Improving Natural Products Identification through Molecular Features Orientated Precursor Ions Selection and Targeted MS/MS Analysis: A Case study of Zhi-Ke-Yang-Yin capsule

Hongping Wang [a], Qiong Yin [a], ZiJian Wang [a], Ping Peng [a], Chunlan Fan [c], Run Zhang [b], Chen Zhao [a] and Zhaozhou Lin [c]

[a] Scientific Research Institute of Beijing Tongrentang Co., Ltd., Beijing 100011, China

[b] Beijing Tongrentang Technology Development Co., Ltd., Beijing 100079, China

[c] Beijing Zhongyan Tongrentang Pharmaceutical R & D Co., Ltd., Beijing 100000, China

The first author. Tel.: +86 10 87632655; fax: +86 10 87632655.

E-mail address: sungirl9626@163.com

Supplementary Data

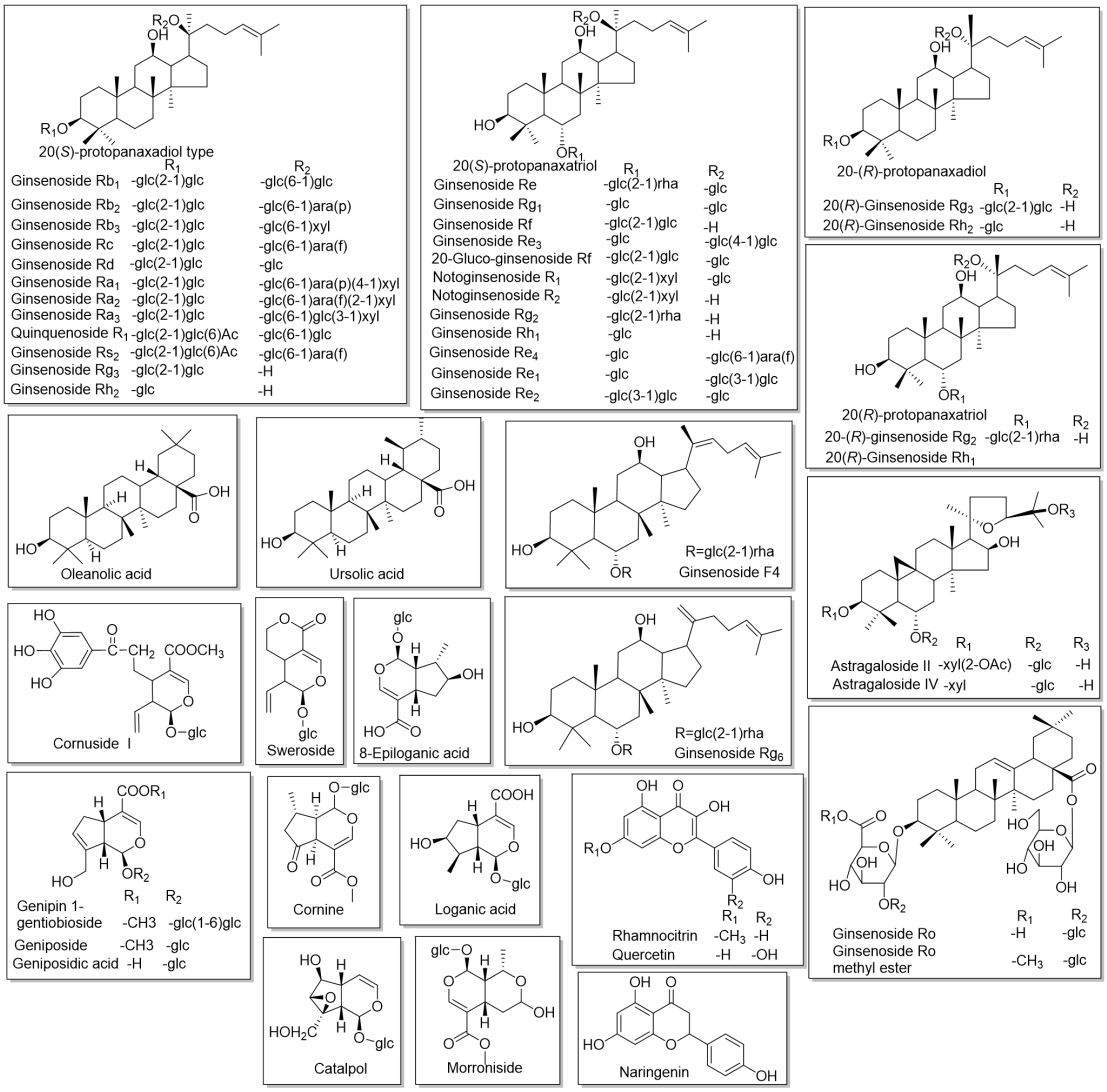

Fig. S1 The structures of the reference standards.

S1 Optimization of the chromatographic conditions and mass spectrometric conditions of ZKYY extract

1) Optimization of the chromatographic conditions of ZKYY extract

A Vanquish™ Flex UHPLC system (Thermo Scientific, USA), equipped with a binary pump and a thermostatted column compartment, was used to perform the separation of the multiple components.

Two types of chromatographic columns, including Waters ACQUITY UPLC® BEH C_{18} column (2.1 x 100 mm, 1.7 μm) and Waters ACQUITY UPLC® HSS T3 column (2.1 x 100 mm, 1.8 μm), were used to perform the separation of multiple components. Good separations of multiple components were obtained on Waters ACQUITY UPLC® BEH C_{18} column (2.1 x 100 mm, 1.7 μm) which was finally selected to analyze ZKYY extract.

The mobile phase system of methanol aqueous solution, methanol-formic acid aqueous solution, acetonitrile aqueous solution and acetonitrle-formic acid aqueous solution were investigated in our study. We found that acetonitrle-formic acid aqueous solution offers good separation of multiple components, so it was chosen as the mobile phase system.

The elution gradient was also optimized by constantly adjusting the proportion of the mobile phase A (0.1% formic acid/water, v/v) and mobile phase B (acetonitrile) and the optimized elution gradient was 0-7 min, 2-20% B; 7-10 min, 20-25% B; 10-20 min, 25-40% B; 20-25 min, 40-65% B; 25-30min，65％B-95％B; 30-31min, 95％B-95％B.

The influence of different column temperatures (25°C, 30°C and 35°C) was also investigated. We found when the column temperature was set at 35°C, not only the lower column pressure but also better separations of multiple components were obtained. Thus, 35°C was much suitable for us.

Taking all of the aforementioned factors into account, we established the chromatographic conditions as follows: A Waters ACQUITY UPLC® BEH C_{18} column (2.1 x 100 mm, 1.7 μm) coupled with a ACQUITY UPLC® BEH C_{18} VanGuard™ Pre-Column (2.1 x 5 mm, 1.7 μm) was employed to perform the

chromatographic separation of ZKYY extract using mobile phase A (0.1% formic acid/water, v/v) and mobile phase B (acetonitrile) by the following gradient elution program: 0-7 min, 2-20% B; 7-10 min, 20-25% B; 10-20 min, 25-40% B; 20-25 min, 40-65% B; 25-30min，65％B-95％B; 30-31min, 95％B-95％B. The flow rate was 0.3 mL/min and the temperature was set at 35℃. The injection volume was 2 uL.

2) Optimization of the mass spectrometric conditions of ZKYY extract

High-accuracy mass spectrometric data were recorded on Orbitrap Exploris 240 mass spectrometer (Thermo Scientific, USA) equipped with Heated ESI source.

Due to all kinds of constituents exhibited significantly stronger ion responses in negative-ion mode than in positive-ion mode, the instrument was operated in negative-ion mode.

The MS parameters were selectively optimized and the collision energy were optimized. Fixed collision energy 35V and stepped collision energy 30%, 45% and 60% (in normalized collision energy type) were compared in our study. From Fig. S2, we found when performing the above collision energy separately, there was no much difference in the MS spectra of flavonoids (B), iridoids (C), phenylethanoid glycosides (D), phenylpropanoids (E) and ionones (F). However, most saponins such as ginsenoside Rd (A) produced relatively lower abundance of $[M-H]^-$ ion but higher abundance of fragmentation ions at collision energy 35V and exhibited relatively higher abundance of $[M-H]^-$ ion but lower abundance of fragmentation ions at stepped collision energy 30%, 45% and 60% (in normalized collision energy type). It can be seen, probably 35V was much suitable for saponins. Thus, taking saponins, flavonoids, iridoids, phenylethanoid glycosides, phenylpropanoids and ionones into consideration, fixed 35V was finally selected as the collision energy.

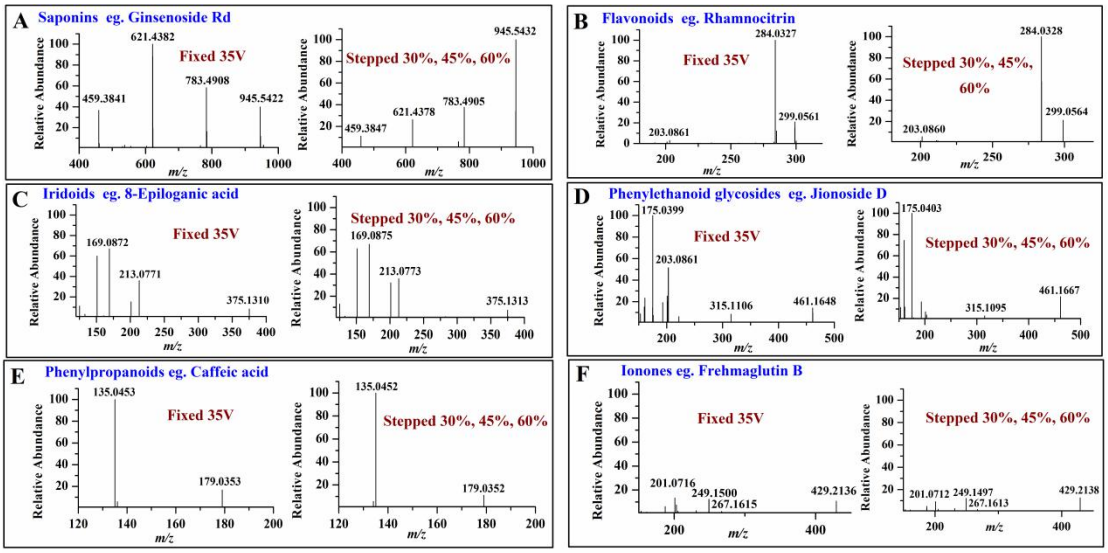

Fig. S2 The MS spectra of saponins (A), flavonoids (B), iridoids (C), phenylethanoid glycosides (D), phenylpropanoids (E) and ionones (F) in fixed collision energy 35V and stepped collision energy 30%, 45% and 60% (in normalized collision energy type).

S2 Identification of saponins

Except for ginsenosides identified mentioned in text, other known compounds and their isomerized, acetylated and malonylated compounds were also identified. Thirty-four triterpenoids, namely, ginsenoside Re_3 (**R2**), ginsenoside Re_4 (**R3**), 20-Glc-Rf (**R5**), ginsenoside Re_1 (**R7**), notoginsenoside R_1 (**R9**), ginsenoside Re_2 (**R10**), ginsenoside Rg1 (**R16**), ginsenoside Re (**R17**), ginsenoside Rf (**R42**), notoginsenoside R_2 (**R47**), ginsenoside Ra_2 (**R55**), ginsenoside Ra_3 (**R58**), ginsenoside Rb_1 (**R59**), 20(*S*)-ginsenoside Rg_2 (**R60**), 20(*S*)-ginsenoside Rh_1 (**R61**), 20(*R*)-ginsenoside Rg_2 (**R68**), ginsenoside Rc (**R70**), 20(*R*)-ginsenoside Rh_1 (**R71**), ginsenoside Ra_1 (**R72**), ginsenoside Ro (**R74**), ginsenoside Rb_2 (**R81**), ginsenoside Rb_3 (**R82**), quinquenoside R_1 (**R86**), ginsenoside Rs_2 (**R91**), ginsenoside Rd (**R92**), ginsenoside Ro methyl ester (**R113**), ginsenoside F4 (**R129**), ginsenoside Rg_6 (**R133**), 20(*S*)-ginsenoside Rg_3 (**R139**), 20(*R*)-ginsenoside Rg_3 (**R141**), 20(*S*)-ginsenoside Rh_2 (**R147**), 20(*R*)-ginsenoside Rh_2 (**R148**), astragaloside IV (**H13**), astragaloside II (**H18**), were confirmed and validated by comparing the mass spectra, retention times and fragmentation pathways with those of reference standards. Then, the fragmentation pathways were used to deduce the other compounds.

R18, **R23**, **R25** and **R29** owned the same not only precursor ion but also the same fragmentation pathways and fragmentation ions as those of ginsenoside Re, so that they were tentatively assigned as the isomers of ginsenoside Re. Similarly, the isomers of the other reference standards were characterized, and **R39** as well as **R65** were identified as ginsenoside Rb_1 isomer while **R53**, **R56** as well as **R62** were

characterized as ginsenoside Ro isomer. **R41**, **R46**, **R50** and **R64** were the isomers of notoginsenoside R4 or ginsenoside Ra_3, and **R104**, **R112** as well as **R134** were the isomers of ginsenoside Rd. **R124** was elucidated as isomerized ginsenoside Rg_2 while **R88** and **R96** were elucidated as the isomerized quinquenoside R_1. **R11** was the isomer of notoginsenoside R_1.

Other known ginsenosides including **R4**, **R8**, **R13**, **R31**, **R32**, **R40**, **R48**, **R51**, **R80**, **R84**, **R89**, **R90**, **R99**, **R101**, **R103**, **R109**, **R116**, **R117**, **R119**, **R122**, **R125**, **R136**, **R142**, **R145** and **R146** were tentatively assigned according to their diagnostic ions and the successively losses of a series of saccharide moiety. Their isomers, which own the same precursor ions, fragmentation pathways and fragmentation ions as the above known compounds were tentatively characterized. **R1**, **R20**, **R26**, **R30** and **R34** were tentatively identified as floralginsenoside P and its isomers. All fragmentation ions were detailed in Table S1.

Except for some isomers were founded, the acetylated and malonylated of known ginsenosides were also detected. After loss of acetyl (42 Da), the remaining fragmentation ions of **R27** and **R36** were the same as those of the reference standard of ginsenoside Re, thus, **R27** and **R36** were deduced as acetyl-ginsenoside Re. Similarly, **R95** was deduced as acetyl-ginsenoside Rd, while **R135**, **R137** and **R140** were deduced as acetyl-ginsenoside Rg_3. **R107** and **R111** were deduced as acetyl-pseudo-ginsenoside RC_1. The remaining fragmentation ions of **R22** were the same as those of the reference standard of ginsenoside Rg1 after loss of malonyl (86 Da), therefore, **R22** was characterized as malonyl-ginsenoside Rg_1. **R24** was

characterized as malonyl-ginsenoside Re while **R94** was identified as malonyl-ginsenoside Rd in the same way. Also, **R28**, **R45**, **R54**, **R57**, **R66**, **R67**, **R69**, **R73**, **R75**, **R77**, **R79**, **R83**, **R85**, **R100**, **R106**, **R123** and **R126** were identified as the malonyl compounds of corresponding reference standards.

Except for ginsenosides, 25 stragalus saponins were also detected and most of them produced the diagnostic ion at *m/z* 489.3580 by successively losses of a series of acetyl and saccharide moiety. The detailed fragmentation ions were shown in Table S1.

S3 Identification of flavonoids

Except for identified flavonoids mentioned in text, other known compounds and their isomers were also characterized. **H84** was extracted at *m/z* 315.0873 with a mass deviation of 1.27 ppm, indicating its molecular formula was $C_{17}H_{16}O_6$. In its MS/MS spectrum, the fragmentation ions at *m/z* 285.0409 and 257.0464 suggested the successive losses of OCH_2 and CO from $[M-H]^-$ ion, respectively, while *m/z* 241.0522 and 211.1346 indicated the successive losses of CO_2 and OCH_2 from *m/z* 285.0409, respectively. Thus, **H84** was tentatively deduced as 2′, 4′-Dihydroxy-5, 6-Dimethyisoflavaone, a known compound isolated from *Astragalus membranaceus*. Similarly, other known compounds such as **H27**-**H29**, **H32**, **H34**-**H36**, **H46**, **H47**, **H57**, **H58**, **H59**, **H64**-**H66**, **H69**, **H70**, **H72**, **H76**, **H77**, **H81**, **H82**, **H87**, **H88**, **S67**, **S69**, **S74**-**S76**, **S77**, **S78**, **S80**, **S81**, **S86** and **S87** were tentatively characterized. Beyond that, the isomers of known compounds were also characterized. For instance, the extracted precursor ion of **H37**, **H41**, **H49**, **H53**, **H61**, **H80**, **H85** and **H90** was

observed at *m/z* 285.0768, which was the same as that of **H69**, indicating their molecular formula was $C_{16}H_{14}O_5$. Their fragmentation ions were observed the same as those of **H69** at *m/z* 270.0513 and 228.0424 suggesting CH_3 and C_2H_2O were successively eliminated from the precursor ion. Thus, **H37**, **H41**, **H49**, **H53**, **H61**, **H80**, **H85** and **H90** were tentatively assigned as vesticarpan isomers.

Actually, the sugar moieties of the flavonoids existing in forms of glycosides were always firstly eliminated from the precursor ions in their targeted analysis and then followed by a series of neutral losses of small molecular. The precursor ion of **S80** was extracted at *m/z* 593.1508 with a mass derivation of 0.34 ppm suggesting its molecular formula was $C_{27}H_{30}O_{15}$. The fragmentation ions at *m/z* 285.0410 suggesting Gal and Rha were eliminated from the precursor ion and the ions at *m/z* 267.0302 and 241.0510 indicating H_2O and CO_2 were eliminated from *m/z* 285.0410. Thus, **S80** was deduced as a known compound kaempferol-3-O-α-L-Rhamnosyl(1-6)-β-D-galactoside. The precursor ions as well as the fragmentation ions of **S64**, **S66**, **S70**, **S72** and **S83** were the same as **S80,** thus, they were tentatively assigned as the isomers of kaempferol-3-O-α-L-Rhamnosyl(1-6)-β-D-galactoside. In the same way, the other known compounds and isomers were tentatively assigned, the fragmentation ions were shown in Table S2.

