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 acetonitrile-formic acid aqueous solution were investigated in our study. We found that acetonitrile-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; 25-30 min, 65%B-95% B; 30-31 min, 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; 25-30 min, 65%B-95%B; 30-31 min, 95%B-95%B. The flow rate was 0.3 mL/min and the temperature was set at 35°C. 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 Re₃ (R2), ginsenoside Re₄ (R3), 20-Glc-Rf (R5), ginsenoside Re₁ (R7), notoginsenoside R₁ (R9), ginsenoside Re₂ (R10), ginsenoside Rg₁ (R16), ginsenoside Re (R17), ginsenoside Rf (R42), notoginsenoside R₂ (R47), ginsenoside Ra₂ (R55), ginsenoside Ra₃ (R58), ginsenoside Rb₁ (R59), 20(S)-ginsenoside Rg₂ (R60), 20(S)-ginsenoside Rh₁ (R61), 20(R)-ginsenoside Rg₂ (R68), ginsenoside Re (R70), 20(R)-ginsenoside Rh₁ (R71), ginsenoside Ra₁ (R72), ginsenoside Ro (R74), ginsenoside Rb₂ (R81), ginsenoside Rb₃ (R82), quinquenoside R₁ (R86), ginsenoside Rs₂ (R91), ginsenoside Rd (R92), ginsenoside Ro methyl ester (R113), ginsenoside F₄ (R129), ginsenoside Rg₆ (R133), 20(S)-ginsenoside Rg₃ (R139), 20(R)-ginsenoside Rg₃ (R141), 20(S)-ginsenoside Rh₂ (R147), 20(R)-ginsenoside Rh₂ (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 Rb₁ 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 Ra3, and R104, R112 as well as R134 were the isomers of ginsenoside Rd. R124 was elucidated as isomerized ginsenoside Rg2 while R88 and R96 were elucidated as the isomerized quinuenoside R1. R11 was the isomer of notoginsenoside R1.

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 Rg3. R107 and R111 were deduced as acetyl-pseudo-ginsenoside RC1. 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 Rg1. 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_{2}H_{2}O 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_{2}O and CO_{2} were eliminated from \( m/z \) 285.0410. Thus, S80 was deduced as a known compound kaempferol-3-O-\alpha-L-Rhamnosyl(1-6)-\beta-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-\alpha-L-Rhamnosyl(1-6)-\beta-D-galactoside. In the same way, the other known compounds and isomers were tentatively assigned, the fragmentation ions were shown in Table S2.

