-H	491.1187	1.63	[M-H-glc]329.0677 [M-H-glc-CH_3]313.0381 [M-H-glc-2CH_3]299.0192 [M-H-glc-2CH_3-CO]270.0126 [M-H-glc-2CH_3-2CO]242.0222	rhamnazin-3-O- β-D-glucoside	EC	flavonoids
122	26.111	$C_{42}H_{72}O_{15}$	+HCOO	861.4821		[M-H]815.4787 [M-H-glc]653.4281 [M-H-2glc]491.3813 [M-H-2glc-CH_3OH]459.3421	hosenkoside I	IB	saponins
123	26.338	$C_{20}H_{18}O_6$	+H	355.1171	1.45	[M+H-CO]337.1062 [M+H-$C_2H_4O_2$] 295.0960 [M+H-H_2O-C_3H_6O]279.0644 [$C_7H_4O_3$]137.0236	3’’-hydroxypsoralenolc	PC	flavonoids
124	26.465	$C_{48}H_{72}O_{21}$	-H	983.4492	0.101683	[M-H-glc]821.4113 [M-H-glc-GluA]645.3664 [2GluA-H_2O]351.0621 [GluA-H]193.0355 [[2×$C_6H_8O_6$-H]-COOH-H_2O]113.0225	licoricesaponin A3	GU	saponins
125	26.699	$C_{50}H_{74}O_{22}$	-H	1025.4598	0.097517	[(2GluA-rha)-H]497.1153 [(GluA-rha)-H]339.0927 [(GluA-rha)-H_2O-H]321.0798 [rha-H]163.0576 [xyl-H_2O]113.0218	uralsaponin X	GU	saponins
126	26.757	$C_{34}H_{40}O_{15}$	-H	687.2285	1.37	[M-H-rha(2-1)rha-CO]367.1180 [M-H-rha(2-1)rha-CH_3-CO]352.0945 [M-H-rha(2-1)rha-CH_3-CO]351.0872 [M-H-rha(2-1)rha-CH_3-2CO]323.0924	icariside Ⅱ-xyl(OAc)	EB	flavonoids

127	26.773	$C_{35}H_{40}O_{16}$	+HCOO	761.2285	1.87	[M-H-furan acid]571.1806 [M-H-furan acid-$C_2H_2O_2$]513.1747 [M-H-furan acid-glc]409.1284 [M-H-furan acid-glc-$C_2H_2O_2$]367.1177 [M-H-furan acid-glc-$C_2H_2O_2$-O]351.0877 [M-H-furan acid-glc-$C_2H_2O_2$-COO]323.0931	icaritin+C2H2O+furan acid+glc	EB	flavonoids
128	26.791	$C_{50}H_{82}O_{22}$	-H	1033.5198	2.03	[M-H-xyl]901.4734 [M-H-xyl-glc]739.4270 [M-H-xyl-2glc]577.3646	asparagoside F	AC	saponins
129	26.816	$C_{42}H_{72}O_{14}$	+HCOO	845.4905	-0.71	[M-H-glc]637.4258 [M-H-2glc]475.3792 [M-H-2glc-C_6H_{12}]391.2812 [2glc-H-$C_4H_8O_4$]221.0689	ginsenoside Rf*	PG	saponins
130	26.822	$C_{39}H_{48}O_{19}$	-H	819.2702	1.18	[M-H-glc]657.219 [M-H-glc-H2O]639.2058 [M-H-rha-furan acid]529.1701 [M-H-glc-furan acid]513.1772 [M-H-rha-furan acid-glc]367.1180 [M-H-rha-furan acid-glc-CH_2]352.0943 [M-H-rha-furan acid-glc-CH_3]351.0886 [M-H-rha-furan acid-glc-CH_3-CO]323.0909	anhydroicaritin-3-O-rhamnodide(1-2)-furan acid-7-O-glucoside	EB	flavonoids
131	26.930	$C_{42}H_{72}O_{14}$	+HCOO	845.4905	-0.71	[M-H-rha]653.4365 [M-H-rha-glc]491.3800	pseudo-ginsenoside F_{11}	PG	saponins
132	26.955	$C_{11}H_7O_3$	+H	187.0397	3.74	[M+H-CO]159.0447 [M+H-COO]143.0496 [M+H-2CO]131.0497 [M+H-CO-COO]115.0547	psoralen*	PC	others
133	26.988	$C_{50}H_{82}O_{22}$	-H	1033.5214	2.03	[M-H-xyl]901.4734 [M-H-xyl-glc]739.4270 [M-H-xyl-2glc]577.3646	asparagoside F	AC	saponins

134	27.129	$C_{51}H_{84}O_{22}$	+HCOO	1093.5405	2.83	[M-H]1047.5366 [M-H-rha]901.4767 [M-H-glc]885.4818 [M-H-glc-rha]739.4250 [M-H-glc-2rha]577.3732	asparasaponin I	PG/AC	saponins
135	27.269	$C_{48}H_{74}O_{20}$	-H	969.4692	0.21	[M-H-H_2O]951.4542 [M-H-H_2O-COO]907.4683 [M-H-rha]823.3719 [M-H-rha-GluA]647.3920 [(2GluA-rha)-H]497.1158 [(2GluA-rha)-H-H_2O-]435.1133 [(GluA-rha)-H]339.0955 [(GluA-rha)-H-H_2O]321.0841	licoricesaponin J2+rha	GU	saponins
136	27.372	$C_{45}H_{74}O_{18}$	+HCOO	947.4832	2.64	[M-H]901.48 [M-glc-H]739.429 [M-2glc-H]577.3702	shatavarin IX	AC	saponins
137	27.536	$C_{44}H_{64}O_{18}$	-H	879.401	1.12	[2GluA-H_2O]351.0571 [GluA-H]193.0356 [GluA-COOH-H_2O]113.0208	licoricesaponin E2+COO+O	GU	saponins
138	27.663	$C_{20}H_{18}O_6$	+H	355.1174	0.61	[M+H-CO]337.1068 [M+H-C_4H_8O]283.0597 [M+H-C_4H_8O-CO-CO_2]211.0391 [M+H-$C_{11}H_{14}O_3$]161.0236 [M+H-$C_{12}H_{14}O_3$]149.0240	erythrinin C	PC	flavonoids
139	27.693	$C_{11}H_7O_3$	+H	187.0398	4.28	[M+H-CO]159.0437 [M+H-COO]143.0493 [M+H-2CO]131.0497 [M+H-CO-COO]115.0546	isopsoralen*	PC	others
140	27.740	$C_{41}H_{70}O_{13}$	+HCOO	815.4791	3.50	[M-H-xyl]637.4279 [M-H-xyl-glc]475.3779 [M-H-xyl-glc-H_2O]391.2823	notoginsenoside-R2	PG	saponins