Table S1 Saponins from ZKYY

No.	t_R (min)	Molecular formula	Measured value (*m/z*)	Diff (ppm)	Product ions	Compound name
Saponins from *panax ginseng*						
R1	10.12	$C_{53}H_{90}O_{23}$	1093.5817	2.01	799.4976[M-H-Ara-Glc]$^-$, 637.4310[M-H-Ara-2Glc]$^-$,	Floralginsenoside P/isomer

					475.3813[M-H-Ara-3Glc]$^-$	
R2	10.57	$C_{48}H_{82}O_{19}$	961.5381	0.94	799.4852[M-H-Glc]$^-$, 637.4333[M-H-2Glc]$^-$, 475.3802[M-H-3Glc]$^-$	Ginsenoside Re_3 [a]
R3	10.96	$C_{47}H_{80}O_{18}$	931.5259	-0.75	799.4870[M-H-Ara(f)]$^-$, 637.4312[M-H-Ara(f)-Glc]$^-$, 475.3810[M-H-Ara(f)-2Glc]$^-$	Ginsenoside Re_4 [a]
R4	11.04	$C_{53}H_{90}O_{22}$	1077.5845	0.00	945.5450[M-H-Ara]$^-$, 783.4838[M-H-Ara-Glc]$^-$, 637.4318[M-H-Ara-Glc-Rha]$^-$, 475.3777[M-H-Ara-2Glc-Rha]$^-$	Floralginsenoside M/Floralginsenoside N
R5	11.18	$C_{48}H_{82}O_{19}$	961.5378	0.62	799.4838[M-H-Glc]$^-$, 637.4320[M-H-2Glc]$^-$, 475.3791[M-H-3Glc]$^-$	20-Gluco-ginsenoside Rf [a]
R6	11.31	$C_{54}H_{92}O_{23}$	1107.5961	0.90	945.5485[M-H-Glc]$^-$, 783.4889[M-H-2Glc]$^-$, 637.4330[M-H-2Glc-Rha]$^-$, 475.3810[M-H-3Glc-Rha]$^-$	Protopanaxatriol+3Glc+Rha
R7	11.32	$C_{48}H_{82}O_{19}$	961.5381	0.94	799.4897[M-H-Glc]$^-$, 637.4309[M-H-2Glc]$^-$, 475.3794[M-H-3Glc]$^-$,	Ginsenoside Re_1 [a]
R8	11.39	$C_{53}H_{90}O_{22}$	1077.5846	0.09	945.5465[M-H-Ara]$^-$, 799.4873[M-H-Ara-Rha]$^-$, 637.4344[M-H-Ara-Rha-Glc]$^-$, 475.3777[M-H-Ara-Rha-2Glc]$^-$	Floralginsenoside M/Floralginsenoside N
R9	11.49	$C_{47}H_{80}O_{18}$	931.5272	0.64	799.4841[M-H-Xyl]$^-$, 637.4319[M-H-Xyl-Glc]$^-$, 475.795[M-H-Xyl-2Glc]$^-$	Notoginsenoside R_1 [a]
R10	11.60	$C_{48}H_{82}O_{19}$	961.5377	0.52	799.4895[M-H-Glc]$^-$, 637.4328[M-H-2Glc]$^-$, 475.3805[M-H-3Glc]$^-$	Ginsenoside Re_2 [a]
R11	11.81	$C_{47}H_{80}O_{18}$	931.5276	1.07	799.4841[M-H-Xyl]$^-$, 637.4303[M-H-Xyl-Glc]$^-$, 475.3780[M-H-Xyl-2Glc]$^-$	Notoginsenoside R_1 isomer
R12	11.89	$C_{54}H_{92}O_{23}$	1107.5970	1.72	945.5467[M-H-Glc]$^-$, 783.4889[M-H-2Glc]$^-$, 637.430[M-H-2Glc-Rha]$^-$, 475.3810[M-H-3Glc-Rha]$^-$	Protopanaxatriol+3Glc+Rha
R13	12.01	$C_{54}H_{92}O_{24}$	1123.5905	0.45	961.5388[M-H-Glc]$^-$, 799.4835[M-H-2Glc]$^-$, 637.4330[M-H-3Glc]$^-$, 475.3788[M-H-4Glc]$^-$	Koryoginsenoside R_2
R14	12.08	$C_{54}H_{92}O_{23}$	1107.5941	-0.90	945.5471[M-H-Glc]$^-$, 783.4981[M-H-2Glc]$^-$,	Protopanaxatriol+3Glc+Rha

					637.4370[M-H-2Glc-Rha]$^-$, 475.3776[M-H-3Glc-Rha]$^-$	
R15	12.09	$C_{48}H_{82}O_{19}$	961.5362	-1.04	799.4890[M-H-Glc]$^-$, 637.4329[M-H-2Glc]$^-$, 475.3800[M-H-3Glc]$^-$	Notoginsenoside N isomer
R16	12.16	$C_{42}H_{72}O_{14}$	799.4849	0.63	637.4355[M-H-Glc]$^-$, 475.3808[M-H-2Glc]$^-$	Ginsenoside Rg_1 [a]
R17	12.20	$C_{48}H_{82}O_{18}$	945.5431	0.85	783.4901[M-H-Glc]$^-$, 637.4330[M-H-Glc-Rha]$^-$, 475.3795[M-H-2Glc-Rha]$^-$	Ginsenoside Re [a]
R18	12.38	$C_{48}H_{82}O_{18}$	945.5433	1.06	783.4897[M-H-Glc]$^-$, 637.4321[M-H-Glc-Rha]$^-$, 475.3792[M-H-2Glc-Rha]$^-$	Re isomer
R19	12.55	$C_{53}H_{90}O_{22}$	1077.5848	0.28	945.5455[M-H-Ara]$^-$, 799.4869[M-H-Ara-Rha]$^-$, 637.4371[M-H-Ara-Rha-Glc]$^-$, 475.3776[M-H-Ara-Rha-2Glc]$^-$	Floralginsenoside M isomer/Floralginsenoside N isomer
R20	12.58	$C_{53}H_{90}O_{23}$	1093.5812	1.55	799.4867[M-H-Ara-Glc]$^-$, 637.4344[M-H-Ara-2Glc]$^-$, 475.3759[M-H-Ara-3Glc]$^-$	Floralginsenoside P/isomer
R21	12.90	$C_{48}H_{82}O_{19}$	961.5363	-0.94	799.3902[M-H-Glc]$^-$, 637.3571[M-H-2Glc]$^-$, 475.3743[M-H-3Glc]$^-$	Notoginsenoside N isomer
R22	12.90	$C_{45}H_{74}O_{17}$	885.4840	-0.90	637.4316[M-H-Malonyl-Glc]$^-$, 475.3779[M-H-Malonyl-2Glc]$^-$	Malonyl-ginsenoside Rg_1
R23	13.08	$C_{48}H_{82}O_{18}$	945.5412	-1.16	783.4919[M-H-Glc]$^-$, 637.4326[M-H-Glc-Rha]$^-$, 475.3794[M-H-2Glc-Rha]$^-$	Ginsenoside Re isomer
R24	13.43	$C_{51}H_{84}O_{21}$	1031.5428	0.10	945.5392[M-H-Malonyl]$^-$, 783.4880[M-H-Malonyl-Glc]$^-$, 637.4326[M-H-Malonyl-Glc-Rha]$^-$, 475.3799[M-H-Malonyl-2Glc- Rha]$^-$	Malonyl-ginsenoside Re
R25	13.44	$C_{48}H_{82}O_{18}$	945.5433	1.06	783.4930[M-H-Glc]$^-$, 637.4330[M-H-Glc-Rha]$^-$, 475.3818[M-H-2Glc-Rha]$^-$	Ginsenoside Re isomer
R26	13.52	$C_{53}H_{90}O_{23}$	1093.5802	0.64	799.4709[M-H-Ara-Glc]$^-$, 637.4294[M-H-Ara-2Glc]$^-$, 475.3743[M-H-Ara-3Glc]$^-$	Floralginsenoside P/isomer
R27	13.54	$C_{50}H_{84}O_{19}$	987.5520	-0.91	945.5434[M-H-Ac]$^-$, 783.4855[M-H-Ac-Glc]$^-$, 637.4315[M-H-Ac-Glc-Rha]$^-$, 475.3791[M-H-Ac-2Glc-Rha]$^-$	Acetyl-ginsenoside Re
R28	13.64	$C_{45}H_{74}O_{17}$	885.4843	-0.56	637.4310[M-H-Malonyl-Glc]$^-$, 475.3799[M-H-Malonyl-2Glc]$^-$	Malonyl-ginsenoside Rf

R29	13.88	$C_{48}H_{82}O_{18}$	945.5437	1.48	783.4935[M-H-Glc]$^-$, 637.4331[M-H-Glc-Rha]$^-$, 475.3801[M-H-2Glc-Rha]$^-$	Ginsenoside Re isomer
R30	14.11	$C_{53}H_{90}O_{23}$	1093.5811	1.46	799.4862[M-H-Ara-Glc]$^-$, 637.4322[M-H-Ara-2Glc]$^-$, 475.3789[M-H-Ara-3Glc]$^-$	Floralginsenoside P/isomer
R31	14.12	$C_{48}H_{82}O_{19}$	961.5377	0.52	799.4824[M-H-Glc]$^-$, 637.4315[M-H-2Glc]$^-$, 475.3791[M-H-3Glc]$^-$	Notoginsenoside N
R32	14.34	$C_{48}H_{82}O_{19}$	961.5372	0.00	799.4862[M-H-Glc]$^-$, 637.4277[M-H-2Glc]$^-$, 475.3796[M-H-3Glc]$^-$	Vina-ginsenoside R_4
R33	14.40	$C_{54}H_{92}O_{24}$	1123.5907	0.62	961.5371[M-H-Glc]$^-$, 799.4849 [M-H-2Glc]$^-$, 637.4293[M-H-3Glc]$^-$, 475.3767[M-H-4Glc]$^-$	Koryoginsenoside R_2 isomer
R34	14.47	$C_{53}H_{90}O_{23}$	1093.5814	1.74	799.4885[M-H-Ara-Glc]$^-$, 127637.4363[M-H-Ara-2Glc]$^-$, 475.3785[M-H-Ara-3Glc]$^-$	Floralginsenoside P/isomer
R35	15.46	$C_{48}H_{82}O_{19}$	961.5384	1.25	799.4858[M-H-Glc]$^-$, 637.4312[M-H-2Glc]$^-$, 475.3802[M-H-3Glc]$^-$	Vina-ginsenoside R_4 isomer
R36	15.53	$C_{50}H_{84}O_{19}$	987.5526	-0.30	945.5323[M-H-Ac]$^-$, 783.4905[M-H-Ac-Glc]$^-$, 637.4360[M-H-Ac-Glc-Rha]$^-$, 475.3814[M-H-Ac-2Glc-Rha]$^-$	Acetyl-ginsenoside Re
R37	15.89	$C_{60}H_{102}O_{28}$	1269.6488	0.71	1107.5858[M-H-Glc]$^-$, 945.5471[M-H-2Glc]$^-$, 783.4899[M-H-3Glc]$^-$, 621.4368[M-H-4Glc]$^-$, 459.3851[M-H-5Glc]$^-$	Protopanaxadiol+5Glc
R38	16.19	$C_{48}H_{82}O_{19}$	961.5389	1.77	799.4788[M-H-Glc]$^-$, 637.4316[M-H-2Glc]$^-$, 475.3803[M-H-3Glc]$^-$	Vina-ginsenoside R_4 isomer
R39	16.25	$C_{54}H_{92}O_{23}$	1107.5951	0.00	945.5400[M-H-Glc]$^-$, 783.4893[M-H-2Glc]$^-$, 621.4345[M-H-3Glc]$^-$, 459.3834[M-H-4Glc]$^-$	Ginsenoside Rb_1 isomer
R40	16.26	$C_{42}H_{72}O_{14}$	799.4854	1.25	637.4312[M-H-Glc]$^-$, 475.3799[M-H-2Glc]$^-$	Ginsenoside Ia
R41	16.36	$C_{59}H_{100}O_{27}$	1239.6377	0.24	1107.5924[M-H-Glc]$^-$, 945.5419[M-H-Glc-Xyl]$^-$, 783.4904 [M-H-2Glc-Xyl]$^-$, 621.4343[M-H-3Glc-Xyl]$^-$,	Notoginsenoside R_4 isomer/Ginsenoside Ra_3 isomer

					459.3808[M-H-4Glc-Xyl]-	
R42	16.51	$C_{42}H_{72}O_{14}$	799.4849	0.63	637.4326[M-H-Glc]-, 475.3797[M-H-2Glc]-	Ginsenoside Rf [a]
R43	16.55	$C_{59}H_{100}O_{27}$	1239.6381	0.56	1107.5955[M-H-Glc]-, 945.5423[M-H-Glc-Xyl]-, 783.4895[M-H-2Glc-Xyl]-, 621.4370[M-H-3Glc-Xyl]-, 459.3840[M-H-4Glc-Xyl]-	Notoginsenoside R_4
R44	16.76	$C_{48}H_{82}O_{19}$	961.5388	1.66	799.4815[M-H-Glc]-, 637.4232[M-H-2Glc]-, 475.3837[M-H-3Glc]-	Vina-ginsenoside R_4 isomer
R45	16.88	$C_{62}H_{102}O_{30}$	1325.6359	-1.43	1239.6378[M-H-Malonyl]-, 1107.5916[M-H-Malonyl-Xyl]-, 945.5457[M-H-Malonyl-Xyl-Glc]-, 783.4895[M-H-Malonyl-Xyl-2Glc]-, 621.4343[M-H-Malonyl-Xyl-3Glc]-, 459.3822[M-H-Malonyl-Xyl-4Glc]-	Malonyl-notoginsenoside R_4
R46	16.98	$C_{59}H_{100}O_{27}$	1239.6383	0.73	1107.5941[M-H-Glc]-, 945.5395[M-H-Glc-Xyl]-, 783.4912[M-H-2Glc-Xyl]-, 621.4358[M-H-3Glc-Xyl]-, 459.3817[M-H-4Glc-Xyl]-	Notoginsenoside R_4 isomer/Ginsenoside Ra_3 isomer
R47	17.17	$C_{41}H_{70}O_{13}$	769.4743	0.65	637.4322[M-H-Xyl]-, 475.3795[M-H-Xyl-Glc]-	Notoginsenoside R_2 [a]
R48	17.23	$C_{44}H_{74}O_{15}$	841.4943	-0.71	799.4834[M-H-Ac]-, 637.4298[M-H-Ac-Glc]-, 475.3789[M-H-Ac-2Glc]-	Yesanchinoside D
R49	17.42	$C_{58}H_{98}O_{26}$	1209.6273	0.41	1077.5818[M-H-Xyl]-, 945.5433[M-H-Xyl-Ara]-, 783.4882[M-H-Xyl-Ara-Glc]-, 621.4371[M-H-X2yl-Ara-2Glc]-, 459.3804[M-H-Xyl-Ara-3Glc]-	Ginsenoside Ra_1 isomer/Ginsenoside Ra_2 isomer
R50	17.49	$C_{59}H_{100}O_{27}$	1239.6375	0.08	1107.5958[M-H-Glc]-, 945.5432[M-H-Glc-Xyl]-, 783.4883[M-H-2Glc-Xyl]-, 621.4380[M-H-3Glc-Xyl]-, 459.3831[M-H-4Glc-Xyl]-	Notoginsenoside R_4 isomer/Ginsenoside Ra_3 isomer
R51	17.49	$C_{41}H_{70}O_{13}$	769.4744	0.78	637.4319[M-H-Ara]-, 475.3796[M-H-Ara-Glc]-	Ginsenoside F_3/Ginsenoside F_5
R52	17.52	$C_{44}H_{74}O_{15}$	841.4954	0.59	799.4853[M-H-Ac]-, 637.4254[M-H-Ac-Glc]-, 475.3789[M-H-Ac-2Glc]-	Yesanchinoside D isomer
R53	17.52	$C_{48}H_{76}O_{19}$	955.4902	-0.10	793.4329[M-H-Glc]-, 731.4350[M-H-Glc-CO_2-H_2O]-,	Ginsenoside Ro isomer

					569.3911[M-H-2Glc-H_2O-CO_2]$^-$,	
R54	17.62	$C_{62}H_{102}O_{30}$	1325.6356	-1.66	1239.6321[M-H-Malonyl]$^-$, 1107.5948[M-H-Malonyl-Xyl]$^-$, 945.5408[M-H-Malonyl-Xyl-Glc]$^-$, 783.4899[M-H-Malonyl-Xyl-2Glc]$^-$, 621.4373[M-H-Malonyl-Xyl-3Glc]$^-$, 459.3832[M-H-Malonyl-Xyl-4Glc]$^-$	Malonyl-notoginsenoside R_4 isomer/Malonyl-ginsenoside Ra_3 isomer
R55	17.69	$C_{58}H_{98}O_{26}$	1209.6262	-0.50	1077.5858[M-H-Xyl]$^-$, 945.5461[M-H-Xyl-Ara(f)]$^-$, 783.4919[M-H-Xyl-Ara(f)-Glc]$^-$, 621.4398[M-H-Xyl-Ara(f)-2Glc]$^-$, 459.3864[M-H-Xyl-Ara(f)-3Glc]$^-$	Ginsenoside Ra_2 [a]
R56	17.77	$C_{48}H_{76}O_{19}$	955.4907	0.42	793.4390[M-H-Glc]$^-$, 613.3750[M-H-2Glc-H_2O]$^-$, 455.3515[M-H-2Glc-Glu A]$^-$	Ginsenoside Ro isomer
R57	17.84	$C_{62}H_{102}O_{30}$	1325.6376	-0.15	1239.6368[M-H-Malonyl]$^-$, 1107.6024[M-H-Malonyl-Xyl]$^-$, 945.5449[M-H-Malonyl-Xyl-Glc]$^-$, 783.4921[M-H-Malonyl-Xyl-2Glc]$^-$, 621.4388[M-H-Malonyl-Xyl-3Glc]$^-$, 459.3872[M-H-Malonyl-Xyl-4Glc]$^-$	Malonyl-notoginsenoside R_4 isomer/Malonyl-ginsenoside Ra_3 isomer
R58	17.86	$C_{59}H_{100}O_{27}$	1239.6375	0.08	1107.5958[M-H-Glc]$^-$, 945.5416[M-H-Glc-Xyl]$^-$, 783.4886[M-H-2Glc-Xyl]$^-$, 621.4367[M-H-3Glc-Xyl]$^-$, 459.3842[M-H-4Glc-Xyl]$^-$	Ginsenoside Ra_3 [a]
R59	17.90	$C_{54}H_{92}O_{23}$	1107.5958	0.63	945.5414[M-H-Glc]$^-$, 783.4903[M-H-2Glc]$^-$, 621.4366[M-H-3Glc]$^-$, 459.3860[M-H-4Glc]$^-$	Ginsenoside Rb_1 [a]
R60	17.96	$C_{42}H_{72}O_{13}$	783.4893	-0.26	637.4333[M-H-Rha]$^-$, 475.3715[M-H-Rha-Glc]$^-$	Ginsenoside 20(*S*)-Rg_2 [a]
R61	17.98	$C_{36}H_{62}O_9$	637.4317	0.16	475.3786[M-H-Glc]$^-$	Ginsenoside 20(*S*)-Rh_1 [a]
R62	17.99	$C_{48}H_{76}O_{19}$	955.4897	-0.63	793.4382[M-H-Glc]$^-$, 613.3737[M-H-2Glc-H_2O]$^-$, 455.3526[M-H-2Glc-Glu A]$^-$	Ginsenoside Ro isomer
R63	18.04	$C_{58}H_{98}O_{26}$	1209.6265	-0.25	1077.5839[M-H-Xyl]$^-$, 945.5435[M-H-Xyl-Ara]$^-$, 783.4897[M-H-Xyl-Ara-Glc]$^-$, 621.4370[M-H-Xyl-Ara-2Glc]$^-$, 459.3864[M-H-Xyl-Ara-3Glc]$^-$	Ginsenoside Ra_1 isomer/Ginsenoside Ra_2 isomer
R64	18.08	$C_{59}H_{100}O_{27}$	1239.6389	1.21	1107.5950[M-H-Glc]$^-$, 945.5428[M-H-Glc-Xyl]$^-$, 783.4910[M-H-2Glc-Xyl]$^-$,	Notoginsenoside R_4 isomer/Ginsenoside Ra_3 isomer