| 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 |
| R2  | 10.57 | C₄₉H₆₀O₁₉ | 961.5381 | 0.94 | 475.3813[M-H-Ara-3Glc]⁻, 799.4852[M-H-Glc]⁻, 637.4333[M-H-2Glc]⁻, 475.3802[M-H-3Glc]⁻, Ginsenoside Re₃⁺ |
|-----|-------|-------------|---------|------|---------------------------------------------------------------|
| R3  | 10.96 | C₄₇H₆₀O₁₈ | 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 Re₄⁺ |
| R4  | 11.04 | C₅₃H₆₀O₂₂ | 1077.5845 | 0.00 | 945.5450[M-H-Ara]⁻, 783.4838[M-H-Ara-Glc]⁻, 637.4318[M-H-Ara-Glc-Rha]⁻, Floralginsenoside M/Floralginsenoside N |
| R5  | 11.18 | C₄₉H₆₀O₁₉ | 961.5378 | 0.62 | 799.4838[M-H-Glc]⁻, 637.4320[M-H-2Glc]⁻, 475.3791[M-H-3Glc]⁻, 20-Gluco-ginsenoside Rf⁺ |
| R6  | 11.31 | C₅₃H₆₀O₂₃ | 1107.5961 | 0.90 | 945.5485[M-H-Glc]⁻, 783.4889[M-H-2Glc]⁻, 637.4330[M-H-2Glc-Rha]⁻, Protopanaxatriol+3Glc+Rha |
| R7  | 11.32 | C₄₉H₆₀O₁₉ | 961.5381 | 0.94 | 799.4897[M-H-Glc]⁻, 637.4309[M-H-2Glc]⁻, 475.3794[M-H-3Glc]⁻, Ginsenoside Re₅⁺ |
| R8  | 11.39 | C₅₃H₆₀O₂₂ | 1077.5846 | 0.09 | 945.5465[M-H-Ara]⁻, 799.4873[M-H-Ara-Rha]⁻, 637.4344[M-H-Ara-Rha-Glc]⁻, Floralginsenoside M/Floralginsenoside N |
| R9  | 11.49 | C₄₇H₆₀O₁₈ | 931.5272 | 0.64 | 799.4841[M-H-Xyl]⁻, 637.4319[M-H-Xyl-Glc]⁻, 475.795[M-H-Xyl-2Glc]⁻, Notoginsenoside R₁⁺ |
| R10 | 11.60 | C₄₉H₆₀O₁₉ | 961.5377 | 0.52 | 799.4895[M-H-Glc]⁻, 637.4328[M-H-2Glc]⁻, 475.3805[M-H-3Glc]⁻, Ginsenoside Re₂⁺ |
| R11 | 11.81 | C₄₇H₆₀O₁₈ | 931.5276 | 1.07 | 799.4841[M-H-Xyl]⁻, 637.4303[M-H-Xyl-Glc]⁻, 475.3780[M-H-Xyl-2Glc]⁻, Notoginsenoside R₁ isomer |
| R12 | 11.89 | C₅₃H₆₀O₂₃ | 1107.5970 | 1.72 | 945.5467[M-H-Glc]⁻, 783.4889[M-H-2Glc]⁻, 637.4330[M-H-2Glc-Rha]⁻, Protopanaxatriol+3Glc+Rha |
| R13 | 12.01 | C₅₃H₆₀O₂₄ | 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 R₂ |
| R14 | 12.08 | C₅₃H₆₀O₂₃ | 1107.5941 | -0.90 | 945.5471[M-H-Glc]⁻, 783.4981[M-H-2Glc]⁻, Protopanaxatriol+3Glc+Rha |
| R15 | 12.09 | C_{44}H_{82}O_{19} | 961.5362 | -1.04 | 637.4370[M-H-2Glc-Rha]^−, 475.3776[M-H-3Glc-Rha]^− | 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}\textsuperscript{a} |
| R17 | 12.20 | C_{44}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\textsuperscript{a} |
| R18 | 12.38 | C_{44}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/\textsuperscript{a}isomer |
| R21 | 12.90 | C_{44}H_{82}O_{19} | 961.5363 | -0.94 | 799.3902[M-H-Glc]^−, 637.4371[M-H-Glc-Rha]^−, 475.3743[M-H-3Glc]^− | Notoginsenoside N isomer |
| R22 | 12.90 | C_{43}H_{74}O_{17} | 885.4840 | -0.90 | 637.4316[M-H-Malonyl-Glc]^−, 475.3789[M-H-Malonyl-2Glc]^− | Malonyl-ginsenoside Rg_{1} |
| R23 | 13.08 | C_{44}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_{44}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/\textsuperscript{a}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_{43}H_{74}O_{17} | 885.4843 | -0.56 | 637.4310[M-H-Malonyl-Glc]^−, 475.3799[M-H-Malonyl-2Glc]^− | Malonyl-ginsenoside Re |
| 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_{33}H_{60}O_{23} | 1093.5811 | 1.46 | 799.4862[M-H-Ara-Glc], 637.4322[M-H-Ara-2Glc], 475.3789[M-H-Ara-3Glc] | Floralginosenoside 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_{33}H_{60}O_{23} | 1123.5907 | 0.62 | 961.5371[M-H-Glc], 799.4849[M-H-2Glc], 475.3796[M-H-3Glc] | Vina-ginsenoside R4 |
| R33 | 14.40 | C_{33}H_{60}O_{23} | 1093.5814 | 1.74 | 799.4885[M-H-Ara-Glc], 127637.4363[M-H-Ara-2Glc], 475.3785[M-H-Ara-3Glc] | Floralginosenoside P isomer |
| R34 | 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 R4 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 R4 isomer |
| R39 | 16.25 | C_{54}H_{82}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 Rb1 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_{50}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 R4 isomer |
| R42  | 16.51  | C_{52}H_{72}O_{14} | 799.4849  | 0.63  | 459.3808[M-H-4Glc-Xyl]^- | Ginsenoside Rf<sup>a</sup> |