141	27.847	$C_{58}H_{98}O_{26}$	-H	1209.6257	0.50	[M-H-xyl]1077.5767 [M-H-glc]1047.5662 [M-H-xyl-ara]945.5800 [M-H-xyl-glc]915.5544 [M-H-xyl-ara-glc]783.4742 [M-H-xyl-ara-2glc]621.4344 [M-H-xyl-ara-glc]459.3873	ginsenoside Ra2	PG	saponins
142	27.992	$C_{59}H_{100}O_{27}$	-H	1239.6368	0.48	[M-H-xyl]1107.6053 [M-H-glc]1077.5989 [M-H-xyl-glc]945.5400 [M-H-xyl-2glc]783.4747 [M-H-xyl-3glc]621.4548 [M-H-xyl-4glc]459.3822 [(2glc-xyl)-H]455.1296 [(glc-xyl)-H-$C_4H_8O_4$]191.0536 [glc-H]161.0449	ginsenoside Ra3	PG	saponins
143	28.080	$C_{54}H_{92}O_{23}$	-H	1107.5931	1.81	[M-H-glc]945.5292 [M-H-2glc]783.4892 [M-H-3glc]621.4330 [M-H-4glc]459.3786 [2glc-H-$C_4H_8O_4$]221.0672	ginsenoside Rb1*	PG	saponins
144	28.242	$C_{53}H_{82}O_{25}$	-H	1117.5038	3.042486	[M-H-$C_5H_6O_6$]955.4906 [M-H-$C_5H_6O_6$-glc]793.4349 [M-H-$C_5H_6O_6$-2glc]613.3726 [M-H-$C_5H_6O_6$-2glc-COOH]569.3801 [M-H-$C_5H_6O_6$-2glc-COOH-xyl]455.3518	achyranthoside D	AB	saponins
145	28.331	$C_{51}H_{82}O_{21}$	+HCOO	1075.5321	0.37	[M-H-rha]883.4733 [M-H-2rha]737.4191 [M-H-2rha-glc]575.3458	oligofurostanoside A	AC	saponins

146	28.363	$C_{41}H_{70}O_{13}$	+HCOO	815.4792	2.38	[M-H-ara(f)]637.4438 [M-H-ara(f)-glc]475.3759 [M-H-ara(f)-glc-C_6H_{12}]391.2945	ginsenoside F5	PG	saponins
147	28.443	$C_{42}H_{72}O_{13}$	+HCOO	829.4956	-0.84	[M-H-rha]637.4286 [M-H-rha-H_2O]619.4304 [M-H-rha-glc]475.3783 [M-H-rha-glc-C_6H_{12}]391.2824	ginsenoside Rg2*	PG	saponins
148	28.566	$C_{15}H_{10}O_6$	+H	287.0541	0.00	[M-H-CO]257.0426 [M-H-CO-H_2O]239.0350 [M-H-2CO]229.0476 [M-H-2CO-H_2O]211.0392 [M-H-3CO-H_2O]183.0404	kaempferol*	EU/EC	flavonoids
149	28.634	$C_{53}H_{90}O_{22}$	+HCOO	1123.5898	0.27	[M-H-ara(f)]945.5590 [M-H-glc]915.5355 [M-H-ara-glc]783.4892 [M-H-ara-glc-H_2O]765.4685 [M-H-ara-2glc]621.4295 [M-H-ara-3glc]459.3806 [2glc-H-$C_4H_8O_4$]221.0655 [(glc-ara)-H-$C_4H_8O_4$]191.0516 [glc-H]161.0457 [ara-h]131.0337	ginsenoside Rc*	PG	saponins
150	28.635	$C_{58}H_{98}O_{26}$	-H	1209.6268	-0.41	[M-H-xyl]1077.5789 [M-H-glc]1047.5684 [M-H-xyl-ara]945.5458 [M-H-xyl-glc]915.5389 [M-H-xyl-ara-glc]783.4892 [M-H-xyl-ara-2glc]621.4308 [M-H-xyl-ara-glc]459.3773	ginsenoside Ra1	PG	saponins

151	28.659	$C_{48}H_{74}O_{19}$	-H	953.4728	1.89	[M-H-H_2O]935.4668 [M-H-rha-glc-H_2O-2COOH]537.3459 [(2GluA-rha)-H]497.1143 [(GluA-rha)-H]339.0944 [(GluA-rha)-H-H_2O]321.0819	licoricesaponin C2+rha+2H	GU	saponins
152	28.702	$C_{36}H_{62}O_9$	+HCOO	683.4368	0.44	[M-H-glc]475.3826 [M-H-glc-C_6H_{12}]391.2880	ginsenoside F1	PG	saponins
153	28.708	$C_{48}H_{72}O_{19}$	-H	951.4602	1.26	[M-H-H_2O]933.4532 [M-H-rha]805.4003 [M-H-rha-H_2O-COOH]743.3967 [M-H-rha-glc-H_2O]625.3383 [M-H-rha-glc-H_2O-2COOH]535.3436 [(2GluA-rha)-H]497.1196 [M-H-rha-glc-H_2O-GluA]465.3016 [(GluA-rha)-H-H_2O]321.0816	licoricesaponin C2+rha	GU	saponins
154	28.803	$C_{20}H_{20}O_5$	+H	341.1382	0.59	[M+H-H_2O]323.1298 [M+H-H_2O-C_4H_6]269.0775 [M+H-2H_2O-C_4H_6]251.0708 [M+H-C_8H_8O]221.0788 [M+H-C_8H_8O-H_2O]203.0695 [M+H-C_8H_8O-H_2O-C_4H_6]149.0228 [M-$C_{11}H_{13}O_3$]147.0440 [M+H-C_8H_8O-H_2O-C_4H_6-CO]121.0275 [M-$C_{11}H_{13}O_3$-CO]119.0480	brosimacutin E brosimacutin D	PC	flavonoids
155	28.903	$C_{27}H_{30}O_{11}$	-H	529.171	1.01	[M-H-rha]383.1130 [M-H-rha-C_5H_{11}]312.0634 [M-H-rha-C_4H_7-OCH_3]297.0402 [M-H-rha-C_4H_7-OCH_3-CO]269.0449	caohuoside C	EB	flavonoids

156	28.909	$C_{20}H_{20}O_5$	+H	341.1380	1.17	[M+H-H_2O]323.1296 [M+H-H_2O-C_4H_6]269.0774 [M+H-2H_2O-C_4H_6]251.0706 [M+H-C_8H_8O]221.0787 [M+H-C_8H_8O-H_2O]203.0694 [M+H-C_8H_8O-H_2O-C_4H_6]149.0227 [M-$C_{11}H_{13}O_3$]147.0444 [M+H-C_8H_8O-H_2O-C_4H_6-CO]121.0270 [M-$C_{11}H_{13}O_3$-CO]119.0481	brosimacutin E brosimacutin D	PC	flavonoids
157	29.015	$C_{45}H_{74}O_{17}$	-H	885.4837	1.81	[M-H-rha]739.4236 [M-H-rha-glc]577.3783	asparanin B	AC	saponins
158	29.069	$C_{16}H_{12}O_7$	+H	317.0658	2.52	[M-CH_3]300.0280 [M-H-CH_3-CO]271.0228 [M-CH_3-2CO-OH]227.0356 [M-$C_8H_8O_3$]164.0092 [M-$C_8H_8O_4$]148.0135	isorhamnetin*	EC	flavonoids
159	29.087	$C_{48}H_{76}O_{19}$	-H	955.4895	0.837266	[M-H-glc]793.4376 [M--H-glc-COOH-H_2O]731.4369 [M-H-2glc]613.3748 [M-H-2glc-COOH]569.3832 [M-H-2glc-2COOH]523.3776 [M-H-2glc-xyl-COOH]455.3528	ginsenoside Ro*	PG/AB	saponins
160	28.919	$C_{53}H_{90}O_{22}$	+HCOO	1123.5906	-0.45	[M-H-ara(p)]945.5380 [M-H-glc]915.5237 [M-H-ara(p)-glc]783.4878 [M-H-ara(p)-glc-H_2O]765.4806 [M-H-ara(p)-2glc]621.4304 [M-H-ara(p)-3glc]459.3796 [M-H-ara(p)-3glc-C_6H_{12}]375.2900 [2glc-H-$C_4H_8O_4$]221.0661 [(glc-ara)-H-$C_4H_8O_4$]191.0554	ginsenoside Rb2*	PG	saponins