					621.4371[M-H-3Glc-Xyl]⁻, 459.3814[M-H-4Glc-Xyl]⁻	Ginsenoside Ra_3 isomer
R65	18.13	$C_{54}H_{92}O_{23}$	1107.5953	0.18	945.5416[M-H-Glc]⁻, 783.4929[M-H-2Glc]⁻, 621.4357[M-H-3Glc]⁻, 459.3875[M-H-4Glc]⁻	Ginsenoside Rb_1 isomer
R66	18.18	$C_{62}H_{102}O_{30}$	1325.6371	-0.53	1239.6327[M-H-Malonyl]⁻, 1107.5933[M-H-Malonyl-Xyl]⁻, 945.5469[M-H-Malonyl-Xyl-Glc]⁻, 783.4915[M-H-Malonyl-Xyl-2Glc]⁻, 621.4376[M-H-Malonyl-Xyl-3Glc]⁻, 459.3820[M-H-Malonyl-Xyl-4Glc]⁻	Malonyl-ginsenoside Ra_3
R67	18.25	$C_{57}H_{94}O_{26}$	1193.5942	-1.09	1107.5786[M-H-Malonyl]⁻, 945.5470[M-H-Malonyl-Glc]⁻, 783.4943[M-H-Malonyl-2Glc]⁻, 621.4411[M-H-Malonyl-3Glc]⁻, 459.3854[M-H-Malonyl-4Glc]⁻	Malonyl-ginsenoside Rb_1
R68	18.29	$C_{42}H_{72}O_{13}$	783.4895	0.00	637.4319[M-H-Rha]⁻, 475.3794[M-H-Rha-Glc]⁻	Ginsenoside 20(*R*)-Rg_2 [a]
R69	18.38	$C_{62}H_{102}O_{30}$	1325.6383	0.38	1239.6388[M-H-Malonyl]⁻, 1107.59573[M-H-Malonyl-Xyl]⁻, 945.5438[M-H-Malonyl-Xyl-Glc]⁻, 783.4890[M-H-Malonyl-Xyl-2Glc]⁻, 621.4385[M-H-Malonyl-Xyl-3Glc]⁻, 459.3852[M-H-Malonyl-Xyl-4Glc]⁻	Malonyl-notoginsenoside R_4 isomer/Malonyl-ginsenoside Ra_3 isomer
R70	18.46	$C_{53}H_{90}O_{22}$	1077.5848	0.28	945.5436[M-H-Ara(f)]⁻, 783.4905[M-H-Ara(f)-Glc]⁻, 621.4355[M-H-Ara(f)-2Glc]⁻, 459.3866[M-H-Ara(f)-3Glc]⁻	Ginsenoside Rc [a]
R71	18.48	$C_{36}H_{62}O_9$	637.4325	1.41	475.3795[M-H-Glc]⁻	Ginsenoside 20(*R*)-Rh_1 [a]
R72	18.54	$C_{58}H_{98}O_{26}$	1209.6263	-0.41	1077.5829[M-H-Xyl]⁻, 945.5496[M-H-Xyl-Ara(p)]⁻, 783.4918[M-H-Xyl-Ara(p)-Glc]⁻, 621.4398[M-H-Xyl-Ara(p)-2Glc]⁻, 459.3823[M-H-Xyl-Ara(p)-3Glc]⁻	Ginsenoside Ra_1 [a]
R73	18.58	$C_{57}H_{94}O_{26}$	1193.5953	-0.17	1107.5951[M-H-Malonyl]⁻, 945.5403[M-H-Malonyl-Glc]⁻, 783.4901[M-H-Malonyl-2Glc]⁻, 621.4357[M-H-Malonyl-3Glc]⁻, 459.3842[M-H-Malonyl-4Glc]⁻	Malonyl-ginsenoside Rb_1 isomer
R74	18.70	$C_{48}H_{76}O_{19}$	955.4907	0.42	793.4379[M-H-Glc]⁻, 731.4362[M-H-Glc-CO_2-H_2O]⁻, 613.3737[M-H-2Glc-H_2O]⁻, 569.3851[M-H-2Glc-H_2O-CO_2]⁻,	Ginsenoside Ro [a]

					455.3528[M-H-2Glc-Glu A]$^-$	
R75	18.78	$C_{56}H_{92}O_{25}$	1163.5842	-0.60	1077.5850[M-H-Malonyl]$^-$, 945.5405[M-H-Malonyl-Ara(f)]$^-$, 783.4891[M-H-Malonyl-Ara(f)-Glc]$^-$, 621.4354[M-H-Malonyl-Ara(f)-2Glc]$^-$, 459.3852[M-H-Malonyl-Ara(f)-3Glc]$^-$	Malonyl-ginsenoside Rc
R76	18.86	$C_{58}H_{98}O_{26}$	1209.6248	-1.65	1077.5869[M-H-Xyl]$^-$, 945.5433[M-H-Xyl-Ara]$^-$, 783.4961[M-H-Xyl-Ara-Glc]$^-$, 621.4344[M-H-Xyl-Ara-2Glc]$^-$, 459.3845[M-H-Xyl-Ara-3Glc]$^-$	Ginsenoside Ra_1 isomer/Ginsenoside Ra_2 isomer
R77	18.96	$C_{62}H_{102}O_{30}$	1325.6382	0.30	1239.6331[M-H-Malonyl]$^-$, 1107.5958[M-H-Malonyl-Xyl]$^-$, 945.5432[M-H-Malonyl-Xyl-Glc]$^-$, 783.4890[M-H-Malonyl-Xyl-2Glc]$^-$, 621.4368[M-H-Malonyl-Xyl-3Glc]$^-$, 459.3842[M-H-Malonyl-Xyl-4Glc]$^-$	Malonyl-notoginsenoside R_4 isomer/Malonyl-ginsenoside Ra_3 isomer
R78	19.03	$C_{58}H_{98}O_{26}$	1209.6252	-1.32	1077.5842[M-H-Xyl]$^-$, 945.5430[M-H-Xyl-Ara]$^-$, 783.4901[M-H-Xyl-Ara-Glc]$^-$, 621.4365[M-H-Xyl-Ara-2Glc]$^-$, 459.3849[M-H-Xyl-Ara-3Glc]$^-$	Ginsenoside Ra_1 isomer/Ginsenoside Ra_2 isomer
R79	19.03	$C_{57}H_{94}O_{26}$	1193.5946	-0.75	1107.6008[M-H-Malonyl]$^-$, 945.5464[M-H-Malonyl-Glc]$^-$, 783.4849[M-H-Malonyl-2Glc]$^-$, 621.4401[M-H-Malonyl-3Glc]$^-$, 459.3840[M-H-Malonyl-4Glc]$^-$	Malonyl-ginsenoside Rb_1 isomer
R80	19.07	$C_{47}H_{74}O_{18}$	925.4801	0.43	793.4316[M-H-Xyl/Ara]$^-$, 613.3721[M-H-Xyl/Ara(f)-Glc-H_2O]$^-$, 455.3538[M-H-Xyl/Ara(f)-Glc-GluA]$^-$	Pseudo-ginsenoside-RT_1
R81	19.10	$C_{53}H_{90}O_{22}$	1077.5848	0.28	945.5414[M-H-Ara(p)]$^-$, 783.4916[M-H-Ara(p)-Glc]$^-$, 621.4418[M-H-Ara(p)-2Glc]$^-$, 459.3886[M-H-Ara(p)-3Glc]$^-$	Ginsenoside Rb_2 [a]
R82	19.28	$C_{53}H_{90}O_{22}$	1077.5854	0.84	945.5438[M-H-Xyl]$^-$, 783.4904[M-H-Xyl-Glc]$^-$, 621.4388[M-H-Xyl-2Glc]$^-$, 459.3851[M-H-Xyl-3Glc]$^-$	Ginsenoside Rb_3 [a]
R83	19.39	$C_{56}H_{92}O_{25}$	1163.5847	-0.17	1077.5853[M-H-Malonyl]$^-$, 945.5468[M-H-Malonyl-Ara(p)]$^-$, 783.4906[M-H-Malonyl-Ara(p)-Glc]$^-$	Malonyl-ginsenoside Rb_2

					, 621.4352[M-H-Malonyl-Ara(p)-2Glc]-, 459.3855[M-H-Malonyl-Ara(p)-3Glc]-	
R84	19.45	$C_{47}H_{74}O_{18}$	925.4797	0.00	793.4379[M-H-Xyl]-, 613.3748[M-H-Xyl-Glc-H_2O]-, 455.3550[M-H-Xyl-Glc-Glu A]-	Pseudoginsenoside-RT_1
R85	19.55	$C_{56}H_{92}O_{25}$	1163.5849	0.00	1077.5847[M-H-Malonyl]-, 945.5458[M-H-Malonyl-Xyl]-, 783.4883[M-H-Malonyl-Xyl-Glc]-, 621.4370[M-H-Malonyl-Xyl-2Glc]-, 459.3842[M-H-Malonyl-Xyl-3Glc]-	Malonyl-ginsenoside Rb_3
R86	19.76	$C_{56}H_{94}O_{24}$	1149.6056	-0.09	1107.5984[M-H-Ac]-, 945.5443[M-H-Ac-Glc]-, 783.4930[M-H-Ac-2Glc]-, 621.4387[M-H-Ac-3Glc]-, 459.3842 [M-H-Ac-4Glc]-	Quinquenoside R_1 [a]
R87	19.84	$C_{42}H_{66}O_{14}$	793.4377	0.38	631.3846[M-H-Glc]-, 455.3521[M-H-Glc-Glu A]-	Chikusetsusaponin IV_a isomer
R88	19.99	$C_{56}H_{94}O_{24}$	1149.6072	1.30	1107.5972[M-H-Ac]-, 945.5375[M-H-Ac-Glc]-, 783.5005[M-H-Ac-2Glc]-, 621.4395[M-H-Ac-3Glc]-, 459.3839[M-H-Ac-4Glc]-	Quinquenoside R_1 isomer
R89	20.25	$C_{42}H_{66}O_{14}$	793.4368	-0.76	631.3853[M-H-Glc]-, 455.3568[M-H-Glc-Glu A]-	Chikusetsusaponin IV_a
R90	20.28	$C_{60}H_{100}O_{27}$	1251.6389	1.20	1209.6250[M-H-Ac]-, 1077.5850[M-H-Ac-Xyl]-, 945.5430[M-H-Ac-Xyl-ara(p)]-, 783.4898[M-H-Ac-Xyl-ara(p)-Glc]-, 621.4366[M-H-Ac-Xyl-ara(p)-2Glc]-, 459.3861[M-H-Ac-Xyl-ara(p)-3Glc]-	Ginsenoside Ra_5
R91	20.38	$C_{55}H_{92}O_{23}$	1119.5959	0.71	1077.5864[M-H-Ac]-, 945.5432[M-H-Ac-Ara(f)]-, 783.4931[M-H-Ac-Ara(f)-Glc]-, 621.4388[M-H-Ac-Ara(f)-2Glc]-, 459.3846[M-H-Ac-Ara(f)-3Glc]-	Ginsenoside Rs_2 [a]
R92	20.47	$C_{48}H_{82}O_{18}$	945.5430	0.74	783.4905[M-H-Glc]-, 621.4374[M-H-2Glc]-, 459.3848[M-H-3Glc]-	Ginsenoside Rd [a]
R93	20.70	$C_{60}H_{100}O_{27}$	1251.6397	1.84	1209.6279[M-H-Ac]-, 1077.5851[M-H-Ac-Xyl]-, 945.5422[M-H-Ac-Xyl-ara(p)]-,	Ginsenoside Ra_5 isomer

					783.4895[M-H-Ac-Xyl-ara(p)-Glc]$^-$, 621.4377[M-H-Ac-Xyl-ara(p)-2Glc]$^-$, 459.3824[M-H-Ac-Xyl-ara(p)-3Glc]$^-$	
R94	20.75	$C_{51}H_{84}O_{21}$	1031.5425	-0.19	945.5433[M-H-Malonyl]$^-$, 783.4901[M-H-Malonyl-Glc]$^-$, 621.4374[M-H-Malonyl-2Glc]$^-$, 459.3849[M-H-Malonyl-3Glc]$^-$	Malonyl-ginsenoside Rd
R95	20.91	$C_{50}H_{84}O_{19}$	987.5528	-0.10	945.5475[M-H-Ac]$^-$, 783.4435[M-H-Ac-Glc]$^-$, 621.3635[M-H-Ac-2Glc]$^-$, 459.3287[M-H-Ac-3Glc]$^-$	Acetyl-ginsenoside Rd
R96	20.95	$C_{56}H_{94}O_{24}$	1149.6045	-1.04	1107.5840[M-H-Ac]$^-$, 945.5441[M-H-Ac-Glc]$^-$, 783.4883[M-H-Ac-2Glc]$^-$, 621.4357[M-H-Ac-3Glc]$^-$, 459.3830[M-H-Ac-4Glc]$^-$	Quinquenoside R_1 isomer
R97	20.99	$C_{47}H_{74}O_{18}$	925.4813	1.73	793.4382[M-H-Xyl/Ara]$^-$, 613.3756[M-H-Xyl/AraGlc-H_2O]$^-$, 455.3536[M-H-Xyl/Ara-Glc-Glu A]$^-$	Pseudo-ginsenoside-RT_1 isomer/Chikusetsusaponin IV isomer
R98	20.95	$C_{55}H_{92}O_{23}$	1119.5952	0.09	1077.5868[M-H-Ac]$^-$, 945.5418[M-H-Ac-Ara(p)]$^-$, 783.4923[M-H-Ac-Ara(p)-Glc]$^-$, 621.4371[M-H-Ac-Ara(p)-2Glc]$^-$, 459.3832[M-H-Ac-Ara(p)-3Glc]$^-$	Ginsenoside Rs_2 isomer
R99	21.11	$C_{62}H_{102}O_{27}$	1277.6539	0.70	1209.6308[M-H-(*E*)-but-2-enoyl]$^-$, 1077.5824[M-H-(*E*)-but-2-enoyl-Xyl]$^-$, 945.5358[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)]$^-$, 783.4861[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)-Glc]$^-$, 621.4417[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)-2Glc]$^-$, 459.3851[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)-3Glc]$^-$	Ginsenoside Ra_4 isomer
R100	21.23	$C_{53}H_{86}O_{22}$	1073.5527	-0.47	945.5427[M-H-Malonyl-Ac]$^-$, 783.4915[M-H-Malonyl-Ac-Glc]$^-$, 621.4370[M-H-Malonyl-Ac-2Glc]$^-$, 459.3838[M-H-Malonyl-Ac-3Glc]$^-$	Acetyl+Malonyl+Ginsenoside Rd
R101	21.41	$C_{58}H_{96}O_{24}$	1175.6215	0.17	1107.5950[M-H-(*E*)-but-2-enoyl]$^-$, 945.5409[M-H-(*E*)-but-2-enoyl-Glc]$^-$, 783.4881[M-H-(*E*)-but-2-enoyl-2Glc]$^-$,	Ginsenoside Ra_6

					621.4368[M-H-(*E*)-but-2-enoyl-3Glc]⁻, 459.3838[M-H-(*E*)-but-2-enoyl-4Glc]⁻	
R102	21.44	$C_{60}H_{100}O_{27}$	1251.6384	0.80	1209.6195[M-H-Ac]⁻, 1077.5830[M-H-Ac-Xyl]⁻, 945.5414[M-H-Ac-Xyl-ara(p)]⁻, 783.4885[M-H-Ac-Xyl-ara(p)-Glc]⁻, 621.4354[M-H-Ac-Xyl-ara(p)-2Glc]⁻, 459.3880[M-H-Ac-Xyl-ara(p)-3Glc]⁻	Ginsenoside Ra_5 isomer
R103	21.50	$C_{46}H_{76}O_{15}$	867.5113	0.81	799.4869[M-H-(*E*)-but-2-enoyl]⁻, 637.4230[M-H-(*E*)-but-2-enoyl-Glc]⁻, 475.3830[M-H-(*E*)-but-2-enoyl-2Glc]⁻	Koryoginsenoside R_1/Ginsenoside Re_6
R104	21.54	$C_{48}H_{82}O_{18}$	945.5416	-0.74	783.4899[M-H-Glc]⁻, 621.4362[M-H-2Glc]⁻, 459.3837[M-H-3Glc]⁻	Ginsenoside Rd isomer
R105	21.74	$C_{58}H_{96}O_{24}$	1175.6213	0.00	1107.4648[M-H-(*E*)-but-2-enoyl]⁻, 27945.5414[M-H-(*E*)-but-2-enoyl-Glc]⁻, 783.4913[M-H-(*E*)-but-2-enoyl-2Glc]⁻, 621.4352[M-H-(*E*)-but-2-enoyl-3Glc]⁻, 459.3857[M-H-(*E*)-but-2-enoyl-4Glc]⁻,	Ginsenoside Ra_6 isomer
R106	21.84	$C_{53}H_{86}O_{22}$	1073.5527	-0.47	987.5481[M-H-Malonyl]⁻, 945.5444[M-H-Malonyl-Ac]⁻, 783.4901[M-H-Malonyl-Ac-Glc]⁻, 621.4376[M-H-Malonyl-Ac-2Glc]⁻, 459.3846[M-H-Malonyl-Ac-3Glc]⁻	Acetyl+Malonyl+Ginsenoside Rd
R107	21.85	$C_{52}H_{86}O_{20}$	1029.5642	0.78	945.5521[M-H-2Ac]⁻, 783.5035[M-H-2Ac-Glc]⁻, 621.4399[M-H-2Ac-2Glc]⁻, 459.3840[M-H-2Ac-3Glc]⁻	Acetyl-pseudo-ginsenoside RC_1
R108	21.86	$C_{62}H_{102}O_{27}$	1277.6537	0.55	1209.6394[M-H-(*E*)-but-2-enoyl]⁻, 1077.5834[M-H-(*E*)-but-2-enoyl-Xyl]⁻, 945.5376[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)]⁻, 783.4856[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)-Glc]⁻, 621.4391[M-H-(*E*)-but-2-enoyl-Xyl-	Ginsenoside Ra_4

					ara(p)-2Glc]$^-$, 459.3857[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)-3Glc]$^-$	
R109	22.05	$C_{57}H_{94}O_{23}$	1145.6122	1.22	1077.5836[M-H-(*E*)-but-2-enoyl]$^-$, 945.5428[M-H-(*E*)-but-2-enoyl-Ara]$^-$, 783.4880[M-H-(*E*)-but-2-enoyl-Ara-Glc]$^-$, 621.4377[M-H-(*E*)-but-2-enoyl-Ara-2Glc]$^-$, 459.3861[M-H-(*E*)-but-2-enoyl-Ara-3Glc]$^-$	Ginsenoside Ra_7/Ginsenoside Ra_8/Ginsenoside Ra_9
R110	22.06	$C_{58}H_{96}O_{25}$	1191.6165	0.25	945.5482[M-H-2Ac-Glc]$^-$, 783.4897[M-H-2Ac-2Glc]$^-$, 621.4391[M-H-2Ac-3Glc]$^-$, 459.3807[M-H-2Ac-4Glc]$^-$	Acetyl-quinquenoside R_1
R111	22.11	$C_{52}H_{86}O_{20}$	1029.5645	1.07	945.5443[M-H-2Ac]$^-$, 783.4893[M-H-2Ac-Glc]$^-$, 621.4373[M-H-2Ac-2Glc]$^-$, 459.3841[M-H-2Ac-3Glc]$^-$	Acetyl-pseudo-ginsenoside RC_1
R112	22.13	$C_{48}H_{82}O_{18}$	945.5441	1.90	783.4899[M-H-Glc]$^-$, 621.4385[M-H-2Glc]$^-$, 459.3848[M-H-3Glc]$^-$	Ginsenoside Rd isomer
R113	22.13	$C_{49}H_{78}O_{19}$	969.5059	0.00	807.4559[M-H-Glc]$^-$, 645.4022[M-H-2Glc]$^-$, 455.3533[M-H-2Glc-CH_2-Glu A]$^-$	Ginsenoside Ro methyl ester [a]
R114	22.37	$C_{58}H_{96}O_{25}$	1191.6169	0.59	945.5467[M-H-2Ac-Glc]$^-$, 783.4882[M-H-2Ac-2Glc]$^-$, 621.4377[M-H-2Ac-3Glc]$^-$, 459.3858[M-H-2Ac-4Glc]$^-$	Acetyl-quinquenoside R_1 isomer
R115	22.38	$C_{58}H_{96}O_{24}$	1175.6218	0.43	1107.5952[M-H-(*E*)-but-2-enoyl]$^-$, 945.5443[M-H-(*E*)-but-2-enoyl-Glc]$^-$, 783.4917[M-H-(*E*)-but-2-enoyl-2Glc]$^-$, 621.4363[M-H-(*E*)-but-2-enoyl-3Glc]$^-$, 459.3848[M-H-(*E*)-but-2-enoyl-4Glc]$^-$	Ginsenoside Ra_6 isomer
R116	22.53	$C_{47}H_{80}O_{17}$	915.5324	0.76	783.4891[M-H-Xyl]$^-$, 621.4368[M-H-Xyl-Glc]$^-$, 459.3842[M-H-Xyl-2Glc]$^-$	Vina-ginsenoside R_{16}
R117	22.55	$C_{57}H_{94}O_{23}$	1145.6121	1.13	1077.5864[M-H-(*E*)-but-2-enoyl]$^-$, 945.5388[M-H-(*E*)-but-2-enoyl-Ara]$^-$	Ginsenoside Ra_7/Ginsenoside