|------|--------|-------------------|-----------|-------|--------------------------|---------------------------|
|      |        |                   |           |       | 637.4326[M-H-Glc]^-,     |                           |
|      |        |                   |           |       | 475.3797[M-H-2Glc]^-,     |                           |
| R43  | 16.55  | C_{58}H_{100}O_{27} | 1239.6381 | 0.56  | 1107.5955[M-H-Glc]^-,     | Notoginsenoside R₄       |
|      |        |                   |           |       | 945.5423[M-H-Glc-Xyl]^-,  |                           |
|      |        |                   |           |       | 783.4895[M-H-2Glc-Xyl]^-,  |                           |
|      |        |                   |           |       | 621.4370[M-H-3Glc-Xyl]^-,  |                           |
|      |        |                   |           |       | 459.3840[M-H-4Glc-Xyl]^-,  |                           |
| R44  | 16.76  | C_{43}H_{62}O_{19} | 961.5388  | 1.66  | 799.4815[M-H-Glc]^-,      | Vina-ginsenoside R₄ isomer|
|      |        |                   |           |       | 637.4232[M-H-2Glc]^-,      |                           |
|      |        |                   |           |       | 475.3837[M-H-3Glc]^-,      |                           |
| R45  | 16.88  | C_{62}H_{102}O_{30} | 1325.6359 | -1.43 | 1239.6378[M-H-Malonyl]^-  | Malonyl-notoginsenoside R₄|
|      |        |                   |           |       | 1107.5916[M-H-Malonyl-Xyl]^-|                           |
|      |        |                   |           |       | 945.5457[M-H-Malonyl-Xyl-Glc]^-|                       |
|      |        |                   |           |       | 783.4915[M-H-Malonyl-Xyl-2Glc]^-|                   |
|      |        |                   |           |       | 621.4358[M-H-Malonyl-Xyl-3Glc]^-|                   |
|      |        |                   |           |       | 459.3822[M-H-Malonyl-Xyl-4Glc]^-|                   |
| R46  | 16.98  | C_{58}H_{100}O_{27} | 1239.6383 | 0.73  | 1107.5941[M-H-Glc]^-,     | Notoginsenoside R₄ isomer/Ginsenoside Ra₃ isomer|
|      |        |                   |           |       | 945.5395[M-H-Glc-Xyl]^-,   |                           |
|      |        |                   |           |       | 783.4912[M-H-2Glc-Xyl]^-,  |                           |
|      |        |                   |           |       | 621.4358[M-H-3Glc-Xyl]^-,  |                           |
|      |        |                   |           |       | 459.3817[M-H-4Glc-Xyl]^-,  |                           |
| R47  | 17.17  | C_{41}H_{70}O_{13} | 769.4743  | 0.65  | 637.4322[M-H-Xyl]^-,      | Notoginsenoside R₂<sup>a</sup> |
|      |        |                   |           |       | 475.3795[M-H-Xyl-Glc]^-,   |                           |
|      |        |                   |           |       | 799.4834[M-H-Ac]^-,       |                           |
|      |        |                   |           |       | 637.4298[M-H-Ac-Glc]^-,    |                           |
|      |        |                   |           |       | 475.3789[M-H-Ac-2Glc]^-,   |                           |
| R48  | 17.23  | C_{44}H_{72}O_{15} | 841.4943  | -0.71 | 1077.5818[M-H-Xyl]^-,     | Yesanchinoside D          |
|      |        |                   |           |       | 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]^-,|                         |
| R49  | 17.42  | C_{58}H_{98}O_{26} | 1209.6273 | 0.41  | 1077.5818[M-H-Xyl]^-,     | Ginsenoside Ra₁ isomer/Ginsenoside Ra₂ isomer |
|      |        |                   |           |       | 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]^-,|                         |
| R50  | 17.49  | C_{59}H_{100}O_{27} | 1239.6375 | 0.08  | 1107.5958[M-H-Glc]^-,     | Notoginsenoside R₄ isomer/Ginsenoside Ra₃ isomer |
|      |        |                   |           |       | 945.5432[M-H-Glc-Xyl]^-,   |                           |