						[glc-H]161.0457 [ara-H]131.0336			
161	29.126	$C_{20}H_{18}O_5$	+H	339.1228	-0.29	[M+H-H_2O]321.1131 [M+H-H_2O-C_3H_6]279.0653 [M+H-C_4H_8O]267.0655 [M+H-C_4H_8O-CO]239.0680 [M+H-C_4H_8O-2CO]211.0819 [M+H-C_4H_8O-3CO]183.0805 [M+H-C_4H_8O-3CO-H_2O]165.0697 [M+H-$C_{13}H_{14}O_2$]137.0223	psoralenol	PC	flavonoids
162	29.397	$C_{53}H_{90}O_{22}$	+HCOO	1123.5903	-0.18	[M-H-xyl]945.5320 [M-H-glc]915.5317 [M-H-xyl-glc]783.4809 [M-H-xyl-glc-H2O]765.4724 [M-H-xyl-2glc]621.4298 [M-H-xyl-3glc]459.3826 [M-H-xyl-3glc-C_6H_{12}]375.2808	ginsenoside Rb3*	PG	saponins
163	29.483	$C_{27}H_{30}O_{11}$	-H	529.1711	0.82	[M-H-rha]383.1134 [M-H-rha-CH_3]368.0912 [M-H-rha-C_5H_{11}]312.0629 [M-H-rha-C_4H_7-OCH_3]297.0398 [M-H-rha-C_4H_7-OCH_3-CO]269.0451	anhydroicaritin-3'-OH-7-*O*-rhamnose	EB	flavonoids

164	29.607	$C_{42}H_{62}O_{17}$	-H	837.3907	0.835929	[M-GluA]661.3500 [M-2GluA]485.3150 [2GluA-H_2O]351.0533 [GluA-H]193.0348 [GluA-COOH-H_2O]113.0236	licoricesaponin G2	GU	saponins
165	29.616	$C_{16}H_{12}O_6$	+H	301.0705	3.99	[M-H-CH_3]284.0309 [M-H-CH_3-CO]255.0284 [M-H-CH_3-2CO]227.0367 [M-H-CH_3-3CO199.0380	kaempferide	EC	flavonoids
166	29.672	$C_{50}H_{76}O_{21}$	-H	1011.4771	3.460274	[(2GluA-rha)-H]497.109 [(GluA-rha)-H]339.0973 [(GluA-rha)-H_2O-H]321.0869 [xyl-H_2O]113.0245	licoricesaponin D3	GU	saponins
167	29.793	$C_{42}H_{60}O_{16}$	-H	819.3787	2.684954	[2GluA-H_2O]351.0541 [GluA-H]193.0329 [GluA-COOH-H_2O]113.0216	licoricesaponin E2	GU	saponins
168	29.8	$C_{56}H_{94}O_{24}$	+HCOO	1195.6125	-1.09	[M-H-Acetyl]1107.5973 [M-H-Acetyl-H_2O]1089.5854 [M-H-Acetyl-glc]945.5294 [M-H-Acetyl-2glc]783.4822 [M-H-Acetyl-2glc-H_2O]765.4799 [M-H-Acetyl-3glc]621.4253 [M-H-Acetyl-4glc]459.3896	acetyl-ginsenoside Rb1	PG	saponins
169	29.859	$C_{48}H_{72}O_{20}$	-H	967.4532	1.240369	[M-H-rha-gluA]645.3467 [2gluA-rha-H]497.1129 [2gluA-rha-H]339.0944	yunganoside L1	GU	saponins

170	29.937	$C_{47}H_{74}O_{18}$	-H	925.4791	1.188572	[M-H-glc]763.4275 [M-H-glc-COOH]719.4517 [M-H-glc-COOH-H2O]701.4286 [M-H-glc-ara]629.3989 [M-H-glc-ara-O]613.3823 [M-H-glc-ara-O-COOH]570.3914 [M-H-glc-ara-O-COOH-xyl]455.3452	chikusetsusaponin IV	AB	saponins
171	29.994	$C_{44}H_{64}O_{17}$	-H	863.4056	1.71	[M-H-COO]819.4060 [M-H-H_2O-COO]801.4058 [M-H-GluA]687.3737 [2GluA-H_2O]351.0571 [GluA-H]193.0356 [GluA-COOH-H_2O]113.0208	licoricesaponin E2+COO	GU	saponins
172	30.257	$C_{36}H_{62}O_9$	+HCOO	683.4357	2.05	[M-H-glc]475.3749	ginsenoside Rh1*	PG	saponins
173	30.385	$C_{20}H_{18}O_6$	+H	355.1071	1.45	[M+H-C_4H_8]299.0519 [M+H-$C_9H_9O_4$]173.0541 [M+H-C_4H_8-$C_9H_6O_4$]121.0255	desmethylicaritin	EB	flavonoids
174	30.447	$C_{26}H_{28}O_{10}$	-H	499.1608	0.400672	[M-rha]353.1031 [M-H-rha-H]352.0958	baohuoside Ⅱ	EB	flavonoids
175	30.47	$C_{48}H_{82}O_{18}$	+HCOO	991.5470	0.81	[M-H-glc]783.4828 [M-H-2glc]621.4426 [M-H-3glc]459.3837 [M-H-3glc-C_6H_{12}]375.2908	ginsenoside Rd*	PG	saponins
176	30.561	$C_{27}H_{30}O_{11}$	-H	529.1699	3.08	[M-H-glc]367.1185 [M-H-glc-CO]339.0859	icariside I	EB	flavonoids
177	30.601	$C_{15}H_{12}O_4$	-H	255.0658	1.96	[M-H-C_8H_7O]135.0079 [M-H-$C_7H_3O_3$]119.0498 [M-H-C_8H_7O]91.0174	isoliquiritigenin*	GU	flavonoids
178	30.859	$C_{16}H_{12}O_4$	+H	269.0809	-1.85	[M-CH_3]253.0503 [M-CH_2-CO]226.0601	formonontin*	GU	flavonoids

						[M-CH_3-2CO]197.0575			
179	30.912	$C_{42}H_{66}O_{14}$	-H	793.4358	2.772743	[M-H-glc]631.3844 [M-H-glc-H_2O]613.3764 [M-H-glc-CO_2-H_2O]569.3856 [M-H-glc-GluA]455.3528	chikusetsusaponin IVa	AB	saponins
180	31.031	$C_{55}H_{92}O_{23}$	+HCOO	1165.5996	0.89	[M-H-Acetyl]1077.5825 [M-H-Acetyl-xyl]945.5439 [M-H-Acetyl-glc]915.5369 [M-H-Acetyl-glc-xyl]783.4821 [M-H-Acetyl-2glc-xyl]621.4202 [M-H-Acetyl-3glc-xyl]459.3882	ginsenoside Rs2 ginsenoside Rs1	PG	saponins
181	31.031	$C_{17}H_{12}O_8$	+H	345.0605	0.00	[M+H-CH_3]330.0359 [M+H-CH_3OH]313.032	3,3',4'-trimethylellagic acid	EC	others
182	31.49	$C_{48}H_{82}O_{18}$	+HCOO	991.5479	-0.10	[M-H-glc]783.5014 [M-H-2glc]621.4474 [M-H-3glc]459.4002	gypenoside XVII*	PG	saponins
183	31.815	$C_{33}H_{40}O_{15}$	-H	675.2294	0	[M-rha(2-1)glc]367.1177 [M-H-rha(2-1)glc]366.1114 [M-H-rha(2-1)glc-CH_3]351.0876 [M-rha(2-1)glc-CH_3]352.0927 [M-H-rha(2-1)glc-CH_3-CO]323.0920	sagittatosideA	EB	flavonoids
184	31.904	$C_{16}H_{12}O_7$	+H	317.0653	4.10	[M-CH_3]300.0229 [M-H-$C_8H_6O_3$]165.0191 [M-H-$C_8H_6O_4$]149.0221 [M-H-$C_8H_6O_4$-CO]121.0283	rhamnetin	EC	flavonoids
185	31.922	$C_{42}H_{62}O_{16}$	-H	821.3948	1.46	[M-H-CO_2-H_2O]759.3976 [M-H-GluA]645.3641 [M-H-2GluA]469.3331 [2GluA-H-H_2O]351.0569	glycyrrhizic acid*	GU	saponins