					, 783.4950[M-H-(*E*)-but-2-enoyl-Ara-Glc]⁻, 621.4338[M-H-(*E*)-but-2-enoyl-Ara-2Glc]⁻, 459.3842[M-H-(*E*)-but-2-enoyl-Ara-3Glc]⁻	Ra_8/Ginsenoside Ra_9
R118	22.55	$C_{58}H_{96}O_{25}$	1191.6167	0.42	945.5460[M-H-2Ac-Glc]⁻, 783.4899[M-H-2Ac-2Glc]⁻, 621.4369[M-H-2Ac-3Glc]⁻, 459.3852[M-H-2Ac-4Glc]⁻	Acetyl-quinquenoside R_1 isomer
R119	22.61	$C_{47}H_{80}O_{17}$	915.5328	1.20	783.4875[M-H-Xyl]⁻, 621.4374[M-H-Xyl-Glc]⁻, 459.3851[M-H-Xyl-2Glc]⁻	Gypenoside IX
R120	22.65	$C_{62}H_{102}O_{27}$	1277.6533	0.23	1209.6272[M-H-(*E*)-but-2-enoyl]⁻, 1077.5864[M-H-(*E*)-but-2-enoyl-Xyl]⁻, 945.5404[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)]⁻, 783.4888[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)-Glc]⁻, 621.4302[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)-2Glc]⁻, 459.3837[M-H-(*E*)-but-2-enoyl-Xyl-ara(p)-3Glc]⁻	Ginsenoside Ra_4 isomer
R121	22.67	$C_{58}H_{96}O_{25}$	1191.6169	0.59	945.5380[M-H-2Ac-Glc]⁻, 783.4918[M-H-2Ac-2Glc]⁻, 621.4365[M-H-2Ac-3Glc]⁻, 459.3831[M-H-2Ac-4Glc]⁻	Acetyl-quinquenoside R_1 isomer
R122	22.72	$C_{47}H_{80}O_{17}$	915.5332	1.64	783.4983[M-H-Ara(f)]⁻, 621.4363[M-H-Ara(f)-Glc]⁻, 459.3858[M-H-Ara(f)-2Glc]⁻	Notoginsenoside Fe
R123	22.72	$C_{53}H_{86}O_{22}$	1073.5532	0.00	945.5435[M-H-Malonyl-Ac]⁻, 783.4878[M-H-Malonyl-Ac-Glc]⁻, 621.4377[M-H-Malonyl-Ac-2Glc]⁻, 459.3854[M-H-Malonyl-Ac-3Glc]⁻	Acetyl+Malonyl+Ginsenoside Rd
R124	22.87	$C_{42}H_{72}O_{13}$	783.4908	1.66	621.4396[M-H-Glc]⁻, 475.3831[M-H-Rha-Glc]⁻	Ginsenoside Rg_2 isomer
R125	22.91	$C_{57}H_{94}O_{23}$	1145.6123	1.31	1077.5928[M-H-(*E*)-but-2-enoyl]⁻, 945.5350[M-H-(*E*)-but-2-enoyl-Ara]⁻, 783.4876[M-H-(*E*)-but-2-enoyl-Ara-Glc]⁻, 621.4327[M-H-(*E*)-but-2-enoyl-Ara-	Ginsenoside Ra_7/Ginsenoside Ra_8/Ginsenoside Ra_9

					2Glc]$^-$, 459.3839[M-H-(*E*)-but-2-enoyl-Ara-3Glc]$^-$	
R126	23.24	$C_{53}H_{86}O_{22}$	1073.5530	-0.19	987.5375[M-H-Malonyl]$^-$, 945.5438[M-H-Malonyl-Ac]$^-$, 783.4887[M-H-Malonyl-Ac-Glc]$^-$, 621.4371[M-H-Malonyl-Ac-2Glc]$^-$, 459.3844[M-H-Malonyl-Ac-3Glc]$^-$	Acetyl+Malonyl+Ginsenoside Rd
R127	23.25	$C_{57}H_{94}O_{23}$	1145.6089	-1.66	1077.5844[M-H-(*E*)-but-2-enoyl]$^-$, 945.5438[M-H-(*E*)-but-2-enoyl-Ara]$^-$, 783.4897[M-H-(*E*)-but-2-enoyl-Ara-Glc]$^-$, 621.4393[M-H-(*E*)-but-2-enoyl-Ara-2Glc]$^-$, 459.3865[M-H-(*E*)-but-2-enoyl-Ara-3Glc]$^-$	Ginsenoside Ra_7 ismoer/Ginsenoside Ra_8 isomer/Ginsenoside Ra_9 isomer
R128	23.25	$C_{58}H_{96}O_{25}$	1191.6168	0.50	945.5350[M-H-2Ac-Glc]$^-$, 783.4876[M-H-2Ac-2Glc]$^-$, 621.4327 [M-H-2Ac-3Glc]$^-$, 459.3839[M-H-2Ac-4Glc]$^-$	Acetyl-quinquenoside R_1 isomer
R129	23.36	$C_{42}H_{70}O_{12}$	765.4796	0.91	619.4214[M-H-Rha]$^-$, 457.3696[M-H-Rha-Glc]$^-$	Ginsenoside F4 [a]
R130	23.38	$C_{42}H_{66}O_{14}$	793.4376	0.25	631.3884[M-H-Glc]$^-$, 455.3553[M-H-Glc-Glu A]$^-$	Zingibroside R_1 isomer
R131	23.56	$C_{48}H_{81}O_{17}$	929.5485	1.18	783.4911[M-H-Rha]$^-$, 621.4376[M-H-Rha-Glc]$^-$, 459.3846[M-H-Rha-2Glc]$^-$	Protopanaxadiol+Rha+2Glc
R132	23.60	$C_{58}H_{96}O_{25}$	1191.6167	0.42	945.5438[M-H-2Ac-Glc]$^-$, 783.4897[M-H-2Ac-2Glc]$^-$, 621.4393 [M-H-2Ac-3Glc]$^-$, 459.3865[M-H-2Ac-4Glc]$^-$	Acetyl-quinquenoside R_1 isomer
R133	23.64	$C_{42}H_{70}O_{12}$	765.4795	0.78	619.4216[M-H-Rha]$^-$, 457.3698[M-H-Rha-Glc]$^-$	Ginsenoside Rg6 [a]
R134	23.73	$C_{48}H_{82}O_{18}$	945.5425	0.21	783.4922[M-H-Glc]$^-$, 621.4371[M-H-2Glc]$^-$, 459.3831[M-H-3Glc]$^-$	Ginsenoside Rd isomer
R135	23.92	$C_{44}H_{74}O_{14}$	825.5000	0.00	783.4901[M-H-Ac]$^-$, 621.4351[M-H-Ac-Glc]$^-$, 459.3853[M-H-Ac-2Glc]$^-$	Acetyl-ginsenoside Rg_3
R136	24.04	$C_{42}H_{66}O_{14}$	793.4367	-0.88	631.3837[M-H-Glc]$^-$, 455.3500[M-H-Glc-Glu A]$^-$	Zingibroside R_1
R137	24.28	$C_{44}H_{74}O_{14}$	825.5006	0.73	783.4900[M-H-Ac]$^-$, 621.4313[M-H-Ac-Glc]$^-$,	Acetyl-ginsenoside Rg_3

					459.3844[M-H-Ac-2Glc]$^-$	
R138	24.49	$C_{42}H_{66}O_{14}$	793.4380	0.76	631.3829[M-H-Glc]$^-$, 455.3611[M-H-Glc-Glu A]$^-$	Zingibroside R_1 isomer
R139	24.68	$C_{42}H_{72}O_{13}$	783.4904	1.15	621.4378[M-H-Glc]$^-$, 459.3845[M-H-2Glc]$^-$	Ginsenoside 20(*S*)-Rg_3 [a]
R140	24.72	$C_{44}H_{74}O_{14}$	825.5006	0.73	783.4950[M-H-Ac]$^-$, 621.4360[M-H-Ac-Glc]$^-$, 459.3793[M-H-Ac-2Glc]$^-$	Acetyl-ginsenoside Rg_3
R141	24.87	$C_{42}H_{72}O_{13}$	783.4903	1.02	621.4376[M-H-Glc]$^-$, 459.3851[M-H-2Glc]$^-$	Ginsenoside 20(*R*)-Rg_3 [a]
R142	25.48	$C_{41}H_{70}O_{12}$	753.4779	-1.33	621.4398[M-H-Ara]$^-$ 459.3819[M-H-Ara-Glc]$^-$	Ginsenoside MC
R143	25.87	$C_{65}H_{100}O_{21}$	1215.6663	-1.32	955.4944[M-H-Polyacetylene]$^-$, 793.4407[M-H-Polyacetylene-Glc]$^-$, 455.3534[M-H-Polyacetylene-2Glc-Glu A]$^-$	Polyacetyleneginsenoside -Ro isomer
R144	26.04	$C_{65}H_{100}O_{21}$	1215.6658	-1.73	793.4395[M-H-Polyacetylene-Glc]$^-$, 455.3527[M-H-Polyacetylene-2Glc-Glu A]$^-$	Polyacetyleneginsenoside -Ro isomer
R145	26.17	$C_{36}H_{62}O_8$	621.4362	-0.64	459.3872[M-H-Glc]$^-$	Ginsenoside Compound K
R146	26.19	$C_{65}H_{100}O_{21}$	1215.6680	0.08	955.4922[M-H-Polyacetylene]$^-$, 793.4376[M-H-Polyacetylene-Glc]$^-$, 455.3531[M-H-Polyacetylene-2Glc-Glu A]$^-$	Polyacetyleneginsenoside -Ro
R147	27.14	$C_{36}H_{62}O_8$	621.4360	-0.97	459.3807[M-H-Glc]$^-$	Ginsenoside 20(*S*)-Rh_2 [a]
R148	27.27	$C_{36}H_{62}O_8$	621.4371	0.80	459.3869[M-H-Glc]$^-$	Ginsenoside 20(*R*)-Rh_2 [a]
Saponins from *Astragali Radix*						
H1	14.71	$C_{47}H_{78}O_{19}$	945.5070	1.16	783.4504[M-H-Glc]$^-$, 489.3577[M-H-2Glc-Xyl]$^-$	Astragaloside VII
H2	16.03	$C_{47}H_{78}O_{19}$	945.5063	0.42	783.4534[M-H-Glc]$^-$, 489.3585[M-H-2Glc-Xyl]$^-$	Astragaloside V
H3	16.67	$C_{49}H_{80}O_{20}$	987.5167	0.20	945.5074[M-H-Ac]$^-$, 927.4952[M-H-Ac-H_2O]$^-$, 783.4525[M-H-Ac-Glc]$^-$, 765.4435[M-H-Ac-Glc-H_2O]$^-$, 621.3989[M-H-Ac-2Glc]$^-$, 489.3623[M-H-Ac-2Glc-Xyl]$^-$	Agroastragaloside IV isomer
H4	16.90	$C_{41}H_{68}O_{14}$	783.4536	-0.64	621.3996[M-H-Glc]$^-$, 489.3577[M-H-Glc-Xyl]$^-$	Isoastragaloside IV
H5	17.11	$C_{49}H_{80}O_{20}$	987.5170	0.51	945.5097[M-H-Ac]$^-$, 783.4512[M-H-Ac-Glc]$^-$, 489.3643[M-H-Ac-2Glc-Xyl]$^-$	Agroastragaloside IV isomer

H6	17.69	$C_{49}H_{80}O_{20}$	987.5159	-0.61	945.5087 [M-H-Ac]$^-$, 927.4955[M-H-Ac-H_2O]$^-$, 783.4543[M-H-Ac-Glc]$^-$, 765.4478[M-H-Ac-Glc-H_2O]$^-$, 621.3989[M-H-Ac-2Glc]$^-$, 489.3623[M-H-Ac-2Glc-Xyl]$^-$	Agroastragaloside IV isomer
H7	17.77	$C_{43}H_{70}O_{15}$	825.4646	1.21	783.4485[M-H-Ac]$^-$, 621.3974[M-H-Ac-Glc]$^-$, 489.3589[M-H-Ac-Glc-Xyl]$^-$	Astragaloside II isomer
H8	18.28	$C_{51}H_{82}O_{21}$	1029.5266	-0.39	945.5078[M-H-2Ac]$^-$, 927.4976[M-H-2Ac-H_2O]$^-$, 783.4511[M-H-2Ac-Glc]$^-$, 765.4457[M-H-2Ac-Glc-H_2O]$^-$	Agroastragaloside III isomer
H9	18.40	$C_{47}H_{78}O_{19}$	945.5051	-0.85	783.4573[M-H-Glc]$^-$, 489.3593[M-H-2Glc-Xyl]$^-$	Astragaloside VI
H10	18.72	$C_{51}H_{82}O_{21}$	1029.5265	-0.49	927.5116[M-H-2Ac-H_2O]$^-$, 765.4478[M-H-2Ac-H_2O-Glc]$^-$	Agroastragaloside III isomer
H11	18.80	$C_{43}H_{70}O_{15}$	825.4640	0.48	783.4541 [M-H-Ac]$^-$, 621.3977[M-H-Ac-Glc]$^-$, 489.3585[M-H-Ac-Glc-Xyl]$^-$	Astragaloside II isomer
H12	19.48	$C_{49}H_{80}O_{20}$	987.5172	0.71	945.5061 [M-H-Ac]$^-$, 927.4971[M-H-Ac-H_2O]$^-$, 783.4526[M-H-Ac-Glc]$^-$, 765.4396[M-H-Ac-H_2O-Glc]$^-$, 621.4099[M-H-Ac-2Glc]$^-$, 489.3492[M-H-Ac-2Glc-Xyl]$^-$	Agroastragaloside IV isomer
H13	19.72	$C_{41}H_{68}O_{14}$	783.4535	0.51	621.3884[M-H-Glc]$^-$, 489.3532[M-H-Glc-Xyl]$^-$	Astragaloside IV [a]
H14	19.90	$C_{43}H_{70}O_{15}$	825.4645	1.09	783.4624[M-H-Ac]$^-$, 621.3972[M-H-Ac-Glc]$^-$, 489.3575[M-H-Ac-Glc-Xyl]$^-$	Astragaloside II isomer
H15	20.22	$C_{49}H_{80}O_{20}$	987.5171	0.61	945.5200[M-H-Ac]$^-$, 783.4661[M-H-Ac-Glc]$^-$, 489.3623[M-H-Ac-2Glc-Xyl]$^-$	Agroastragaloside IV isomer
H16	20.64	$C_{43}H_{70}O_{15}$	825.4642	0.73	783.4567[M-H-Ac]$^-$, 489.3588[M-H-Ac-Glc-Xyl]$^-$	Astragaloside II isomer
H17	20.70	$C_{51}H_{82}O_{21}$	1029.5267	-0.29	945.5063[M-H-2Ac]$^-$, 927.4969[M-H-2Ac-H_2O]$^-$, 783.4714[M-H-2Ac-Glc]$^-$, 765.4423[M-H-2Ac-Glc-H_2O]$^-$, 621.4058783.4714[M-H-2Ac-2Glc]$^-$	Agroastragaloside III
H18	21.44	$C_{43}H_{70}O_{15}$	825.4644	0.97	783.4563[M-H-Ac]$^-$, 621.3985[M-H-Ac-Glc]$^-$, 489.3577[M-H-Ac-Glc-Xyl]$^-$	Astragaloside II [a]

H19	21.62	$C_{43}H_{70}O_{15}$	825.4639	0.36	783.4533[M-H-Ac]$^-$, 621.3995[M-H-Ac-Glc]$^-$, 489.3585[M-H-Ac-Glc-Xyl]$^-$	Astragaloside II isomer
H20	22.17	$C_{47}H_{76}O_{17}$	911.5016	1.32	765.4301[M-H-Rha]$^-$	Astragaloside VIII
H21	22.23	$C_{49}H_{80}O_{20}$	987.5167	0.20	945.5215[M-H-Ac]$^-$, 783.4659[M-H-Ac-Glc]$^-$, 489.3621[M-H-Ac-2Glc-Xyl]$^-$	Agroastragaloside IV
H22	22.25	$C_{48}H_{78}O_{18}$	941.5106	-0.42	795.4499[M-H-Rha]$^-$	Soyasaponin I
H23	22.96	$C_{45}H_{72}O_{16}$	867.4746	0.46	765.5357[M-H-2Ac-H_2O]$^-$	Astragaloside I
H24	23.44	$C_{47}H_{76}O_{17}$	911.5011	0.77	765.4304[M-H-Rha]$^-$	Astragaloside VIII isomer
H25	23.61	$C_{47}H_{74}O_{17}$	909.4855	0.77	783.4506[M-H-3Ac]$^-$, 765.4476[M-H-3Ac-H_2O]$^-$	Acetylastragaloside I

a: Compound identified by comparison with the reference standards .