|      |        |                   |           |       | 783.4883[M-H-2Glc-Xyl]^-,  |                           |
|      |        |                   |           |       | 621.4380[M-H-3Glc-Xyl]^-,  |                           |
|      |        |                   |           |       | 459.3831[M-H-4Glc-Xyl]^-,  |                           |
| R51  | 17.49  | C_{41}H_{70}O_{13} | 769.4744  | 0.78  | 637.4319[M-H-Ara]^-,      | Ginsenoside F₃/Ginsenoside F₅ |
|      |        |                   |           |       | 475.3796[M-H-Ara-Glc]^-,   |                           |
|      |        |                   |           |       | 799.4853[M-H-Ac]^-,       |                           |
|      |        |                   |           |       | 637.4254[M-H-Ac-Glc]^-,    |                           |
|      |        |                   |           |       | 475.3789[M-H-Ac-2Glc]^-,   |                           |
| R52  | 17.52  | C_{44}H_{72}O_{15} | 841.4954  | 0.59  | 793.4329[M-H-Glc]^-,      | Yesanchinoside D isomer   |
|      |        |                   |           |       | 731.4350[M-H-Glc-CO₂H₂O]^-|                           |
|      |        |                   |           |       | 841.4954[M-H-Glc-CO₂H₂O]^-|                           |
| R54 | 17.62 | C_{62}H_{102}O_{30} | 1325.6356 | -1.66 | 569.3911[M-H-2Glc-H_2O-CO_2]^+; 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]^- |
| 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]^- |
| 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]^- |
| 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]^- |
| R60 | 17.96 | C_{42}H_{72}O_{13} | 783.4893 | -0.26 | 637.4333[M-H-Rha]^-; 475.3715[M-H-Rha-Glc]^- |
| R61 | 17.98 | C_{36}H_{62}O_{9} | 637.4317 | 0.16 | 475.3786[M-H-Glc]^- |
| R62 | 17.99 | C_{48}H_{78}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]^- |
| 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]^- |
| 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/Notoginsenoside Ra_3 isomer |
| Entry | R | Mass  | Molecular Formula | Molar Mass | Charge | 
|-------|---|-------|-------------------|-----------|-------| 
| R65   | 18.13 | 1107.5953 | C_{56}H_{92}O_{23} | 1107.5953 | 0.18 | Ginkgoside Ra₃ isomer 
| R66   | 18.18 | 1325.6371 | C_{62}H_{102}O_{30} | 1325.6371 | -0.53 | Ginkgoside Rb₁ isomer 
| R67   | 18.25 | 1193.5942 | C_{57}H_{94}O_{26} | 1193.5942 | -1.09 | Malonylginkgoside Ra₃ 
| R68   | 18.29 | 783.4895  | C_{42}H_{72}O_{13} | 783.4895  | 0.00  | Malonylginkgoside Rb₁ 
| R69   | 18.38 | 1325.6383 | C_{62}H_{102}O_{30} | 1325.6383 | 0.38  | Malonylnotoginkgoside Ra₄ isomer/Malonylginkgoside Ra₃ isomer 
| R70   | 18.46 | 1077.5848 | C_{53}H_{90}O_{22} | 1077.5848 | 0.28  | Ginkgoside Re₃ 
| R71   | 18.48 | 637.4325  | C_{36}H_{62}O_{9}  | 637.4325  | 1.41  | Ginkgoside 20(R)-Rg₂ a 
| R72   | 18.54 | 1209.6263 | C_{35}H_{98}O_{26} | 1209.6263 | -0.41 | Ginkgoside Ra₁ a 
| R73   | 18.58 | 1193.5953 | C_{57}H_{94}O_{26} | 1193.5953 | -0.17 | Malonylginkgoside Rb₁ isomer 
| R74   | 18.70 | 955.4907  | C_{48}H_{76}O_{19} | 955.4907  | 0.42  | Ginkgoside Ro a |
| R75  | 18.78 | C_{58}H_{92}O_{25} | 1163.5842 | -0.60 | 455.3528[M-H-2Glc-Glu A]^-; 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 Ra1 isomer/Ginsenoside Ra2 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 R4 isomer/Malonyl-ginsenoside Ra3 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 Ra1 isomer/Ginsenoside Ra2 isomer |
| R79  | 19.03 | C_{55}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 Rb1 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-H2O]^-; 455.3538[M-H-Xyl/Ara(f)-Glc-Glu A]^-; Pseudo-ginsenoside-RT1 |
| R81  | 19.10 | C_{55}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 Rb2^a |
| R82  | 19.28 | C_{55}H_{96}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 Rb3^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 Rb2 |