						[GluA-H]193.0353 [GluA-H-CO_2-H_2O]113.0243			
186	32.351	$C_{47}H_{80}O_{17}$	+HCOO	961.5348	2.60	[M-H-ara]783.4910 [M-H-ara-glc]621.4313 [M-H-ara-2glc]459.3711	notoginsenoside Fe*	PG	saponins
187	32.499	$C_{27}H_{30}O_{11}$	-H	529.1725	-1.82	[M-H-glc]367.1168 [M-H-glc-H]366.1110 [M-H-glc-H-CH_3]351.0889 [M-H-glc-H-CH_3-CO]323.0929	anhydroicaritin-3-*O*-glucoside	EB	flavonoids
188	32.78	$C_{32}H_{38}O_{14}$	-H	645.2167	3.409696	[M-rha(2-1)xyl]367.1169 [M-H-rha(2-1)xyl]366.1095 [M-H-rha(2-1)xyl-CH_3]351.0864 [M-H-rha(2-1)xyl-CH_3-CO]323.0908	sagittatoside B*	EB	flavonoids
189	32.945	$C_{33}H_{40}O_{14}$	-H	659.233	2.275366	[M-rha(2-1)rha]367.1172 [M-H-rha(2-1)rha-CH_3]351.0860 [M-H-rha(2-1)rha-CH_3-CO]323.0909	2"-*O*-rhamnosylikariside Ⅱ	EB	flavonoids
190	33.134	$C_{47}H_{80}O_{17}$	+HCOO	961.5375	-0.21	[M-H-xyl]783.4910 [M-H-xyl-glc]621.4313 [M-H-xyl-2glc]459.3711	ginsenoside compound O	PG	saponins
191	33.221	$C_{17}H_{12}O_4$	+H	281.0801	2.63	[M+H-H_2O]263.0696 [M+H-H_2O-CO]235.0738 [M+H-C_8H_9O]161.0238 [M+H-C_8H_6O-OH]147.0447 [C_8H_7O]119.0497	3-methylflavone-8-carboxylic acid	PC	flavone
192	33.525	$C_{42}H_{64}O_{16}$	-H	823.4084	4.614943	[2GluA-H_2O]351.0577 [GluA-H]193.0330 [GluA-COOH-H_2O]113.0229	licoricesaponin J2	GU	saponins
193	33.96	$C_{42}H_{70}O_{12}$	+HCOO	811.4823	2.59	[M-H-rha]619.4182 [M-H-rha-glc]457.3578	ginsenoside Rg4	PG	saponins

194	34.121	$C_{20}H_{20}O_4$	+H	325.1441	-1.85	[M-C_4H_7]269.0819 [M+H-C_8H_8O]205.0866 [M-C_8H_8O-C_4H_7]149.0241 [M-C_8H_8O-C_4H_7-H_2O]131.0132 [M-C_8H_8O-C_4H_7-CO]121.0284 [M-$C_{12}H_{13}O_3$]119.0491	bavachin	PC	flavonoids
195	34.316	$C_{42}H_{62}O_{15}$	-H	805.3993	2.855718	[2GluA-H_2O]351.0543 [GluA-H]193.0364 [GluA-COOH-H_2O]113.0225	licoricesaponin C2	GU	saponins
196	34.423	$C_{42}H_{70}O_{12}$	+HCOO	811.4839	0.62	[M-H-rha]619.4196 [M-H-rha-glc]457.3526	ginsenoside Rg6*	PG	saponins
197	34.635	$C_{20}H_{20}O_5$	+H	341.1392	-2.35	[M+H-H_2O]323.1286 [M+H-H_2O-C_4H_6]269.0827 [M+H-C_8H_8O]221.0811 [M+H-C_8H_8O-H_2O]203.0697 [M+H-C_8H_8O-H_2O-C_4H_6]149.0243 [M-$C_{11}H_{13}O_3$]147.0437 [M-$C_{11}H_{13}O_3$-CO]119.0506	bavachromanol	PC	flavonoids
198	34.798	$C_{42}H_{64}O_{15}$	-H	807.4152	2.477034	[M-H-CO2-H2O]745.4140 [M-H-GluA]631.3826 [M-H-2GluA]455.3484 [2GluA-H-H_2O]351.0564 [2GluA-H-H_2O-CO_2]289.0572 [GluA-H]193.0350 [GluA-H-CO_2-H_2O]113.0244	licoricesaponin B2	GU	saponins
199	34.836	$C_{27}H_{30}O_{10}$	-H	513.1759	1.364053	[M-H-rha]367.1161 [M-H-rha-H]366.1114 [M-H-rha-CH_2]352.0934 [M-H-rha-CH_3]351.0868 [M-H-rha-CH_3-CO]323.0917 [M-H-rha-CH_3-CO-CO_2]279.0297	icariside Ⅱ	EB	flavonoids

200	34.901	$C_{42}H_{72}O_{13}$	+HCOO	829.4932	2.17	[M-H-glc]621.4340 [M-H-2glc]459.3979	ginsenoside F2*	PG	saponins
201	34.935	$C_{36}H_{60}O_8$	+HCOO	665.4261	0.60	[M-H-glc]457.3620	ginsenoside Rk3*	PG	saponins
202	35.324	$C_{33}H_{38}O_{14}$	-H	657.2181	1.18	[M-H-furan acid]513.1769 [M-H-furan acid-rha]367.1177 [M-H-furan acid-rha-H]366.1114 [M-H-furan acid-rha-CH_2]352.0934 [M-H-furan acid-rha-CH_3]351.0871 [M-H-furan acid-rha-CH_3-CO]323.0913 [M-H-furan acid-rha-CH_3-CO-CO_2]279.0289	anhydroicaritin-3-*O*-rhamnose(1-2)-furan acid	EB	flavonoids
203	35.507	$C_{16}H_{12}O_6$	+H	301.071	2.33	[M-H-CH_3]284.0303 [M-H-CO]271.0608 [M-H-CH_3-CO]256.0384 [M-OH-CO]255.0691 [M-H-2CO]243.0630 [M-H-2CO-CH_3OH]211.0365 [M-H-$C_8H_6O_2$]165.0192 [M-H-$C_8H_6O_4$]133.0241	rhamnocitrin	EC	flavonoids
204	35.52	$C_{36}H_{60}O_8$	+HCOO	665.4268	-0.45	[M-H-glc]457.3911	ginsenoside Rh4*	PG	saponins
205	35.573	$C_{48}H_{76}O_{19}$	-H	955.4519	0.837266	[M-H-CO2-$CH_2OHCOOH$]835.4471 [M-H-glc]793.4376 [M--H-glc-COOH-H_2O]731.4369 [M-H-2glc]613.3748 [M-2glc-COOH]569.3832 [M-2glc-2COOH]523.3776 [M-2glc-xyl-COOH]455.3528	achyranthoside C	AB	saponins
206	35.675	$C_{20}H_{18}O_4$	+H	323.1284	-1.86	[M-C_4H_7]267.0650 [M+H-C_5H_8]255.0651 [M-C_4H_7-CO]239.0702 [M-C_4H_7-2CO]211.0754 [M+H-$C_{13}H_{14}O$]137.0240	neobavaisoflavone*	PC	flavonoids