Table S2 Flavonoids from ZKYY

No.	t_R (min)	Molecular formula	Measured value (*m/z*)	Diff (ppm)	Product ions	Compound name
Flavonoids from *Astragali Radix*						
H26	5.31	$C_{22}H_{22}O_{11}$	461.1090	1.30	299.0554[M-H-Glc]$^-$, 284.0328[M-H-Glc-CH_3]$^-$	Kaempferol-4′-methoxy-3-O-β-D-glucopyranoside isomer
H27	6.56	$C_{25}H_{28}O_{11}$	503.1558	0.99	299.0563[M-H-(6'-acetyl)Glc]$^-$, 284.0327[M-H-(6'-acetyl)Glc-CH_3]$^-$,	(-)-Methylinissolin 3-O-β-D-(6'-acetyl)-glucoside
H28	7.18	$C_{21}H_{20}O_9$	415.1032	0.72	253.0495[M-H-Glc]$^-$	daidzein 7-O-β-D-glucoside
H29	7.39	$C_{22}H_{22}O_{11}$	461.1086	0.43	299.0565[M-H-Glc]$^-$, 284.032354[M-H-Glc-CH_3]$^-$	Kaempferol-4′-methoxy-3-O-β-D-glucopyranoside
H30	7.54	$C_{15}H_{10}O_4$	253.0502	0.40	201.0707[M-H-C_2H_2O]$^-$	Daidzein isomer
H31	7.82	$C_{21}H_{20}O_9$	415.1026	-0.72	253.0503[M-H-Glc]$^-$	daidzein 7-O-β-D-glucoside isomer
H32	7.97	$C_{22}H_{22}O_{10}$	445.1140	1.12	430.0913[M-H-CH_3]$^-$, 283.0595[M-H-Glc]$^-$, 268.0370[M-H-CH_3-Glc]$^-$	calycosin-7-O-β-D-glucoside
H33	8.54	$C_{16}H_{12}O_5$	283.0610	1.41	268.0383[M-H-CH_3]$^-$, 240.0429[M-H-CH_3-CO]$^-$,	Calycosin isomer

					239.0355[M-H-CO_2]$^-$, 224.0489[M-H-CO_2-CH_3]$^-$	
H34	8.58	$C_{21}H_{20}O_{12}$	463.0880	0.65	301.0716[M-H-Glc]$^-$	Quercetin-3-O-β-D-glucopyranoside
H35	8.74	$C_{21}H_{20}O_{12}$	463.0882	1.08	301.0715[M-H-Glc]$^-$	Isoquercitrin
H36	8.93	$C_{22}H_{24}O_{10}$	447.1297	1.34	285.0771[M-H-Glc]$^-$, 270.0541[M-H-Glc-CH_3]$^-$	licoagroside D
H37	8.94	$C_{16}H_{14}O_5$	285.0768	1.75	270.0513[M-H-CH_3]$^-$, 228.0424[M-H-CH_3-C_2H_2O]$^-$	Vesticarpan isomer
H38	9.34	$C_{15}H_{10}O_4$	253.0505	1.58	201.0715[M-H-C_2H_2O]$^-$	Daidzein isomer
H39	9.67	$C_{16}H_{12}O_5$	283.0609	1.06	268.0379[M-H-CH_3]$^-$, 240.0430[M-H-CH_3-CO]$^-$, 239.0351[M-H-CO_2]$^-$, 224.0477[M-H-CO_2-CH_3]$^-$	Calycosin isomer
H40	9.71	$C_{16}H_{12}O_6$	299.0562	2.01	284.0337[M-H-CH_3]$^-$, 256.0366[M-H-CH_3-CO]$^-$	Rhamnocitrin isomer
H41	9.77	$C_{16}H_{14}O_5$	285.0768	1.75	270.0455[M-H-CH_3]$^-$	Vesticarpan isomer
H42	9.89	$C_{16}H_{12}O_5$	283.0611	1.77	268.0383[M-H-CH_3]$^-$, 240.0434[M-H-CH_3-CO]$^-$, 239.0356[M-H-CO_2]$^-$, 224.0482[M-H-CO_2-CH_3]$^-$	Calycosin isomer
H43	10.08	$C_{16}H_{12}O_6$	299.0561	1.67	284.0331[M-H-CH_3]$^-$, 269.0460[M-H-OCH_2]$^-$, 256.0384[M-H-CH_3-CO]$^-$	Rhamnocitrin isomer
H44	10.09	$C_{22}H_{22}O_{11}$	461.1086	0.43	446.0839[M-H-CH_3]$^-$, 299.0558[M-H-Glc]$^-$, 284.0324[M-H-Glc-CH_3]$^-$, 269.0450[M-H-Glc-OCH_2]$^-$, 256.0392[M-H-Glc-CH_3-CO]$^-$	Rhamnocitin-3-O-β-D-glucopyranoside isomer
H45	10.20	$C_{15}H_{10}O_4$	253.0503	0.79	201.0710[M-H-C_2H_2O]$^-$	Daidzein isomer
H46	10.21	$C_{16}H_{12}O_5$	283.0609	1.06	268.0381[M-H-CH_3]$^-$, 240.0434[M-H-CH_3-CO]$^-$, 239.0354[M-H-CO_2]$^-$, 224.0488[M-H-CO_2-CH_3]$^{--}$	Calycosin isomer
H47	10.29	$C_{17}H_{14}O_6$	313.0716	1.28	298.0489[M-H-CH_3]$^-$, 283.0254[M-H-OCH_2]$^-$, 270.0534[M-H-CH_3-CO]$^-$, 255.0301[M-H-OCH_2-CO]$^-$	Kumatakenin
H48	10.33	$C_{22}H_{24}O_{10}$	447.1294	0.67	285.0762[M-H-Glc]$^-$	licoagroside D isomer
H49	10.35	$C_{16}H_{14}O_5$	285.0768	1.75	270.0436[M-H-CH_3]$^-$	Vesticarpan isomer

H50	10.40	$C_{16}H_{12}O_6$	299.0561	1.67	284.0326[M-H-CH_3]$^-$	Rhamnocitrin isomer
H51	11.17	$C_{15}H_{10}O_4$	253.0504	1.19	201.0715[M-H-C_2H_2O]$^-$	Daidzein isomer
H52	11.25	$C_{16}H_{12}O_6$	299.0561	1.67	284.0278[M-H-CH_3]$^-$, 269.0359[M-H-OCH_2]$^-$	Rhamnocitrin isomer
H53	11.29	$C_{16}H_{14}O_5$	285.0763	0.00	270.0479[M-H-CH_3]$^-$	Vesticarpan isomer
H54	11.37	$C_{22}H_{22}O_{11}$	461.1090	1.30	299.0571[M-H-Glc]$^-$, 284.0305[M-H-Glc-CH_3]$^-$	Rhamnocitin-3-O-β-D-glucopyranoside isomer
H55	11.50	$C_{15}H_{10}O_5$	269.0455	1.86	241.0504[M-H-CO]$^-$	5,7,4'-Trihydroxy-isoflavonone isomer
H56	11.72	$C_{22}H_{22}O_{11}$	461.1086	0.43	299.0570[M-H-Glc]$^-$, 284.0301[M-H-Glc-CH_3]$^-$	Rhamnocitin-3-O-β-D-glucopyranoside isomer
H57	11.72	$C_{23}H_{24}O_{11}$	475.1240	0.00	267.0659[M-H-Glc-OCH_3-CH_3]	odoratin-7-O- -D-glucopyranoside
H58	11.72	$C_{22}H_{22}O_9$	429.1190	0.93	267.0661[M-H-Glc]$^-$, 252.0432[M-H-Glc-CH_3]$^-$	Ononin
H59	11.77	$C_{15}H_{10}O_4$	253.0505	1.58	201.0712[M-H-C_2H_2O]$^-$	Daidzein
H60	11.77	$C_{22}H_{24}O_{10}$	447.1295	0.89	285.0769[M-H-Glc]$^-$	licoagroside D isomer
H61	11.86	$C_{16}H_{14}O_5$	285.0768	1.75	270.0536[M-H-CH_3]$^-$	Vesticarpan isomer
H62	11.87	$C_{16}H_{12}O_6$	299.0561	1.67	284.0328[M-H-CH_3]$^-$, 269.0454[M-H-OCH_2]$^-$, 256.0379[M-H-CH_3-CO]$^-$	Rhamnocitrin [a]
H63	12.61	$C_{15}H_{10}O_7$	301.0349	0.33	273.0411[M-H-CO]$^-$, 257.0460[M-H-CO_2]$^-$, 245.0458[M-H-2CO]$^-$, 229.0499[M-H-CO_2-CO]$^-$	Quercetin [a]
H64	12.63	$C_{15}H_{10}O_6$	285.0405	2.10	217.0507[M-H-C_3O_2]$^-$	Kaempferol
H65	12.72	$C_{23}H_{26}O_{10}$	461.1450	0.43	299.0939[M-H-Glc]$^-$, 284.0692[M-H-Glc-CH_3]$^-$	(6aR, 11aR)-9,10-Dimethoxypterocarpan-3-O-β-D-glucopyranoside
H66	12.83	$C_{16}H_{12}O_5$	283.0609	1.06	268.0379[M-H-CH_3]$^-$, 240.0431[M-H-CH_3-CO]$^-$, 239.0352[M-H-CO_2]$^-$, 224.0477[M-H-CO_2-CH_3]$^-$	Calycosin

H67	12.84	$C_{16}H_{12}O_6$	299.0562	2.01	284.0337[M-H-CH_3]$^-$	Rhamnocitrin isomer
H68	12.84	$C_{15}H_{10}O_4$	253.0503	0.79	201.0715[M-H-C_2H_2O]$^-$	Daidzein isomer
H69	12.94	$C_{16}H_{14}O_5$	285.0768	1.75	270.0530[M-H-CH_3]$^-$	vesticarpan
H70	13.34	$C_{17}H_{18}O_5$	301.1081	1.66	271.0623[M-H-OCH_2]$^-$, 203.0864[M-H-OCH_2-C_3O_2]$^-$	2′,8-Dihydroxy-4′,7-dimethoxyisoflavan/(3R) -7,2'-Dihydroxy-3',4'-dimethoxyisoflavan/isomucronulatol
H71	13.34	$C_{16}H_{12}O_6$	299.0561	1.67	284.0327[M-H-CH_3]$^-$, 269.0451[M-H-OCH_2]$^-$, 256.0366[M-H-CH_3-CO]$^-$	Rhamnocitrin isomer
H72	13.35	$C_{23}H_{28}O_{10}$	463.1604	0.00	301.1074[M-H-Glc]$^-$, 286.0849[M-H-Glc-CH_3]$^-$, 271.0613[M-H-Glc-2CH_3]$^-$, 256.0374[M-H-Glc-OCH_2]$^-$, 227.0708[M-H-Glc-2CH_3-CO_2]$^-$	3S-(-)-Mucronulatol-7-O-β-D-glucopyranoside/（3R）-7,2’-dihydroxy-3’,4’-dimethoxyisoflavone -7-O-β-D-glucoside
H73	13.36	$C_{16}H_{12}O_4$	267.0662	1.87	252.0430[M-H-CH_3]$^-$, 223.0415[M-H-CO_2]$^-$	Formononetin isomer
H74	13.44	$C_{22}H_{22}O_{11}$	461.1087	0.65	299.0556[M-H-Glc]$^-$, 284.0315[M-H-Glc-CH_3]$^-$, 269.0445299.0556[M-H-Glc-CO]$^-$	Rhamnocitin-3-O-β-D-glucopyranoside
H75	13.61	$C_{16}H_{12}O_6$	299.0562	2.01	284.0328[M-H-CH_3]$^-$	Rhamnocitrin isomer
H76	13.62	$C_{24}H_{24}O_{10}$	471.1295	0.85	267.0671[M-H-(6″-O-acetyl)Glc]$^-$, 252.0419[M-H-(6″-O-acetyl)Glc-CH_3]$^-$	6″-O-acetyl-ononin
H77	14.12	$C_{17}H_{18}O_5$	301.1081	1.66	271.0511[M-H-OCH_2]$^-$, 203.0863[M-H-OCH_2-C_3O_2]$^-$	2′,8-Dihydroxy-4′,7-dimethoxyisoflavan/(3R)-7,2'-Dihydroxy-3',4'-dimethoxyisoflavan/isomucronulatol
H78	14.30	$C_{15}H_{10}O_5$	269.0455	1.86	241.0520[M-H-CO]$^-$	5,7,4'-Trihydroxy-isoflavonone isomer
H79	14.30	$C_{25}H_{28}O_{11}$	503.1556	0.60	299.0942[M-H-(6'-acetyl)Glc]$^-$,	(-)-Methylinissol

					284.0690[M-H-(6'-acetyl)Glc-CH_3]	in 3-O-β-D-(6'-acetyl)-glucoside isomer
H80	14.38	$C_{16}H_{14}O_5$	285.0768	1.75	270.0522[M-H-CH_3]$^-$	Vesticarpan isomer
H81	14.58	$C_{15}H_{10}O_5$	269.0455	1.86	241.0516[M-H-CO]$^-$	5,7,4'-Trihydroxy-isoflavonone
H82	14.96	$C_{17}H_{18}O_5$	301.1081	1.66	286.0861[M-H-CH_3]$^-$, 271.0627[M-H-OCH_2]$^-$, 203.0861[M-H-OCH_2-C_3O_2]$^-$	2′,8-Dihydroxy-4′,7-dimethoxyisoflavan/(3R) -7,2'-Dihydroxy-3',4'-dimethoxyisoflavan/isomucronulatol
H83	15.17	$C_{16}H_{12}O_6$	299.0560	1.34	284.0331[M-H-CH_3]$^-$, 269.0455[M-H-OCH_2]$^-$	Rhamnocitrin isomer
H84	15.25	$C_{17}H_{16}O_6$	315.0873	1.27	285.0409[M-H-OCH_2]$^-$, 257.0464[M-H-OCH_2-CO]$^-$, 241.0522[M-H-OCH_2-CO_2]$^-$, 211.1346[M-H-2OCH_2-CO_2]$^-$	2′,4′-Dihydroxy-5,6-Dimethyisoflavaone
H85	15.51	$C_{16}H_{14}O_5$	285.0768	1.75	270.0480[M-H-CH_3]$^-$	Vesticarpan isomer
H86	15.74	$C_{16}H_{12}O_6$	299.0561	1.67	284.0329[M-H-CH_3]$^-$	Rhamnocitrin isomer
H87	16.42	$C_{16}H_{12}O_5$	283.0611	1.77	268.0377[M-H-CH_3]$^-$, 240.0429[M-H-CH_3-CO]$^-$, 239.0350[M-H-CO_2]$^-$, 224.0482[M-H-CO_2-CH_3]$^-$	Wogonin/Oroxylin A
H88	17.60	$C_{16}H_{12}O_4$	267.0660	1.12	252.0429[M-H-CH_3]$^-$, 223.0405[M-H-CO_2]$^-$	Formononetin
H89	17.78	$C_{16}H_{12}O_6$	299.0556	0.00	284.0340[M-H-CH_3]$^-$, 269.0455[M-H-OCH_2]$^-$	Rhamnocitrin isomer
H90	17.90	$C_{16}H_{14}O_5$	285.0766	1.05	270.0450[M-H-CH_3]$^-$	Vesticarpan isomer
H91	18.45	$C_{16}H_{12}O_6$	299.0560	1.34	284.0325[M-H-CH_3]$^-$, 269.0457[M-H-OCH_2]$^-$	Rhamnocitrin isomer
H92						
Flavonoids from *Corni officinalis*						
S64	5.77	$C_{27}H_{30}O_{15}$	593.1504	-0.34	285.0387[M-H-Gal-Rha]$^-$	Kaempferol-3-O-α-L-rhamnosyl(1-6)-β-D-galactosi

						de isomer
S65	6.03	$C_{21}H_{22}O_{11}$	449.1091	1.56	287.0569[M-H-Glc]$^-$, 269.0457[M-H-$C_6H_{12}O_6$]$^-$	Aromadendrin 7-O-β-D-glucosi de isomer
S66	6.21	$C_{27}H_{30}O_{15}$	593.1508	0.34	431.0997[M-H-Gal]$^-$, 285.0405[M-H-Gal-Rha]$^-$	Kaempferol-3-O-α-L-rhamnosyl(1-6)-β-D-galactosi de isomer
S67	6.91	$C_{21}H_{22}O_{11}$	449.1086	0.45	287.0564[M-H-Glc]$^-$, 269.0456[M-H-$C_6H_{12}O_6$]$^-$, 259.0613[M-H-Glc-CO]$^-$	Aromadendrin 7-O-β-D-glucosi de
S68	7.10	$C_{21}H_{22}O_{11}$	449.1091	1.56	259.0637[M-H-Glc-CO]$^-$	Aromadendrin 7-O-β-D-glucosi de isomer
S69	7.40	$C_{15}H_{12}O_6$	287.0558	0.70	259.0606[M-H-CO]$^-$, 243.0672[M-H-CO_2]$^-$	2R,3R-Trans-aro madendrin
S70	7.53	$C_{27}H_{30}O_{15}$	593.1497	-1.52	285.0407[M-H-Gal-Rha]$^-$, 267.0315[M-H-Gal-Rha-H_2O]$^-$, 241.0507[M-H-Gal-Rha-CO_2]$^-$	Kaempferol-3-O-α-L-rhamnosyl(1-6)-β-D-galactosi de isomer
S71	7.77	$C_{21}H_{22}O_{11}$	449.1089	1.11	287.0569[M-H-Glc]$^-$, 269.0455[M-H-$C_6H_{12}O_6$]$^-$, 259.0633[M-H-Glc-CO]$^-$	Aromadendrin 7-O-β-D-glucosi de isomer
S72	7.77	$C_{27}H_{30}O_{15}$	593.1500	-1.01	285.0414[M-H-Gal-Rha]$^-$, 267.0316[M-H-Gal-Rha-H_2O]$^-$, 241.0513[M-H-Gal-Rha-CO_2]$^-$	Kaempferol-3-O-α-L-rhamnosyl(1-6)-β-D-galactosi de isomer
S73	8.24	$C_{21}H_{18}O_{13}$	477.0670	0.21	301.0374[M-H-GluA]$^-$	Quercetin 3-O-β-D-glucuro nide isomer
S74	8.32	$C_{27}H_{30}O_{16}$	609.1459	0.49	301.0351[M-H-Glc/Gal-Rha]$^-$	Rutin/Naringenin -3-O-α-L-rhamn osyl(1-6)-β-D-ga lactoside
S75	8.45	$C_{27}H_{30}O_{16}$	609.1459	0.49	301.0355[M-H-Glc/Gal-Rha]$^-$	Rutin/Naringenin -3-O-α-L-rhamn osyl(1-6)-β-D-ga lactoside
S76	8.58	$C_{21}H_{20}O_{12}$	463.0880	0.65	301.0347[M-H-Glc/Gal]$^-$, 259.0261[M-H-Glc/Gal-C_2H_2O]$^-$	Quercetin-3-O-β-D-galactopyrano side /Quercetin-3-O-β-D-glucoside
S77	8.65	$C_{21}H_{18}O_{13}$	477.0668	-0.21	301.0358[M-H-GluA]$^-$	Quercetin

						3-O-β-D-glucuronide
S78	8.74	$C_{21}H_{20}O_{12}$	463.0881	0.86	301.0361[M-H-Glc/Gal]$^-$	Quercetin-3-O-β-D-galactopyranoside /Quercetin-3-O-β-D-glucoside
S79	8.80	$C_{21}H_{22}O_{11}$	449.1090	1.34	287.0561[M-H-Glc]$^-$, 269.0466[M-H-$C_6H_{12}O_6$]$^-$	Aromadendrin 7-O-β-D-glucoside isomer
S80	8.92	$C_{27}H_{30}O_{15}$	593.1508	0.34	285.0410[M-H-Gal-Rha]$^-$, 267.0302[M-H-Gal-Rha-H_2O]$^-$, 241.0510[M-H-Gal-Rha-CO_2]$^-$	Kaempferol-3-O-α-L-Rhamnosyl(1-6)-β-D-galactoside
S81	9.07	$C_{20}H_{18}O_{11}$	433.0775	0.92	301.0346[M-H-Xyl]$^-$	Quercetin 3-O-β-D-Xylopyranoside
S82	9.25	$C_{20}H_{18}O_{11}$	433.0773	0.46	301.0346[M-H-Xyl]$^-$	Quercetin 3-O-β-D-Xylopyranoside isomer
S83	9.28	$C_{27}H_{30}O_{15}$	593.1506	0.00	285.0407[M-H-Gal-Rha]$^-$	Kaempferol-3-O-α-L-Rhamnosyl(1-6)-β-D-galactoside isomer
S84	10.18	$C_{15}H_{12}O_6$	287.0560	1.39	243.0652[M-H-CO_2]$^-$	2R,3R-Trans-aromadendrin isomer
S85	11.66	$C_{15}H_{12}O_6$	287.0561	1.74	259.0605[M-H-CO]$^-$	2R,3R-Trans-aromadendrin isomer
S86	11.82	$C_{16}H_{14}O_5$	285.0767	1.40	270.0539[M-H-CH_3]$^-$, 217.0523[M-H-C_3O_2]$^-$	Naringenin-7-O-methylether
S87	14.65	$C_{15}H_{12}O_5$	271.0612	2.21	229.0507[M-H-C_2H_2O]$^-$, 227.0726[M-H-CO_2]$^-$, 203.0862[M-H-C_3O_2]$^-$	Naringenin [a]
Flavonoid from *Chinese yam*						
SY8	19.45	$C_{16}H_{14}O_4$	269.0818	1.49	254.0583[M-H-CH_3]$^-$, 239.0348[M-H-OCH_2]$^-$, 211.0399[M-H-OCH_2-CO]$^-$	3,5-Dimethoxy-2,7-phenanthrenediol

a: Compound identified by comparison with the standard reference.