207	35.87	$C_{42}H_{66}O_{14}$	-H	793.4358	2.772743	[M-H-glc]631.3877 [M-H-glc-H_2O]613.3784 [M-H-glc-CO_2-H_2O]569.3820 [M-H-glc-GluA]455.3516	zingibroside R1	PG/AB	saponins
208	35.880	$C_{21}H_{20}O_6$	+H	369.1334	-0.27	[M-C_4H_7]313.0693 [M-C_5H_{10}]298.0472 [M-C_4H_7-CO]285.0757 [M-C_5H_{10}-CO]270.0510 [M-C_4H_7-CO-CH_2O]255.0635 [M+H-C_5H_{10}-2CO]243.0657 [M-C_4H_7-2CO-CH_2O]227.0703	glycycoumarin	GU	others
209	36.299	$C_{45}H_{72}O_{16}$	+HCOO	913.4806	0.99	[M-H]867.471 [M-H-rha]721.4117 [M-H-2rha]575.3643	astragaloside I	AC	saponins
210	36.514	$C_{20}H_{16}O_6$	+H	353.1026	-1.70	[M+H-H_2O]335.0836 [M+H-$C_{13}H_{12}O_2$]153.0176	licoisoflavone B	GU	flavonoids
211	36.796	$C_{42}H_{72}O_{13}$	+HCOO	829.4946	0.48	[M-H-glc]621.4327 [M-H-2glc]459.3844 [M-H-2glc-C_6H_{12}]375.2900	20-S-ginsenoside-Rg3*	PG	saponins
212	36.831	$C_{20}H_{20}O_4$	+H	325.1442	-2.15	[M-C_4H_7]269.0803 [M+H-C_8H_8O]205.0858 [M-C_8H_8O-C_4H_7]149.0237 [M-$C_{11}H_{13}O_2$]147.0445 [M-C_8H_8O-C_4H_7-CO]121.0286 [M-$C_{12}H_{13}O_3$]119.0495 [M-C_8H_8O-C_4H_7-$_2$CO]93.0342 [M-$C_{12}H_{13}O_3$-CO]91.0551	bavachalcone	PC	flavonoids
213	37.164	$C_{42}H_{72}O_{13}$	+HCOO	829.4946	0.48	[M-H-glc]621.4357 [M-H-2glc]459.3919 [M-H-2glc-C_6H_{12}]375.2813	20-R-ginsenoside-Rg3*	PG	saponins

214	38.174	$C_{22}H_{22}O_6$	+H	383.1489	0.04	[M+H-C_4H_8]327.0865 [M+H-C_4H_8-CO]299.0914 [M+H-C_4H_8-CO-CH_3]284.0675 [M+H-C_4H_8-CH_2O]269.0448	glycyrin	GU	others
215	38.518	$C_{41}H_{70}O_{12}$	+HCOO	799.4818	3.25	[M-H-ara]621.4313 [M-H-ara-glc]459.3876 [M-H-ara-glc-C_6H_{12}]375.2968	ginsenoside Mc	PG	saponins
216	38.541	$C_{22}H_{46}NO_7P$	+H	468.3085	1.07	[M+H-H_2O]450.2977 [P-Ch]184.0735 [P-Ch-H_2O]166.0634 [P-Ch-C_3H_9N]125.0004 [P-Ch-HPO_3]104.1046 [P-Ch-HPO_3-H_2O]86.0995	2-tetradecanoyl-*sn*-glycerol -3-phosphocholine	CE/HK CN/QN	lyso-GPCs
217	38.643	$C_{20}H_{16}O_4$	+H	321.1128	-1.87	[M-CH_3]305.0808 [M+H-CH_3-C_2H_4]279.0649 [M+H-CH_3-C_2H_4-CO]251.0697 [M+H-CH_3-C_2H_4-$_2$CO]223.0754 [M-$C_6H_5O_2$]211.0743 [M-$C_7H_5O_3$]183.0807 [M-$C_7H_5O_3$-H_2O]165.0700 [M+H-$C_{13}H_{12}O$]137.0243	corylin*	PC	flavonoids
218	39.015	$C_{41}H_{70}O_{12}$	+HCOO	799.4838	0.75	[M-H-xyl]621.4258 [M-H-xyl-glc]459.3916	ginsenoside compound Y	PG	saponins
219	39.167	$C_{20}H_{18}O_4$	+H	323.1280	-0.62	[M-C_8H_7O]203.0705 [M-$C_9H_7O_2$]175.0758 [M-$C_{11}H_{11}O_2$]147.0443 [M-$C_{12}H_{11}O_3$]119.0493 [M-$C_{12}H_{11}O_3$-CO]91.0548	bavachromene isobavachromene	PC	flavonoids

220	39.608	$C_{20}H_{20}O_4$	+H	325.1437	-0.62	[M-C_4H_7]269.0813 [M+H-C_8H_8O]205.0856 [M-C_8H_8O-C_4H_7]149.0239 [M-$C_{11}H_{13}O_2$]147.0442 [M-C_8H_8O-C_4H_7-CO]121.0284 [M-$C_{12}H_{13}O_3$]119.0492 [M-C_8H_8O-C_4H_7-2CO]93.0339 [M-$C_{12}H_{13}O_3$-CO]91.0547	isobavachalcone	PC	flavonoids
221	39.919	$C_{20}H_{16}O_5$	+H	337.1070	0.30	[M+H-CO]309.1115 [M-C_4H_7]281.0444 [M-C_4H_7-CO]253.0496 [M-C_4H_7-2CO]225.0545 [M+H-C_4H_7-2CO-OH]209.0591 [M-C_4H_7-3CO]197.0596 [M+H-C_4H_7-3CO-OH]181.0653 [M-C_4H_7-4CO]169.0648	psoralidin*	PC	others
222	39.999	$C_{24}H_{48}NO_7P$	+H	494.3240	0.20	[M+H-H_2O]476.3098 [P-Ch]184.0730 [P-Ch-H_2O]166.0613 [P-Ch-C_3H_9N]125.0008 [P-Ch-HPO_3]104.1084 [P-Ch-HPO_3-H_2O]86.0977	1-[(9Z)-hexadecenoyl]-*sn*-glycero-3-phosphocholine	CE/HK CN/QN	lyso-GPCs
223	40.885	$C_{23}H_{48}NO_7P$	+H	482.3228	2.73	[P-Ch]184.0735 [P-Ch-H_2O]166.0635 [P-Ch-C_3H_9N]125.0002 [P-Ch-HPO_3]104.1054 [P-Ch-HPO_3-H_2O]86.0960	1-pentadecanoyl-*sn*-glycero-3-phosphocholine	CE/HK CN/QN	lyso-GPCs
224	41.090	$C_{20}H_{18}O_6$	-H	353.1027	0.85	[M-CHO_2]308.1060	(-)-asarinin*	XX	others

225	41.645	$C_{25}H_{24}O_5$	+H	405.1689	1.86	[M+H-C_4H_8-CH_2O]319.0966 [M+H-C_4H_7-C_4H_7O]279.0651 [M+H-C_4H_7-C_4H_7O-H_2O]251.0691 [M+H-C_4H_7-C_4H_7O-H_2O-CO]223.0750 [$C_7H_4O_3$]137.0239	osajin	PC	flavonoids
226	41.714	$C_{42}H_{70}O_{12}$	+HCOO	811.4836	0.99	[M-H-glc]603.4244 [M-H-2glc]441.3729	ginsenoside Rk1*	PG	saponins
227	41.761	$C_{26}H_{50}NO_7P$	+H	520.3414	1.54	[M+H-H_2O]502.3297 [M-P-Ch]337.2722 [P-Ch]184.0741 [P-Ch-H_2O]166.0639 [P-Ch-C_3H_9N]125.0002 [P-Ch-HPO_3]104.1072 [P-Ch-HPO_3-H_2O]86.0965	1-linoleoyl-*sn*-glycerol -3-phosphocholine	CE/HK CN/QN	lyso-GPCs
228	42.251	$C_{42}H_{70}O_{12}$	+HCOO	811.4844	0.00	[M-H-glc]603.4263 [M-H-2glc]441.3733	ginsenoside Rg5	PG	saponins
229	42.750	$C_{20}H_{20}O_4$	+H	325.1436	-0.31	[M-C_4H_7]269.0809 [M+H-C_8H_8O]205.0859 [M-C_8H_8O-C_4H_7]149.0242 [M-C_8H_8O-C_4H_7-H_2O]131.0131 [M-C_8H_8O-C_4H_7-CO]121.0288 [M-$C_{12}H_{13}O_3$]119.0459	isobavachin	PC	flavonoids
230	42.972	$C_{18}H_{24}O_2$	+H	273.1848	0.38	[M-C8H15]161.0951 [M+H-C11H20]121.0664 [M+H-C11H20-CH2]107.0493	3-hydroxybakuchiol	PC	others
231	43.452	$C_{24}H_{50}NO_6P$	+H	480.3445	1.87	[P-Ch]184.0741 [P-Ch-H_2O]166.0634 [P-Ch-C_3H_9N]125.0002 [P-Ch-HPO_3]104.1071 [P-Ch-HPO_3-H_2O]86.0966	1-(1Z-hexadecenyl)-*sn*- glycerol -3-phosphocholine	CE/HK CN/QN	lyso-GPCs

232	43.541	$C_{24}H_{50}NO_7P$	+H	496.3394	0.81	[M+H-H2O]478.3302 [M-P-Ch]313.2742 [M+H-C16H30O]258.1097 [P-Ch]184.0744 [P-Ch-H_2O]166.0631 [P-Ch-C_3H_9N]125.0004 [P-Ch-HPO_3]104.1072 [P-Ch-HPO_3-H_2O]86.0966	1-hexadecanoyl-*sn*-glycerol -3-phosphocholine	CE/HK CN/QN	lyso-GPCs
233	43.726	$C_{21}H_{22}O_4$	+H	339.1600	-2.65	[M-C_4H_7]283.0961 [M+H-C_5H_8]271.0962 [M-C_8H_7O]219.1015 [M-C_8H_7O-CH_2-C_4H_6]151.0396 [M-$C_{12}H_{15}O_2$]147.0447 [M-$C_{13}H_{15}O_3$]119.0496 [M-$C_{13}H_{15}O_3$-CO]107.0497	bavachinin	PC	flavonoids
234	43.772	$C_{39}H_{64}O_{12}$	+HCOO	769.4369	0.65	[M-H]723.4327 [M-H-rha]577.3756 [M-H-rha-glc]415.3213 [glc-H]161.0454 [glc-H-H_2O]143.0349 [rha-H-H_2O-CH_2]113.0261 [glc-H-$C_2H_4O_2$]101.0235	sarsasapogenin-3-glucose-22-rhamnose	AC	saponins
235	44.277	$C_{36}H_{62}O_8$	+HCOO	667.4417	1.56	[M-H-glc]459.3910	ginsenoside Rh2*	PG	saponins
236	44.686	$C_{24}H_{52}NO_6P$	+H	482.3617	-1.45	[P-Ch]184.0735 [P-Ch-H_2O]166.0635 [P-Ch-C_3H_9N]125.0002 [P-Ch-HPO_3]104.1054 [P-Ch-HPO_3-H_2O]86.0960	1-*O*-hexadecyl-*sn*-glycerol -3-phosphocholine	CE/HK CN/QN	lyso-GPCs

237	44.910	$C_{25}H_{26}O_4$	+H	391.1911	-1.79	[M-C_4H_7]335.1287 [M-C_4H_7-CH_2]321.1134 [M-C_4H_7-CH_2-C_4H_6]267.0652 [M-C_9H_{15}-CO]239.0703 [M-C_9H_{15}-2CO]211.0748 [M-C_9H_{15}-3CO]183.0811 [M-C_9H_{15}-3CO-H2O]165.0710 [M+H-$C_{18}H_{22}O$]137.0240 [M-C_9H_{15}-C_9H_7O]131.0491	corylifol A*	PC	flavonoids
238	44.952	$C_{26}H_{52}NO_7P$	+H	522.3561	-1.34	[M+H-H_2O]504.3450 [M-P-Ch]339.2892 [P-Ch]184.0741 [P-Ch-H_2O]166.0634 [P-Ch-C_3H_9N]125.0002 [P-Ch-HPO_3]104.1071 [P-Ch-HPO_3-H_2O]86.0966	1-(9Z-octadecenoyl)-*sn*-glycerol -3-phosphocholine	CE/HK CN/QN	lyso-GPCs
239	45.071	$C_{18}H_{32}O_3$	-H	295.2266	4.06	[M-H-H_2O]277.2180 [M-$C_6H_{13}O$]195.1393	13-hode	AB	others
240	45.611	$C_{20}H_{18}O_4$	+H	323.1281	-0.93	[M-C_8H_7O]203.0701 [M-$C_9H_7O_2$]175.0767 [M-$C_{11}H_{11}O_2$]147.0453 [M-$C_{12}H_{11}O_3$]119.0491 [M-$C_{12}H_{11}O_3$-CO]91.0546	bavachromene isobavachromene	PC	flavonoids
241	45.842	$C_{21}H_{20}O_6$	+H	369.1335	-0.54	[M-C_4H_7]313.0710 [M-C_4H_7-CH_3]298.0446 [M-C_4H_7-CH_3-CO]270.0534 [M+H-C_4H_7-CH_3-2CO]243.0632 [M-C_4H_7-CH_3-$C_8H_5O_2$]165.0201	icaritin*	EB	flavonoids

242	46.854	$C_{20}H_{18}O_4$	+H	323.1277	0.31	[M-C_8H_7O]203.0705 [M-C_8H_7O-H_{20}]185.0603 [M-$C_9H_7O_2$]175.0401 [M-C_8H_7O-C_3H_6]161.0235 [M+H-C_4H_7]149.0239 [M-$C_{11}H_{11}O_2$]147.0440	chromenoflavanone	PC	flavonoids
243	48.18	$C_{26}H_{54}NO_7P$	+H	524.3718	-2.10	[M+H-H_2O]506.3625 [M-P-Ch]341.3047 [P-Ch]184.0741 [P-Ch-H_2O]166.0634 [P-Ch-C_3H_9N]125.0002 [P-Ch-HPO_3]104.1071 [P-Ch-HPO_3-H_2O]86.0966	1-octadecanoyl-*sn*-glycero-3-phosphocholine	CE/HK CN/QN	lyso-GPCs
244	48.301	$C_{21}H_{22}O_4$	+H	339.1599	-2.36	[M-C_4H_7]283.0959 [M+H-C_5H_8]271.0965 [M-C_8H_7O]219.1017 [M-C_8H_7O-CH_2-C_4H_6]151.0390 [M-$C_{12}H_{15}O_2$]147.0445 [M-$C_{13}H_{15}O_3$]119.0499 [M-$C_{13}H_{15}O_3$-CO]91.0545	4'-*O*-methylbavachalcone	PC	flavonoids
245	49.161	$C_{26}H_{54}NO_7P$	+H	524.3721	-2.10	[M+H-H_2O]506.3625 [M-P-Ch]341.3047 [P-Ch]184.0741 [P-Ch-H_2O]166.0634 [P-Ch-C_3H_9N]125.0002 [P-Ch-HPO_3]104.1071 [P-Ch-HPO_3-H_2O]86.0966	2-octadecanoyl-*sn*-glycero-3-phosphocholine	CE/HK CN/QN	lyso-GPCs