Table S3 Iridoids from ZKYY

No.	t_R (min)	Molecular formula	Measured value (*m/z*)	Diff (ppm)	Product ions	Compound name
Iridoids from *Rehmanniae Radix*						
D1	1.40	$C_{15}H_{22}O_{10}$	361.1136	0.28	199.0604[M-H-Glc]$^-$, 169.0508[M-H-Glc-CH_2O]$^-$	Catalpol [a]
D2	2.03	$C_{21}H_{32}O_{15}$	523.1665	0.38	199.0614[M-H-2Glc]$^-$, 169.0507[M-H-2Glc-OCH_2]$^-$	Rehmannioside A
D3	2.72	$C_{15}H_{22}O_{10}$	361.1137	0.55	199.0617[M-H-Glc]$^-$ 169.0511[M-H-Glc-CH_2O]$^-$	Monomelittoside
D4	3.12	$C_{27}H_{42}O_{20}$	685.2192	0.15	505.1195[M-H-Glc-H_2O]$^-$, 361.0782[M-H-2Glc]$^-$, 343.0674[M-H-2Glc-H_2O]$^-$, 181.0503[M-H-3Glc-H_2O]$^-$	Rehmannioside D
D5	3.17	$C_{15}H_{24}O_{10}$	363.1295	1.10	201.0711[M-H-Glc]$^-$	Dihydrocatalpo isomer
D6	3.19	$C_9H_{12}O_3$	167.0712	2.39	152.0117[M-H-CH_3]$^-$, 123.0455[M-H-CO_2]$^-$, 108.0218[M-H-CH_3-CO_2]$^-$	6β-hydroxy-2-oxabicyclo[4.3.0]△8-9-nonen-1-one
D7	3.22	$C_{16}H_{22}O_{10}$	373.1140	1.34	329.0873[M-H-CO_2]$^-$, 167.0346[M-H-CO_2-Glc]$^-$	Gardoside
D8	3.27	$C_{21}H_{32}O_{15}$	523.1666	0.57	361.1154[M-H-Glc]$^-$, 199.0609[M-H-2Glc]$^-$	Melittoside
D9	3.30	$C_{15}H_{22}O_{10}$	361.1138	0.83	199.0605[M-H-Glc]$^-$ 169.0511[M-H-Glc-CH_2O]$^-$	Catalpol isomer/ Monomelittoside isomer
D10	3.72	$C_{15}H_{24}O_{10}$	363.1295	1.10	201.0714[M-H-Glc]$^-$	Dihydrocatalpo
D11	3.80	$C_{16}H_{22}O_{10}$	373.1138	0.80	329.0871[M-H-CO_2]$^-$, 167.0349[M-H-CO_2-Glc]$^-$	Geniposidic acid [a]
D12	3.81	$C_{21}H_{34}O_{14}$	509.1872	0.39	185.0494213.0776[M-H-2Glc]$^-$	Rehmannioside C
D13	4.46	$C_{15}H_{24}O_9$	347.1345	0.86	167.0468[M-H-Glc-H_2O]$^-$	Ajugol
D14	4.47	$C_{16}H_{24}O_{10}$	375.1294	0.80	213.0773[M-H-Glc]$^-$, 169.0866[M-H-Glc-CO_2]$^-$	Mussaenosidic acid
D15	4.84	$C_{15}H_{22}O_9$	345.1189	0.87	183.0661[M-H-Glc]$^-$	Aucubin
D16	5.17	$C_{16}H_{24}O_{10}$	375.1291	0.00	213.0776[M-H-Glc]$^-$, 169.0872[M-H-Glc-CO_2]$^-$	8-Epiloganic acid [a]
D17	5.45	$C_{17}H_{26}O_{10}$	389.1450	0.51	227.0942[M-H-Glc]$^-$, 169.0143[M-H-Glc-$OCOCH_2$]$^-$	Ajugoside
D18	6.03	$C_{23}H_{34}O_{15}$	549.1824	0.91	387.1440[M-H-Glc]$^-$, 225.0766[M-H-2Glc]$^-$	Genipin 1-gentiobioside [a]
D19	6.73	$C_{18}H_{26}O_{10}$	401.1451	0.75	167.0716[M-H-Glc-Ac-OCH_2]$^-$	Acetylcatalpol
D20	6.93	$C_{17}H_{24}O_{10}$	387.1296	1.29	225.0782[M-H-Glc]$^-$, 181.0503[M-H-Glc-CO_2]$^-$,	Geniposide [a]

					163.0401[M-H-Glc-CO_2-H_2O]$^-$	
D21	6.94	$C_{31}H_{48}O_{18}$	707.2766	0.57	545.1743[M-H-Glc]$^-$, 383.1188[M-H-2Glc]$^-$	Frehmaglutoside G/Frehmaglutoside G
D22	6.96	$C_{17}H_{26}O_{10}$	389.1449	0.26	227.0930[M-H-Glc]$^-$, 169.0142[M-H-Glc-$OCOCH_2$]$^-$	3,4-Dihydroverbenalin
D23	6.97	$C_{16}H_{26}O_8$	345.1553	1.16	139.1123[M-H-CO_2-Glc]$^-$	5-Deoxylamiol
D24	8.66	$C_{25}H_{32}O_{12}$	523.1818	0.38	361.1681[M-H-Glc]$^-$, 330.1437[M-H-$C_{10}H_9O_4$]$^-$, 193.0508[$C_{10}H_{10}O_4$-H]$^-$, 175.0405[$C_{10}H_{10}O_4$-H-H_2O]$^-$	6-O-Feruloylajugol isomer
D25	8.69	$C_{24}H_{30}O_{13}$	525.1613	0.95	201.0719[M-H-$C_9H_6O_3$-Glc]$^-$	6-O-E-caffeoyl ajugol isomer
D26	9.28	$C_{22}H_{28}O_{11}$	467.1558	1.07	287.0901[M-H-Glc-H_2O]$^-$, 137.0246[$C_7H_6O_3$-H]$^-$	6-O-p-hydroxybenzoate ajugol
D27	9.30	$C_{24}H_{30}O_{13}$	525.1613	0.95	201.0703[M-H-$C_9H_6O_3$-Glc]$^-$	6-O-E-caffeoyl ajugol isomer
D28	9.61	$C_{25}H_{32}O_{12}$	523.1821	0.96	361.1662[M-H-Glc]$^-$, 193.0509[$C_{10}H_{10}O_4$-H]$^-$, 175.0401[$C_{10}H_{10}O_4$-H-H_2O]$^-$	6-O-Feruloylajugol isomer
D29	11.10	$C_{24}H_{30}O_{10}$	477.1765	0.84	315.0876[M-H-Glc]$^-$	Rehmaglutoside A
D30	11.17	$C_{25}H_{32}O_{12}$	523.1816	0.00	193.0508[$C_{10}H_{10}O_4$-H]$^-$, 175.0765[$C_{10}H_{10}O_4$-H-H_2O]$^-$	6-O-Z-Feruloylajugol
D31	11.72	$C_{24}H_{30}O_{13}$	525.1613	0.95	201.0713[M-H-$C_9H_6O_3$-Glc]$^-$	6-O-E-caffeoyl ajugol
D32	14.22	$C_{25}H_{32}O_{12}$	523.1819	0.57	193.0507[$C_{10}H_{10}O_4$-H]$^-$, 175.0401[$C_{10}H_{10}O_4$-H-H_2O]$^-$	6-O-E-Feruloylajugol
Iridoids from *Corni officinalis*						
S1	2.26	$C_{16}H_{22}O_9$	357.1188	0.56	195.0679[M-H-Glc]$^-$, 177.0551[M-H-Glc-H_2O]$^-$	Sweroside isomer
S2	3.22	$C_{16}H_{22}O_{10}$	373.1138	0.80	211.0613[M-H-Glc]$^-$, 167.0346[M-H-Glc-CO_2]$^-$	Secoxyloganin isomer
S3	4.11	$C_{16}H_{22}O_{10}$	373.1137	0.54	211.0613[M-H-Glc]$^-$, 167.0350[M-H-Glc-CO_2]$^-$	Secoxyloganin
S4	4.36	$C_{16}H_{22}O_{11}$	389.1088	1.03	345.1205[M-H-CO_2]$^-$, 301.1531[M-H-2CO_2]$^-$, 227.1404[M-H-Glc]$^-$, 183.0665[M-H-Glc-CO_2]$^-$, 139.0402[M-H-2CO_2-Glc]$^-$	Secologanoside isomer
S5	4.37	$C_{23}H_{36}O_{16}$	567.1924	-0.18	405.1412[M-H-Glc]$^-$, 243.0877[M-H-2Glc]$^-$	cornusglucoside D/E/G/isomer
S6	4.65	$C_{17}H_{26}O_{11}$	405.1400	0.74	243.0871[M-H-Glc]$^-$	Morroniside

						isomer
S7	4.71	$C_{23}H_{36}O_{16}$	567.1924	-0.18	405.1410[M-H-Glc]$^-$, 243.0878[M-H-2Glc]$^-$	cornusglucoside D/E/G/isomer
S8	4.81	$C_{16}H_{24}O_{10}$	375.1292	0.27	213.0775[M-H-Glc]$^-$, 169.0874[M-H-Glc-CO_2]$^-$, 151.0770[M-H-Glc-CO_2-H_2O]$^-$	Loganic acid [a]
S9	4.86	$C_{16}H_{22}O_9$	357.1189	0.84	195.0681[M-H-Glc]$^-$, 177.0569[M-H-Glc-H_2O]$^-$	Sweroside isomer
S10	4.86	$C_{23}H_{36}O_{16}$	567.1925	0.00	243.0878[M-H-2Glc]$^-$	cornusglucoside D/E/G/isomer
S11	5.01	$C_{23}H_{36}O_{16}$	567.1924	-0.18	405.1410[M-H-Glc]$^-$, 243.0880[M-H-2Glc]$^-$	cornusglucoside D/E/G/isomer
S12	5.10	$C_{23}H_{36}O_{16}$	567.1923	-0.35	405.1394[M-H-Glc]$^-$, 243.0880[M-H-2Glc]$^-$	cornusglucoside cornusglucoside D/E/G/isomer
S13	5.25	$C_{23}H_{36}O_{16}$	567.1927	0.35	405.1410[M-H-Glc]$^-$, 243.0872[M-H-2Glc]$^-$	cornusglucoside D/E/G/isomer
S14	5.38	$C_{17}H_{26}O_{10}$	389.1450	0.51	227.0928[M-H-Glc]$^-$, 209.0821[M-H -$C_6H_{12}O_6$]$^-$	β-dihydrocornin
S15	5.43	$C_{23}H_{36}O_{16}$	567.1927	0.35	405.1416[M-H-Glc]$^-$, 243.0885[M-H-2Glc]$^-$	cornusglucoside D/E/G/isomer
S16	5.56	$C_{17}H_{26}O_{11}$	405.1398	0.25	243.0885[M-H-Glc]$^-$, 225.0701[M-H-$C_6H_{12}O_6$]$^-$, 181.0489[M-H-$C_6H_{12}O_6$-CO_2]$^-$	Morroniside [a]
S17	5.82	$C_{16}H_{24}O_{10}$	375.1293	0.53	213.0771[M-H-Glc]$^-$, 169.0871[M-H-Glc-CO_2]$^-$, 151.0765[M-H-Glc-CO_2-H_2O]$^-$	Loganic acid isomer
S18	5.91	$C_{16}H_{22}O_{11}$	389.1087	0.77	345.1190[M-H-CO_2]$^-$, 227.1403[M-H-Glc]$^-$, 183.0663[M-H-Glc-CO_2]$^-$, 139.0770[M-H-2CO_2-Glc]$^-$	Secologanoside
S19	5.94	$C_{18}H_{28}O_{11}$	419.1557	0.95	239.0653[M-H-$C_6H_{12}O_6$]$^-$	7R-O-methylmorroniside
S20	6.15	$C_{17}H_{24}O_{10}$	387.1291	0.00	225.0739[M-H-Glc]$^-$, 165.0513[M-H-Glc-$COOCH_3$]$^-$	Cornine isomer
S21	6.38	$C_{17}H_{24}O_{10}$	387.1295	1.03	225.0768[M-H-Glc]$^-$, 165.0558[M-H-Glc-$COOCH_3$]$^-$	Cornine isomer
S22	6.50	$C_{21}H_{30}O_{14}$	505.1561	0.79	459.1069[M-H-HCOOH]$^-$, 429.0970[M-H-HCOOH-OCH_2]$^-$, 399.0876[M-H-HCOOH-2OCH_2]$^-$, 371.0912[M-H-HCOOH-2OCH_2-CO]$^-$	Logmalicid A isomer/Logmalicid B isomer
S23	6.72	$C_{18}H_{28}O_{11}$	419.1556	0.72	257.0820[M-H-Glc]$^-$, 239.0720[M-H-$C_6H_{12}O_6$]$^-$	7S-O-methylmorroniside
S24	6.81	$C_{17}H_{24}O_{10}$	387.1292	0.26	225.0780[M-H-Glc]$^-$,	Cornine [a]

					165.0530[M-H-Glc-$COOCH_3$]$^-$	
S25	6.83	$C_{11}H_{14}O_5$	225.0767	1.78	195.0652[M-H-OCH_2]$^-$, 181.0772[M-H-CO_2]$^-$	Dehydromorroniside aglycone
S26	6.85	$C_{17}H_{26}O_{10}$	389.1453	1.28	227.0941[M-H-Glc]$^-$, 209.0812[M-H -$C_6H_{12}O_6$]$^-$	Loganin
S27	7.01	$C_{16}H_{22}O_9$	357.1188	0.56	195.0663[M-H-Glc]$^-$, 177.0559[M-H-Glc-H_2O]$^-$	Sweroside [a]
S28	7.42	$C_{17}H_{26}O_{10}$	389.1451	0.77	227.0919[M-H-Glc]$^-$, 209.0822[M-H -$C_6H_{12}O_6$]$^-$	Loganin isomer
S29	7.42	$C_{21}H_{30}O_{14}$	505.1557	0.00	487.1445[M-H-H_2O]$^-$, 389.1441[M-H-HCOOH-$HCOOCH_3$]$^-$, 227.0928[M-H-HCOOH-$HCOOCH_3$-Glc]$^-$ 209.0825[M-H-HCOOH-$HCOOCH_3$-Glc-H_2O]$^-$	Logmalicid A isomer/Logmalicid B isomer
S30	7.50	$C_{21}H_{30}O_{14}$	505.1556	-0.20	487.1473[M-H-H_2O]$^-$, 389.1416[M-H-HCOOH-$HCOOCH_3$]$^-$, 227.0927[M-H-HCOOH-$HCOOCH_3$-Glc]$^-$ 209.0804[M-H-HCOOH-$HCOOCH_3$-Glc-H_2O]$^-$	Logmalicid A/Logmalicid B
S31	7.73	$C_{21}H_{30}O_{14}$	505.1561	0.79	487.1473[M-H-H_2O]$^-$, 389.1416[M-H-HCOOH-$HCOOCH_3$]$^-$, 227.0927[M-H-HCOOH-$HCOOCH_3$-Glc]$^-$, 209.0818[M-H-HCOOH-$HCOOCH_3$-Glc-H_2O]$^-$	Logmalicid A isomer/Logmalicid B isomer
S32	7.73	$C_{17}H_{24}O_{11}$	403.1242	0.25	241.1088[M-H-Glc]$^-$, 197.1183[M-H-Glc-CO_2]$^-$	Kingiside/8-epikingiside
S33	7.86	$C_{21}H_{30}O_{14}$	505.1557	0.00	487.1474[M-H-H_2O]$^-$, 227.0930[M-H-HCOOH-$HCOOCH_3$-Glc]$^-$, 209.0832[M-H-HCOOH-$HCOOCH_3$-Glc-H_2O]$^-$	Logmalicid A/Logmalicid B
S34	7.91	$C_{17}H_{26}O_{10}$	389.1452	1.03	227.0950[M-H-Glc]$^-$	Loganin isomer
S35	8.11	$C_{21}H_{30}O_{14}$	505.1562	0.99	227.0927[M-H-HCOOH-$HCOOCH_3$-Glc]$^-$, 209.0833[M-H-HCOOH-$HCOOCH_3$-Glc-H_2O]$^-$	Logmalicid A isomer/Logmalicid B isomer
S36	8.96	$C_{17}H_{26}O_{11}$	433.1714	0.92	271.0627[M-H-Glc]$^-$, 253.0869[M-H-$C_6H_{12}O_6$]$^-$, 225.0770[M-H-$C_6H_{12}O_6$-CO]$^-$	7-O-ethylmorroniside
S37	9.61	$C_{16}H_{22}O_9$	357.1188	0.56	195.0664[M-H-Glc]$^-$, 177.0567[M-H-Glc-H_2O]$^-$	Sweroside isomer
S38	9.61	$C_{21}H_{24}O_7$	387.1447	0.77	372.1206[M-H-CH_3]$^-$, 357.0978[M-H-2CH_3]$^-$, 341.1096[M-H-CH_3-OCH_3]$^-$	(-)-medioresinol
S39	9.66	$C_{20}H_{22}O_6$	357.1337	-0.28	342.1125[M-H-CH_3]$^-$, 311.0929[M-H-CH_3-OCH_3]$^-$	(+)-pinoresinol/(+)-epipinoresinol

S40	10.04	$C_{24}H_{30}O_9$	461.1816	0.87	446.1563[M-H-CH_3]$^-$	Luzonoid B
S41	10.18	$C_{34}H_{50}O_{20}$	777.2823	0.77	615.2268[M-H-Glc]$^-$	CornusideII
S42	10.32	$C_{24}H_{30}O_{14}$	541.1556	-0.18	379.1035[M-H-Glc]$^-$, 361.0935[M-H-$C_6H_{12}O_6$]$^-$, 331.0670[M-H-$C_6H_{12}O_6$-OCH_2]$^-$	Cornuside I [a]
S43	10.65	$C_{20}H_{22}O_7$	373.1292	1.34	358.1072[M-H-CH_3]$^-$	Cornifins A
S44	10.89	$C_{20}H_{20}O_8$	387.1081	0.26	341.1096[M-H-CH_3-OCH_3]$^-$, 313.1083[M-H-CH_3-OCH_3-CO]$^-$	3,4,3',4'-tetrahydroxy-δ-truxinate

a: Compound identified by comparison with the standard reference.