246	50.105	$C_{25}H_{24}O_4$	+H	389.1746	0.26	[M-C_4H_7]333.1127 [M+H-C_5H_8]321.1116 [M+H-C_6H_8]309.1116 [M-C_6H_{11}]305.0811 [M-C_6H_{11}-CH_2]291.0653 [M+H-C_6H_{11}-C_3H_3]267.0641 [M-C_6H_{11}-CH_2-CO]263.0705 [M+H-C_6H_{11}-C_3H_3-CO]239.0693 [M-$C_{18}H_{20}O$]137.0241	neocorylin	PC	flavonoids
247	50.301	$C_{36}H_{60}O_7$	+HCOO	649.4296	3.079616	[M-H-glc]441.3732	ginsenoside Rk2	PG	saponins
248	50.714	$C_{26}H_{56}NO_6P$	+H	510.3923	-0.78	[M+H-H_2O]492.3478 [M-P-Ch]327.2859 [P-Ch]184.0724 [P-Ch-H_2O]166.0598 [P-Ch-C_3H_9N]125.0006 [P-Ch-HPO_3]104.1062 [P-Ch-HPO_3-H_2O]86.0964	1-heptadecanoyl-*sn*-glycero -3-phosphocholine	CE/HK CN/QN	lyso-GPCs
249	50.975	$C_{36}H_{60}O_7$	+HCOO	649.4301	2.309712	[M-H-glc]441.3727	ginsenoside Rh3	PG	saponins
250	51.074	$C_{28}H_{58}NO_7P$	+H	552.4019	1.81	[M+H-H_2O]534.3951 [P-Ch]184.0722 [P-Ch-H_2O]166.0595 [P-Ch-C_3H_9N]125.0003 [P-Ch-HPO_3]104.1061 [P-Ch-HPO_3-H_2O]86.0963	2-*O*-acetyl-1-*O*-octadecyl-*sn*-glycerol -3-phosphocholine	CE/HK CN/QN	lyso-GPCs
251	52.557	$C_{18}H_{24}O$	+H	257.1900	0.00	[M-C_4H_7]201.1271 [M-C_5H_9]187.1124 [M-C_6H_{11}]173.0956 [M-C_6H_{11}-CH_2]159.0807 [M-C_6H_{11}-C_2H_2]145.0637 [M-C_8H_7O]137.1326 [M-$C_{11}H_{17}$]107.0494	bakuchiol*	PC	others

252	55.862	$C_{30}H_{48}O_3$	+H	457.3664	2.62	[M+H-H_2O]439.3555 [M+H-H_2O-COOH]393.3628 [M-H_2O-$C_{15}H_{22}O_2$]203.1794 [$C_{15}H_{22}O_2$-COOH]189.1636 [$C_{15}H_{22}O_2$-COOH-CH_2]175.1481 [$C_{15}H_{22}O_2$-COOH-2CH_2]161.1332 [$C_{15}H_{22}O_2$-COOH-3CH_2]147.1169 [$C_{15}H_{22}O_2$-COOH-4CH_2]133.1013 [$C_{15}H_{22}O_2$-COOH-5CH_2]119.0866	oleanic acid*	PG	others
253	58.071	$C_{18}H_{32}O_2$	-H	279.2324	1.79	NF	linoleic-acid	PG/EB	others
254	59.467	$C_{40}H_{80}NO_8P$	+H	734.5698	-0.54	[P-Ch]184.0739 [P-Ch-H_2O]166.0634 [P-Ch-C_3H_9N]125.0003 [P-Ch-HPO_3]104.1055 [P-Ch-HPO_3-H_2O]86.0961	colfosceril palmitate	CE/HK CN/QN	lyso-GPCs
255	59.467	$C_{42}H_{82}NO_8P$	+H	760.5851	0.00	[P-Ch]184.0740 [P-Ch-H_2O]166.0645 [P-Ch-C_3H_9N]125.0000 [P-Ch-HPO_3]104.1077 [P-Ch-HPO_3-H_2O]86.0964	1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine	CE/HK CN/QN	lyso-GPCs
256	60.653	$C_{16}H_{32}O_2$	-H	255.2335	-2.35	NF	palmitic acid	AC	others
257	61.450	$C_{18}H_{34}O_2$	-H	281.2491	-1.78	NF	oleic acid	EB	others

*Confirmed with reference compounds

Table. S2 Detailed distinguishing information of 30 pairs of isomers from GLJ.

NO	RT (min)	Formula	Adduct	Observed (*m/z*)	DT (ms)	Predict-CCS (Å²)	Diagnostic ion (*m/z*)	Identification
1	22.54	$C_{42}H_{72}O_{14}$	+HCOO	845.4875	8.75	262.4	-	ginsenoside Rg1*
	26.82	$C_{42}H_{72}O_{14}$	+HCOO	845.4905	8.75	262.4	221.0647	ginsenoside Rf*
	26.93	$C_{42}H_{72}O_{14}$	+HCOO	845.4905	8.25	260.2	653.4096	pseudo-ginsenoside F11*
2	22.54	$C_{48}H_{82}O_{18}$	+HCOO	991.5461	10.11	261.5	391.2911	ginsenoside Re*
	30.47	$C_{48}H_{82}O_{18}$	+HCOO	991.5470	10.57	287.5	375.2908	ginsenoside Rd*
	31.49	$C_{48}H_{82}O_{18}$	+HCOO	991.5479	10.33	286.6	375.2911	gypenoside XVII*
3	28.63	$C_{53}H_{90}O_{22}$	+HCOO	1123.5898	11.60	305.2	-	ginsenoside Rc
	28.92	$C_{53}H_{90}O_{22}$	+HCOO	1123.5906	12.10	306.7	-	ginsenoside Rb2*
	29.40	$C_{53}H_{90}O_{22}$	+HCOO	1123.5903	12.30	306.7	-	ginsenoside Rb3*
4	28.36	$C_{41}H_{70}O_{13}$	+HCOO	815.4792	8.65	258.4	-	notoginsenoside-R2
	27.74	$C_{41}H_{70}O_{13}$	+HCOO	815.4791	8.55	256.5	-	ginsenoside F5
5	28.64	$C_{58}H_{98}O_{26}$	-H	1209.6268	11.80	324.2	-	ginsenoside Ra2
	27.85	$C_{58}H_{98}O_{26}$	-H	1209.6257	12.48	325.6	-	ginsenoside Ra1
6	28.44	$C_{42}H_{72}O_{13}$	+HCOO	829.4956	8.62	260.8	391.2824	ginsenoside Rg2*
	34.90	$C_{42}H_{72}O_{13}$	+HCOO	829.4932	8.90	261.5	391.2814	ginsenoside F2*
	36.80	$C_{42}H_{72}O_{13}$	+HCOO	829.4946	8.75	261.5	375.2913	20-S-ginsenoside-Rg3*
	37.16	$C_{42}H_{72}O_{13}$	+HCOO	829.4946	8.73	261.5	375.2905	20-R-ginsenoside-Rg3*
7	28.70	$C_{36}H_{62}O_{9}$	+HCOO	683.4368	7.20	236.6	-	ginsenoside F1
	30.26	$C_{36}H_{62}O_{9}$	+HCOO	683.4357	7.05	236.6	-	ginsenoside Rh1*
8	32.35	$C_{47}H_{80}O_{17}$	+HCOO	961.5348	9.95	280.8	-	notoginsenoside Fe*
	33.13	$C_{47}H_{80}O_{17}$	+HCOO	961.5375	10.05	282.7	-	ginsenoside compound O
9	33.96	$C_{42}H_{70}O_{12}$	+HCOO	811.4823	8.45	261.4	457.3526	ginsenoside Rg4
	34.42	$C_{42}H_{70}O_{12}$	+HCOO	811.4839	8.90	261.9	457.3578	ginsenoside Rg6*
	42.25	$C_{42}H_{70}O_{12}$	+HCOO	811.4844	9.75	262.6	441.3729	ginsenoside Rk1*

	41.71	$C_{42}H_{70}O_{12}$	+HCOO	811.4836	9.45	262.1	441.3733	ginsenoside Rg5
10	34.94	$C_{36}H_{60}O_{8}$	+HCOO	665.4261	7.05	247.1	-	ginsenoside Rk3*
	35.52	$C_{36}H_{60}O_{8}$	+HCOO	665.4268	7.35	247.8	-	ginsenoside Rh4*
11	39.02	$C_{41}H_{70}O_{12}$	+HCOO	799.4838	8.60	255.4	-	ginsenoside Mc
	38.52	$C_{41}H_{70}O_{12}$	+HCOO	799.4818	8.75	257.7	-	ginsenoside compound Y
12	50.30	$C_{36}H_{60}O_{7}$	+HCOO	649.4296	7.60	246.5	-	ginsenoside Rk2
	50.98	$C_{36}H_{60}O_{7}$	+HCOO	649.4301	7.85	247.1	-	ginsenoside Rh3
13	29.09	$C_{48}H_{76}O_{19}$	-H	955.4895	10.01	293.1	793.4376	ginsenoside Ro*
	35.57	$C_{48}H_{76}O_{19}$	-H	955.4519	9.95	292.5	835.4471	achyranthoside C
14	21.36	$C_{48}H_{82}O_{19}$	+HCOO	1007.5411	10.30	287.5	391.2814	20-*O*-gluginsenoside-Rf
	25.90	$C_{48}H_{82}O_{19}$	+HCOO	1007.5425	10.50	291.5	408.3247	hosenkoside O
15	35.71	$C_{42}H_{66}O_{14}$	-H	793.4358	8.82	269.3	-	zingibroside R1
	30.92	$C_{42}H_{66}O_{14}$	-H	793.4358	7.55	268.8	-	chikusetsusaponin IVa
	21.97	$C_{42}H_{72}O_{15}$	+HCOO	861.4841	8.78	273.9	-	hosenkoside J hosenkoside E
16	23.47	$C_{42}H_{72}O_{15}$	+HCOO	861.4830	9.40	273.9	-	hosenkoside J hosenkoside E
	20.30	$C_{42}H_{72}O_{15}$	+HCOO	861.4835	8.25	268.5	-	hosenkoside N
	25.92	$C_{42}H_{72}O_{15}$	+HCOO	861.4836	8.90	273.9	-	hosenkoside D
	26.11	$C_{42}H_{72}O_{15}$	+HCOO	861.4821	9.35	273.9	-	hosenkoside I
	20.35	$C_{48}H_{82}O_{20}$	+HCOO	1023.5361	10.55	296.9	-	hosenkoside B
17	22.38	$C_{48}H_{82}O_{20}$	+HCOO	1023.5337	10.13	292.7	-	hosenkoside C
	24.16	$C_{48}H_{82}O_{20}$	+HCOO	1023.5356	11.45	296.9	-	hosenkoside A
	20.85	$C_{47}H_{80}O_{19}$	+HCOO	993.5248	10.50	293.5	-	hosenkoside F
18	23.32	$C_{47}H_{80}O_{19}$	+HCOO	993.5264	9.75	289.1	-	hosenkoside G
	25.02	$C_{47}H_{80}O_{19}$	+HCOO	993.5247	11.00	293.5	-	hosenkoside L
	28.90	$C_{27}H_{30}O_{11}$	-H	529.1710	4.67	230.3	383.1130	caohuoside C
19	29.48	$C_{27}H_{30}O_{11}$	-H	529.1711	4.70	230.3	383.1134 368.0912	anhydroicaritin-3'-OH -7-*O*-rhamnose

	30.56	$C_{27}H_{30}O_{11}$	-H	529.1699	4.80	231.2	367.1185	icariside I
	32.50	$C_{27}H_{30}O_{11}$	-H	529.1725	5.05	231.2	366.1110	anhydroicaritin-3-*O*-glucoside
20	25.56	$C_{33}H_{40}O_{15}$	+HCOO	721.2346	5.40	246.3	367.1186	icariin*
	31.82	$C_{33}H_{40}O_{15}$	-H	675.2294	5.40	246.3	366.1114	sagittatoside A
21	18.60	$C_{21}H_{22}O_9$	-H	417.1188	2.77	197.5	-	liquiritin*
	22.88	$C_{21}H_{22}O_9$	-H	417.1194	4.10	201.2	-	isoliquiritin*
22	16.38	$C_{27}H_{32}O_{14}$	-H	579.1717	4.38	226.9	-	glucoliquiritin
	17.58	$C_{27}H_{32}O_{14}$	-H	579.1714	4.55	231.8	-	glucoisoliquiritin
23	18.50	$C_{26}H_{30}O_{13}$	-H	549.1595	4.45	230.6	-	liquiritin apioside*
	22.26	$C_{26}H_{30}O_{13}$	-H	549.1595	4.05	225.6	-	licuraside
24	27.66	$C_{20}H_{18}O_6$	+H	355.1174	2.90	186.0	149.0240	erythrinin C
	30.39	$C_{20}H_{18}O_6$	+H	355.1071	2.77	184.6	121.0255	desmethylicaritin
25	24.49	$C_{15}H_{12}O_4$	-H	255.0654	1.71	155.0	-	liquiritigenin*
	30.60	$C_{15}H_{12}O_4$	-H	255.0658	1.78	157.5	-	isoliquiritigenin*
	34.12	$C_{20}H_{20}O_4$	+H	325.1441	2.65	176.3	-	bavachin
26	36.83	$C_{20}H_{20}O_4$	+H	325.1442	2.75	178.7	-	bavachalcone
	39.61	$C_{20}H_{20}O_4$	+H	325.1437	2.76	178.7	-	isobavachalcone
	42.75	$C_{20}H_{20}O_4$	+H	325.1436	2.68	176.3	-	isobavachin
	35.68	$C_{20}H_{18}O_4$	+H	323.1284	2.65	175.0	267.0649	neobavaisoflavone*
27	45.61	$C_{20}H_{18}O_4$	+H	323.1281	2.63	174.9	175.0758 147.0443	bavachromene isobavachromene
	46.85	$C_{20}H_{18}O_4$	+H	323.1277	2.61	174.3	203.0701	chromenoflavanone
	39.17	$C_{20}H_{18}O_4$	+H	323.1280	2.63	174.9	175.0767 147.0453	bavachromene isobavachromene
28	48.30	$C_{21}H_{22}O_4$	+H	339.1599	2.93	179.9	-	bavachinin
	43.73	$C_{21}H_{22}O_4$	+H	339.1600	2.95	185.5	-	4'-*O*-methylbavachalcone
29	35.51	$C_{16}H_{12}O_6$	+H	301.0710	2.05	164.5	255.0284	rhamnocitrin
	29.62	$C_{16}H_{12}O_6$	+H	301.0705	2.03	164.5	255.0691	kaempferide

30	29.07	$C_{16}H_{12}O_7$	+H	317.0658	2.15	168.3	-	isorhamnetin*
	31.90	$C_{16}H_{12}O_7$	+H	317.0653	2.15	168.3	-	rhamnetin

* Confirmed with reference compounds