Table S4 Phenylethanoid glycosides from ZKYY

No.	t_R (min)	Molecular formula	Measured value (*m/z*)	Diff (ppm)	Product ions	Compound name
D42	4.65	$C_{20}H_{30}O_{12}$	461.1660	0.22	315.1091[M-H-Rha]$^-$, 297.0990[M-H-Rha-H_2O]$^-$, 153.0558[M-H-Rha-Glc]$^-$	Decaffeoylacteoside
D43	4.94	$C_{21}H_{28}O_{13}$	487.1456	0.82	179.0353[M-H-Rha-Glc]$^-$, 161.0247[$C_9H_6O_3$-H]$^-$	Cistanoside F
D44	6.56	$C_{21}H_{32}O_{12}$	475.1818	0.42	329.1248[M-H-Rha]$^-$, 311.1118[M-H-Rha-H_2O]$^-$, 167.0715[M-H-Rha-Glc]$^-$	Darendoside B/Deacyl-martynoside
D45	7.66	$C_{35}H_{46}O_{20}$	785.2508	0.51	623.2194[M-H-$C_9H_6O_3$]$^-$, 605.2052[M-H-$C_9H_6O_3$-H_2O]$^-$, 477.1617[M-H-$C_9H_6O_3$-Rha]$^-$, 461.1667[M-H-$C_9H_6O_3$-Glc]$^-$, 443.1577[M-H-$C_9H_6O_3$-Glc-H_2O]$^-$, 161.0244[$C_9H_6O_3$-H]$^-$	Purpureaside C
D46	8.06	$C_{35}H_{46}O_{19}$	769.2556	0.13	623.2177[M-H-Rha]$^-$, 605.2121[M-H-Rha-H_2O]$^-$, 461.1709[M-H-Rha-Glc]$^-$	Jionoside E
D47	8.54	$C_{36}H_{48}O_{20}$	799.2662	0.13	637.2330[M-H-Glc]$^-$, 623.2192[M-H-$C_{10}H_8O_3$]$^-$, 605.2079[M-H-$C_{10}H_8O_3$-H_2O]$^-$, 477.1617[M-H-$C_{10}H_8O_3$-Rha]$^-$, 175.0401[$C_{10}H_8O_3$-H]$^-$	Jionoside A1/Jionoside A2
D48	8.68	$C_{35}H_{46}O_{20}$	785.2508	0.51	623.2120[M-H-$C_9H_6O_3$]$^-$, 477.1508[M-H-$C_9H_6O_3$-Rha]$^-$, 461.1667[M-H-$C_9H_6O_3$-Glc]$^-$, 443.1560[M-H-$C_9H_6O_3$-Glc-H_2O]$^-$, 161.0245[$C_9H_6O_3$-H]$^-$	Dihoside B
D49	9.11	$C_{29}H_{36}O_{15}$	623.1969	-1.12	461.1664[M-H-$C_9H_6O_3$]$^-$, 315.1078[M-H-$C_9H_6O_3$-Rha]$^-$,	Verbascoside

					161.0245[$C_9H_6O_3$-H]$^-$	
D50	9.33	$C_{37}H_{50}O_{20}$	813.2819	0.25	491.1700[M-H-$C_{10}H_8O_3$-Rha]$^-$, 175.0401[$C_{10}H_8O_3$-H]$^-$	Jionoside B1/Jionoside B2
D51	9.63	$C_{29}H_{36}O_{15}$	623.1971	-0.80	461.1627[M-H-$C_9H_6O_3$]$^-$, 161.0244[$C_9H_6O_3$-H]$^-$	Isoverbascoside
D52	10.34	$C_{30}H_{38}O_{15}$	637.2136	0.74	475.1461[M-H-$C_9H_6O_3$]$^-$, 329.0859[M-H-$C_9H_6O_3$-Rha]$^-$	Leucosceptoside A
D53	10.77	$C_{30}H_{38}O_{15}$	637.2135	0.56	461.1648[M-H-$C_{10}H_8O_3$]$^-$, 315.1106[M-H-$C_{10}H_8O_3$-Rha]$^-$	Jionoside D
D54	11.26	$C_{30}H_{38}O_{15}$	637.2139	1.30	461.1663[M-H-$C_{10}H_8O_3$]$^-$, 315.1101[M-H-$C_{10}H_8O_3$-Rha]$^-$	Leucosceptoside A isomer/Jionoside D isomer
D55	12.21	$C_{31}H_{40}O_{15}$	651.2289	0.00	475.1840[M-H-$C_{10}H_8O_3$]$^-$, 329.1229[M-H-$C_{10}H_8O_3$-Rha]$^-$, 175.0407[$C_{10}H_8O_3$-H]$^-$	Martynoside
D56	13.07	$C_{31}H_{40}O_{15}$	651.2291	0.31	475.1826[M-H-$C_{10}H_8O_3$]$^-$, 329.1237[M-H-$C_{10}H_8O_3$-Rha]$^-$, 175.0402[$C_{10}H_8O_3$-H]$^-$	Martynoside isomer
D57	13.46	$C_{29}H_{36}O_{13}$	591.2080	0.34	283.0615[M-H-$C_9H_6O_3$-Rha]$^-$, 145.0298[$C_6H_{12}O_5$-H]$^-$	Jionoside C

Table S5 Phenylpropanoids from ZKYY

No.	t_R (min)	Molecular formula	Measured value (*m/z*)	Diff (ppm)	Product ions	Compound name
S45	4.15	$C_9H_8O_4$	179.0345	0.56	135.0453[M-H-CO_2]$^-$	Caffeic acid isomer
S46	4.53	$C_9H_8O_3$	163.0396	0.61	119.0504[M-H-CO_2]$^-$	*p*-Hydroxycinnamic acid isomer
S47	5.27	$C_9H_8O_3$	163.0396	0.61	119.0504[M-H-CO_2]$^-$	*p*-Hydroxycinnamic acid isomer
S48	5.33	$C_9H_8O_4$	179.0345	0.56	135.0453[M-H-CO_2]$^-$	Caffeic acid
S49	5.78	$C_9H_8O_3$	163.0396	0.61	119.0504[M-H-CO_2]$^-$	*p*-Hydroxycinnamic acid isomer
S50	5.95	$C_9H_8O_4$	179.0345	0.56	135.0453[M-H-CO_2]$^-$	Caffeic acid isomer
S51	6.55	$C_9H_8O_3$	163.0396	0.61	119.0504[M-H-CO_2]$^-$	*p*-Hydroxycinnamic acid
S52	7.47	$C_{22}H_{22}O_{12}$	477.1036	0.63	313.0566[M-H-$C_9H_8O_3$]$^-$, 169.0143[$C_7H_6O_5$-H]$^-$, 163.0400[$C_9H_8O_3$-H]$^-$	4-O-(6'-O-Galloyl-β-D-glucopyranosyl)-cis-p-coumaric acid isomer
S53	7.51	$C_9H_8O_3$	163.0396	0.61	119.0502[M-H-CO_2]$^-$	*p*-Hydroxycinnamic acid isomer

S54	8.08	$C_{22}H_{22}O_{12}$	477.1039	1.26	459.0923[M-H-H_2O]$^-$, 433.1128[M-H-CO_2]$^-$, 313.0569[M-H-$C_9H_8O_3$]$^-$, 169.0143[$C_7H_6O_5$-H]$^-$, 163.0403[$C_9H_8O_3$-H]$^-$	4-O-(6'-O-Galloyl-β-D-glucopyranosyl)-cis-p-coumaric acid
S55	8.17	$C_{26}H_{36}O_{11}$	523.2184	0.96	361.1655[M-H-Glc]$^-$, 346.1419[M-H-Glc-CH_3]$^-$, 315.1208[M-H-Glc-CH_3-OCH_3]$^-$	(-)-Secoisolariciresinol-9'-O-β-D-glucopyranoside isomer
S56	8.41	$C_{26}H_{34}O_{11}$	521.2028	0.96	359.1506[M-H-Glc]$^-$, 344.1269[M-H-Glc-CH_3]$^-$, 341.1383[M-H-Glc-H_2O]$^-$, 311.0921[M-H-Glc-H_2O-2CH_3]$^-$	(7*S*,8*R*)-Urolignoside/Glochidioboside/(7*S*,8*R*)-Dihydrodehydrodiconiferyl alcohol 9-O-β-D-glucopyranoside
S57	8.66	$C_{26}H_{34}O_{11}$	521.2028	0.96	359.1500[M-H-Glc]$^-$, 344.1250[M-H-Glc-CH_3]$^-$	(7*S*,8*R*)-Urolignoside/Glochidioboside/(7*S*,8*R*)-Dihydrodehydrodiconiferyl alcohol 9-O-β-D-glucopyranoside
S58	8.79	$C_{26}H_{34}O_{11}$	521.2028	0.96	359.1509[M-H-Glc]$^-$, 344.1248[M-H-Glc-CH_3]$^-$, 326.1163[M-H-Glc-H_2O-CH_3]$^-$, 311.0921[M-H-Glc-H_2O-2CH_3]$^-$	(7*S*,8*R*)-Urolignoside/Glochidioboside/(7*S*,8*R*)-Dihydrodehydrodiconiferyl alcohol 9-O-β-D-glucopyranoside
S59	9.23	$C_{26}H_{36}O_{11}$	523.2187	1.53	361.1674[M-H-Glc]$^-$, 346.1414[M-H-Glc-CH_3]$^-$	(-)-Secoisolariciresinol-9'-O-β-D-glucopyranoside isomer
S60	9.46	$C_{26}H_{36}O_{11}$	523.2186	1.34	361.1659[M-H-Glc]$^-$, 346.1414[M-H-Glc-CH_3]$^-$, 315.1249[M-H-Glc-CH_3-OCH_3]$^-$	(-)-Secoisolariciresinol-9'-O-β-D-glucopyranoside
S61	9.83	$C_{26}H_{34}O_{11}$	521.2028	0.96	359.1518[M-H-Glc]$^-$, 344.1253[M-H-Glc-CH_3]$^-$	(-)-Isolariciresinol 3α-O-β-D-glucopyranoside/(-)-Lyoniresinol 3α-β-D-glucopyranoside
S62	9.91	$C_{22}H_{26}O_8$	417.1549	0.00	402.1302[M-H-CH_3]$^-$, 387.1093[M-H-OCH_2]$^-$	(-)Episyringaresinol/ Syringaresinol
S63	10.07	$C_{26}H_{34}O_{11}$	521.2028	0.96	341.1403[M-H-Glc-H_2O]$^-$,	(-)-Isolariciresinol

					326.1163[M-H-Glc-H_2O-CH_3]$^-$, 311.0928[M-H-Glc-H_2O-OCH_2]$^-$	3α-O-β-D-glucopyranoside/(-)-Lyoniresinol 3α-β-D-glucopyranoside

Table S6 Ionones from ZKYY

No.	t_R (min)	Molecular formula	Measured value (*m/z*)	Diff (ppm)	Product ions	Compound name
D33	5.57	$C_{21}H_{34}O_{10}$	445.2076	0.45	265.1467[M-H-H_2O-Glc]$^-$	Frehmaglutoside F
D34	6.69	$C_{16}H_{26}O_8$	345.1553	1.16	183.1028[M-H-Glc]$^-$	Rehmapicroside
D35	6.84	$C_{21}H_{34}O_{10}$	445.2076	0.45	265.1461[M-H-H_2O-Glc]$^-$, 235.1345[M-H-H_2O-Glc-CH_2O]$^-$, 191.1447[M-H-H_2O-Glc-CH_2O-CO_2]$^-$	Frehmaglutoside E
D36	7.22	$C_{19}H_{34}O_9$	405.2128	0.74	213.1499[M-H-Glc-2CH_3]$^-$, 195.1400[M-H-Glc-2CH_3-H_2O]$^-$	Oxyrehmanionoside B
D37	8.04	$C_{10}H_{16}O_3$	183.1023	1.09	139.1129[M-H-CO_2]$^-$	Rehmapicrogenin
D38	10.96	$C_{21}H_{34}O_9$	429.2129	0.93	267.1617[M-H-Glc]$^-$, 249.1500[M-H-Glc-H_2O]$^-$, 231.1394[M-H-Glc-2H_2O]$^-$, 223.1719[M-H-Glc-CO_2]$^-$, 205.1616[M-H-Glc-H_2O-CO_2]$^-$	Frehmaglutin B
D39	12.12	$C_{10}H_{16}O_3$	183.1024	1.64	139.1128[M-H-CO_2]$^-$	Rehmapicrogenin isomer
D40	14.89	$C_{28}H_{40}O_{10}$	535.2544	0.19	417.1024[M-H-C_8H_6O]$^-$, 163.0404[$C_8H_6O_3$-H]$^-$	Frehmaglutoside C
D41	17.81	$C_{12}H_{20}O_3$	211.1339	2.37	183.1396[M-H-CO]$^-$, 168.0661[M-H-CO-CH_3]$^-$, 167.1443[M-H-CO_2]$^-$	Frehmaglutoside A

Table S7 Triterpenoids from ZKYY

No.	t_R (min)	Molecular formula	Measured value (*m/z*)	Diff (ppm)	Product ions	Compound name
Triterpenoids from *Astragali Radix*						
H92	29.09	$C_{30}H_{48}O_3$	455.3529	0.88	437.3365[M-H-H_2O]$^-$, 409.3488[M-H-H_2O-CO]$^-$	Betulinic acid
H93	29.87	$C_{30}H_{48}O_3$	455.3531	1.32	409.3483[M-H-H_2O-CO]$^-$	Oleanolic acid [a]
H94	29.95	$C_{30}H_{48}O_3$	455.3528	0.66	409.3474[M-H-H_2O-CO]$^-$	Ursolic acid [a]
Triterpenoids from *Corni officinalis*						

S88	16.17	$C_{36}H_{58}O_{10}$	649.3941	-1.69	487.3427[M-H-Glc]$^-$	Arjunglucoside II isomer
S89	16.86	$C_{36}H_{58}O_{10}$	649.3954	0.31	487.3418[M-H-Glc]$^-$	Arjunglucoside II
Triterpenoids from *Trichosanthis Radix*						
T1	12.22	$C_{30}H_{48}O_7$	519.3325	0.58	501.3213[M-H-H_2O]$^-$, 459.3167[M-H-C_3H_8O]$^-$, 387.2559[M-H-C_3H_8O-4H_2O]$^-$	Cucurbitacin P isomer
T2	13.46	$C_{30}H_{46}O_7$	517.3171	1.16	499.3054[M-H-H_2O]$^-$, 457.2955[M-H-C_3H_8O]$^-$, 439.2862[M-H-C_3H_8O-H_2O]$^-$, 385.2399[M-H-H_2O-C_2H_4O-C_4H_6O]$^-$	Cucurbitacin R isomer/Dihydrocucurbitacin D isomer /Cucurbitacin O isomer
T3	14.30	$C_{30}H_{48}O_7$	519.3325	0.58	501.3223[M-H-H_2O]$^-$, 459.3122[M-H-C_3H_8O]$^-$, 441.3003[M-H-C_3H_8O-H_2O]$^-$, 423.2924[M-H-C_3H_8O-2H_2O]$^-$, 387.2543[M-H-C_3H_8O-4H_2O]$^-$, 359.2242[M-H-C_3H_8O-4H_2O-CO]$^-$	Cucurbitacin P
T4	14.72	$C_{30}H_{44}O_7$	515.3013	0.78	479.2794[M-H-2H_2O]$^-$, 437.2691[M-H-H_2O-C_3H_8O]$^-$, 385.2089[M-H-H_2O-C_4H_6O-C_2H_2O]$^-$, 341.2123[M-H-H_2O-C_4H_6O-C_2H_2O-C_2H_4O]$^-$	Cucurbitacin D
T5	14.72	$C_{30}H_{46}O_8$	533.3116	0.38	497.2876[M-H-2H_2O]$^-$, 479.2806[M-H-3H_2O]$^-$, 464.2560[M-H-3H_2O-CH_3]$^-$, 437.2689[M-H-2H_2O-C_3H_8O]$^-$, 427.2495[M-H-2H_2O-C_4H_6O]$^-$, 409.2382[M-H-3H_2O-C_4H_6O]$^-$, 385.2419[M-H-2H_2O-C_4H_6O-C_2H_2O]$^-$, 341.2124[M-H-2H_2O-C_4H_6O-C_2H_2O-C_2H_4O]$^-$	Cucurbitacin H
T6	14.96	$C_{30}H_{46}O_8$	533.3118	0.75	479.2751[M-H-3H_2O]$^-$, 427.2480[M-H-2H_2O-C_4H_6O]$^-$, 385.2428[M-H-2H_2O-C_4H_6O-C_2H_2O]$^-$, 341.2119[M-H-2H_2O-C_4H_6O-C_2H_2O-C_2H_4O]$^-$	Cucurbitacin H isomer
T7	16.70	$C_{30}H_{46}O_7$	517.3171	1.16	499.3082[M-H-H_2O]$^-$, 457.2949[M-H-C_3H_8O]$^-$, 455.2816[M-H-H_2O-C_2H_4O]$^-$, 439.2861[M-H-C_3H_8O-H_2O]$^-$,	Cucurbitacin R/ dihydrocucurbitacin D/ cucurbitacin O

T8	16.70	$C_{30}H_{44}O_7$	515.3007	-0.39	385.2377[M-H-H_2O-C_2H_4O-C_4H_6O]$^-$, 367.2302[M-H-2H_2O-C_2H_4O-C_4H_6O]$^-$ 479.2771[M-H-2H_2O]$^-$, 461.2759[M-H-3H_2O]$^-$, 437.2693[M-H-2H_2O-C_2H_2O]$^-$	Cucurbitacin D isomer
T9	16.94	$C_{30}H_{46}O_7$	517.3170	0.97	499.3068[M-H-H_2O]$^-$, 457.2982[M-H-C_3H_8O]$^-$, 439.2863[M-H-C_3H_8O-H_2O]$^-$, 385.2389[M-H-H_2O-C_2H_4O-C_4H_6O]$^-$, 367.2295[M-H-2H_2O-C_2H_4O-C_4H_6O]$^-$	Cucurbitacin R/ dihydrocucurbitacin D/ cucurbitacin O
T10	17.62	$C_{30}H_{46}O_7$	517.3166	0.19	385.2389[M-H-H_2O-C_2H_4O-C_4H_6O]$^-$, 367.2278[M-H-2H_2O-C_2H_4O-C_4H_6O]$^-$	Cucurbitacin R/ dihydrocucurbitacin D/ cucurbitacin O
T11	18.61	$C_{30}H_{44}O_7$	515.3014	0.97	437.2743[M-H-2H_2O-C_2H_2O]$^-$	Cucurbitacin D isomer

a: Compound identified by comparison with the standard reference.

Table S8 Other compounds from ZKYY

No.	t_R (min)	Molecular formula	Measured value (*m/z*)	Diff (ppm)	Product ions	Compound name
Organic acids from *Corni officinalis*						
S90	0.96	$C_6H_8O_7$	191.0196	2.09	173.0460[M-H-H_2O]$^-$, 111.0090[M-H-CO_2-2H_2O]$^-$	Citric acid isomer
S91	1.10	$C_7H_6O_5$	169.0141	2.37	125.0246[M-H-CO_2]$^-$	Gallic acid isomer
S92	1.21	$C_6H_8O_7$	191.0196	2.09	173.0460[M-H-H_2O]$^-$, 147.0305[M-H-CO_2]$^-$, 129.0197[M-H-CO_2-H_2O]$^-$, 111.0091[M-H-CO_2-2H_2O]$^-$	Citric acid
S93	1.50	$C_{13}H_{16}O_{10}$	331.0667	0.60	169.0145[M-H-Glc]$^-$, 125.0250[M-H-Glc-CO_2]$^-$	Gallic acid 4-O-β-D-glucoside
S94	1.68	$C_{13}H_{16}O_{10}$	331.0668	0.91	169.0145[M-H-Glc]$^-$, 125.0247[M-H-Glc-CO_2]$^-$	Gallic acid 4-O-β-D-glucoside isomer
S95	1.84	$C_7H_6O_5$	169.0141	2.37	125.0246[M-H-CO_2]$^-$	Gallic acid
S96	2.50	$C_7H_6O_4$	153.0189	0.65	109.0298[M-H-CO_2]$^-$	3,5-Dihydroxybenzoic acid isomer
S97	3.16	$C_{13}H_{16}O_{10}$	331.0668	0.91	169.0145[M-H-Glc]$^-$, 125.0246[M-H-Glc-CO_2]$^-$	Gallic acid 4-O-β-D-glucosi

						de isomer
S98	3.16	$C_7H_6O_5$	169.0141	2.37	125.0244[M-H-CO_2]$^-$	Gallic acid isomer
S99	3.51	$C_7H_6O_4$	153.0189	0.65	109.0296[M-H-CO_2]$^-$	3,5-Dihydroxybenzoic acid
S100	3.90	$C_{13}H_{16}O_{10}$	331.0671	1.81	169.0145[M-H-Glc]$^-$, 125.0250[M-H-Glc-CO_2]$^-$	Gallic acid 4-O-β-D-glucoside isomer
S101	4.28	$C_8H_8O_5$	183.0297	2.19	168.0065[M-H-CH_3]$^-$, 139.0404[M-H-CO_2]$^-$	Methyl gallate isomer
S102	4.84	$C_8H_8O_3$	151.03971	1.32	123.0453[M-H-CO]$^-$, 108.0456[M-H-CO-CH_3]$^-$	Vanillin isomer
S103	5.02	$C_7H_6O_4$	153.0190	1.31	109.0297[M-H-CO_2]$^-$	3,5-Dihydroxybenzoic acid isomer
S104	5.37	$C_8H_8O_5$	183.0297	2.19	168.0065[M-H-CH_3]$^-$, 139.0401[M-H-CO_2]$^-$	Methyl gallate isomer
S105	5.47	$C_{16}H_{18}O_9$	353.0875	0.57	191.0565[M-H-$C_9H_6O_3$]$^-$, 173.0456[M-H-$C_9H_6O_3$-H_2O]$^-$, 161.0249[$C_9H_6O_3$-H]$^-$, 147.0303[M-H-$C_9H_6O_3$-CO_2]$^-$, 129.0195[M-H-$C_9H_6O_3$-CO_2-H_2O]$^-$, 111.0095[M-H-$C_9H_6O_3$-CO_2-2H_2O]$^-$	Chlorogenic acid isomer
S106	5.82	$C_{16}H_{18}O_9$	353.0875	0.57	191.0562[M-H-$C_9H_6O_3$]$^-$, 173.0458[M-H-$C_9H_6O_3$-H_2O]$^-$, 161.0245[$C_9H_6O_3$-H]$^-$, 129.0191[M-H-$C_9H_6O_3$-CO_2-H_2O]$^-$, 111.0088[M-H-$C_9H_6O_3$-CO_2-2H_2O]$^-$	Chlorogenic acid
S107	5.84	$C_8H_8O_3$	151.0397	1.32	123.0452[M-H-CO]$^-$, 108.0454[M-H-CO-CH_3]$^-$	Vanillin
S108	6.13	$C_7H_6O_4$	153.0191	1.96	109.0296[M-H-CO_2]$^-$	3,5-Dihydroxybenzoic acid isomer
S109	6.63	$C_{16}H_{18}O_9$	353.0877	1.13	111.0090[M-H-$C_9H_6O_3$-CO_2-2H_2O]$^-$	Chlorogenic acid isomer
S110	7.04	$C_{16}H_{18}O_9$	353.0874	0.28	191.0555[M-H-$C_9H_6O_3$]$^-$, 161.0242[$C_9H_6O_3$-H]$^-$, 147.0452[M-H-$C_9H_6O_3$-CO_2]$^-$, 129.0195[M-H-$C_9H_6O_3$-CO_2-H_2O]$^-$, 111.0089[M-H-$C_9H_6O_3$-CO_2-2H_2O]$^-$	Chlorogenic acid isomer
S111	7.83	$C_{16}H_{18}O_9$	353.0879	1.70	191.0560[M-H-$C_9H_6O_3$]$^-$, 111.0093[M-H-$C_9H_6O_3$-CO_2-2H_2O]$^-$	Chlorogenic acid isomer
S112	8.59	$C_{16}H_{18}O_9$	353.0876	0.85	111.0088[M-H-$C_9H_6O_3$-CO_2-2H_2O]$^-$	Chlorogenic acid isomer
S113	9.14	$C_8H_8O_5$	183.0297	2.19	168.0066[M-H-CH_3]$^-$, 139.0399[M-H-CO_2]$^-$	Methyl gallate

Polyphenols from *Chinese yam*						
SY1	11.64	$C_{14}H_{14}O_3$	229.0870	2.18	123.0459[M-H-C_7H_6O]$^-$	2'，3，5-Trihydroxybib enzyl isomer
SY2	12.22	$C_{19}H_{24}O_4$	315.1600	1.27	297.1503[M-H-H_2O]$^-$, 279.1394[M-H-2H_2O]$^-$, 191.1079[M-H-H_2O-C_7H_6O]$^-$, 173.0979[M-H-2H_2O-C_7H_6O]$^-$, 149.0610[M-H-$C_9H_9O_2$]$^-$	(3R,5R)-3,5-Dihydrox y-1,7-bis(4-hydroxyph enyl)-3,5 –heptanediol
SY3	12.40	$C_{14}H_{14}O_3$	229.0870	2.18	123.0453[M-H-C_7H_6O]$^-$	2',3,5-Trihydroxybib enzyl isomer
SY4	13.15	$C_{21}H_{28}O_6$	375.1811	0.80	360.1581[M-H-CH_3]$^-$, 203.0865[M-H-2H_2O-$C_8H_8O_2$]$^-$, 179.0715[M-H-$C_{10}H_{11}O_3$]$^-$, 149.0608[M-H-$C_{10}H_{11}O_3$-OCH_2]$^-$, 135.0452[$C_8H_8O_2$-H]$^-$	(3R,5R)-1,7-Bis(4-hyd roxy-3-methoxyphenyl)-3,5–heptanediol
SY5	13.39	$C_{21}H_{28}O_6$	375.1811	0.80	360.1573[M-H-CH_3]$^-$, 203.0860[M-H-2H_2O-$C_8H_8O_2$]$^-$, 179.0723[M-H-$C_{10}H_{11}O_3$]$^-$, 149.0616[M-H-$C_{10}H_{11}O_3$-OCH_2]$^-$, 135.0453[$C_8H_8O_2$-H]$^-$	(3R,5R)-1,7-Bis(4-hyd roxy-3-methoxyphenyl)-3,5–heptanediol isomer
SY6	13.47	$C_{14}H_{14}O_3$	229.0870	2.18	123.0453[M-H-C_7H_6O]$^-$	2',3,5-Trihydroxybib enzyl
SY7	18.97	$C_{15}H_{16}O_3$	243.1026	2.06	137.0609[M-H-C_7H_6O]$^-$, 122.0374[M-H-C_7H_6O-CH_3]$^-$, 106.0425[M-H-C_7H_6O-OCH_3]$^-$	Batatasin **III**/Bat atasin**IV**

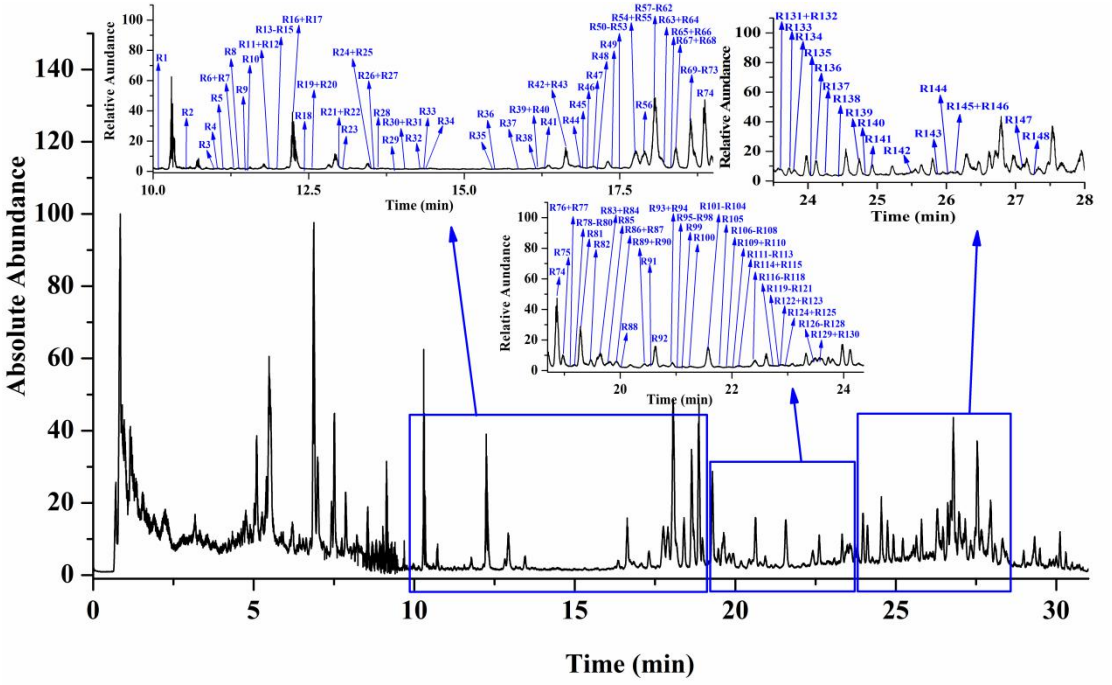

Fig. S3 The LC-MS traces of ginsenosides (saponins) on TIC of ZKYY extract.

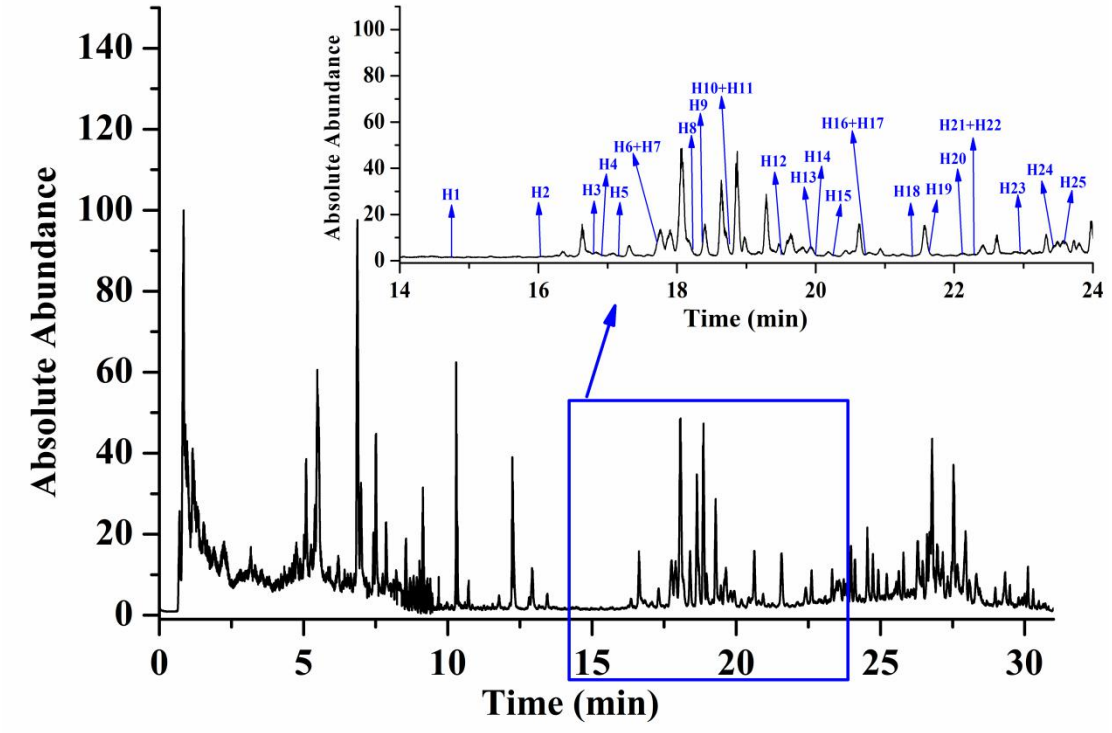

Fig. S4 The LC-MS traces of astragalus saponins on TIC of ZKYY extract.

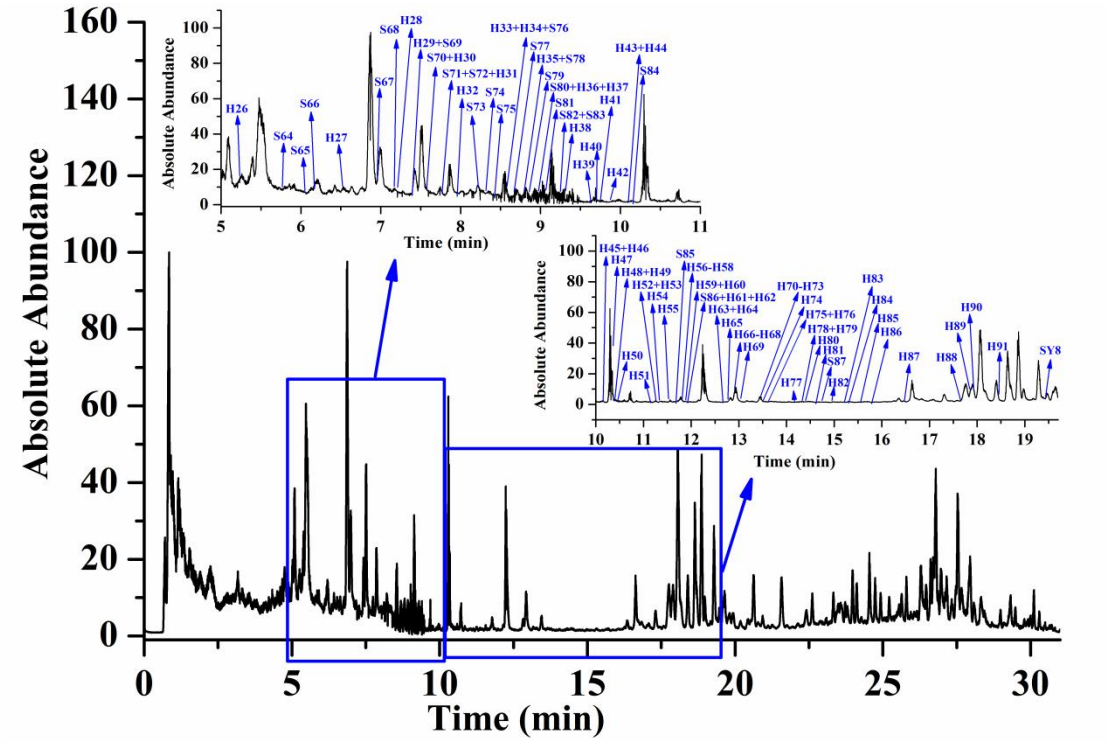

Fig. S5 The LC-MS traces of flavonoids on TIC of ZKYY extract.

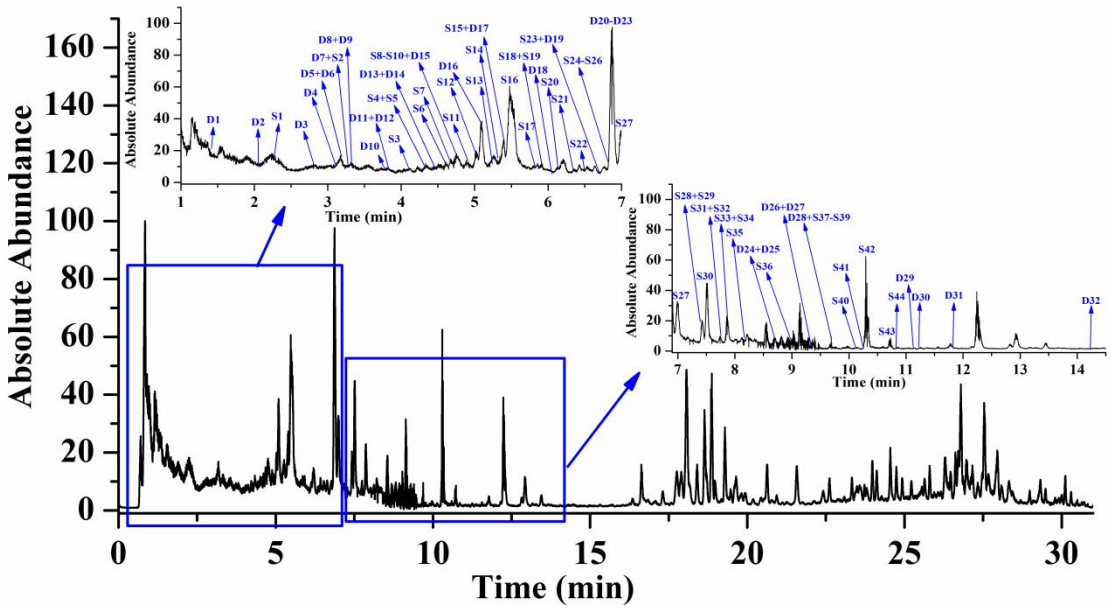

Fig. S6 The LC-MS traces of iridoids on TIC of ZKYY extract.

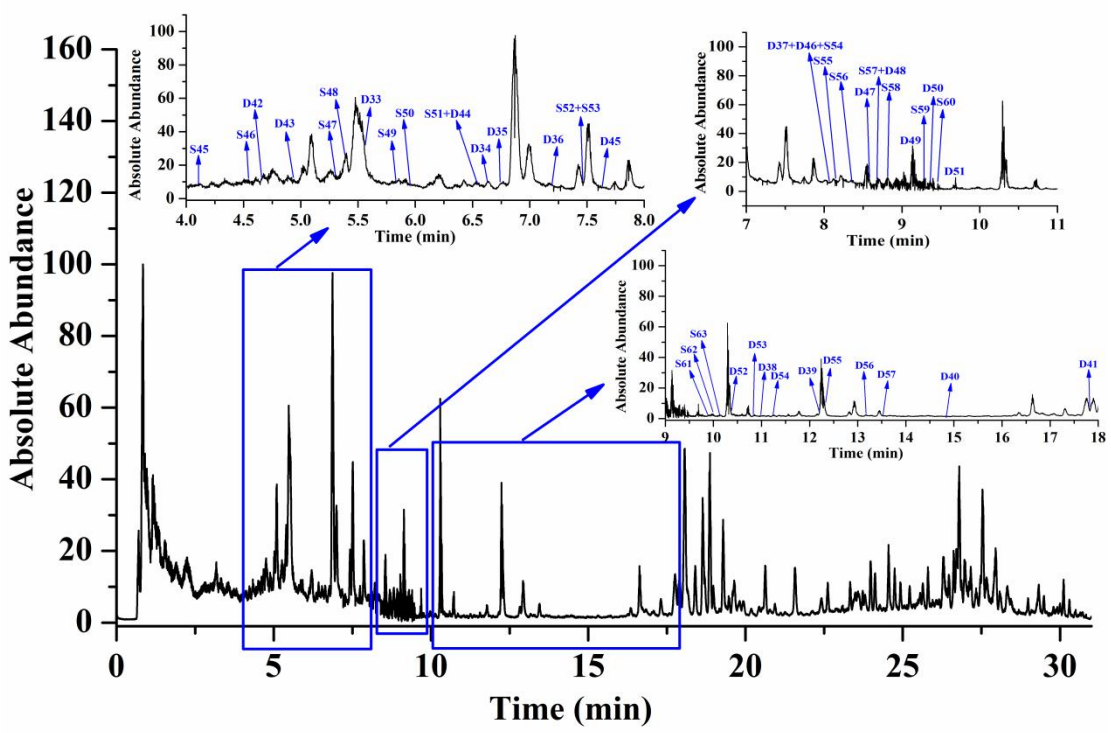

Fig. S7 The LC-MS traces of phenylethanoid glycosides, phenylpropanoids and ionones on TIC of ZKYY extract.