16
17

621.4352[M-H-Malonyl-Ara(p)-2Glc]

459.3855[M-H-Malonyl-Ara(p)-3Glc]

Pseudoginsenoside-RT1

793.4379[M-H-Xyl]−

613.3748[M-H-Xyl-Glc-H2O]−

455.3550[M-H-Xyl-Glc-Glu A]−

Malonyl-ginsenoside Rb3

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]−

Quinquenoside R1 a

1107.5984[M-H-Ac]−

945.5443[M-H-Ac-Glc]−

783.4930[M-H-Ac-2Glc]−

621.4387[M-H-Ac-3Glc]−

Chikusetsusaponin Iva isomer

Quinquenoside R1 isomer

631.3846[M-H-Glc]−

455.3521[M-H-Glc-Glu A]−

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]−

Ginsenoside Ra5

1219.6259[M-H-Ac-Xyl-ara(p)]−

Ginsenoside Rs2 a

1209.6250[M-H-Ac-Xyl-ara(p)]−

1077.5850[M-H-Ac-Xyl]−

945.5430[M-H-Ac-Xyl-ara(p)]−

783.4898[M-H-Ac-Xyl-ara(p)-Glc]−

Ginsenoside Rs5

945.5422[M-H-Ac-Xyl-ara(p)]−

Ginsenoside Rd a

Ginsenoside Rs5 isomer
| R94  | 20.75 | C_{51}H_{84}O_{21} | 1031.5425 | -0.19 | 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]^{-} | Malonyl-ginsenoside Rd |
| R95  | 20.91 | C_{50}H_{84}O_{19} | 987.5528 | -0.10 | 945.5433[M-H-Malonyl]^{-}, 783.4901[M-H-Malonyl-Glc]^{-}, 621.4374[M-H-Malonyl-2Glc]^{-}, 459.3849[M-H-Malonyl-3Glc]^{-} | Acetyl-ginsenoside Rd |
| R96  | 20.95 | C_{52}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]^{-}, 621.3635[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_{2}O]^{-}, 455.3536[M-H-Xyl/Ara-Glc-Glu A]^{-} | Pseudo-ginsenoside-RT_{1} isomer/Chikusetsusaponin IV isomer |
| R98  | 20.95 | C_{52}H_{94}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 R_{s2} 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 R_{a4} 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 R_{a6} |
| Compound | R Value | Molecular Formula | MW | p | Major Adducts |
|----------|---------|-------------------|-----|---|----------------|
| R102     | 21.44   | C_{50}H_{100}O_{27} | 1251.6384 | 0.80 | 621.4368[M-H-(E)-but-2-enoyl-3Glc]⁻, 459.3838[M-H-(E)-but-2-enoyl-4Glc]⁻, 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 R₈ isomer |
| R103     | 21.50   | C_{48}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 R₁/Ginsenoside R₆, |
| 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 R₆ 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 RC₁ |
| 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-]
| Compound | Mespolarity | Molar Mass | Retention Time | M/z Values |
|----------|-------------|------------|----------------|------------|
| R109     | 22.05       | C₂₅H₆₉O₂₃  | 1145.6122      | 1077.5836[M-H-(E)-but-2-enoyl-Xyl-ara(p)-2Glc]⁻, 945.5428[M-H-(E)-but-2-enoyl-Ara-3Glc]⁻, 783.4880[M-H-(E)-but-2-enoyl-Ara-2Glc]⁻, 621.4377[M-H-(E)-but-2-enoyl-Ara-3Glc]⁻, 459.3861[M-H-(E)-but-2-enoyl-Ara-3Glc]⁻ | Ginsenoside Ra₁/Ginsenoside Rb₁/Ginsenoside Ra₆ |
| R110     | 22.06       | C₅₈H₈₀O₂₅  | 1191.6165      | 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 R₁ |
| R111     | 22.11       | C₅₂H₈₆O₂₀  | 1029.5645      | 945.5443[M-H-2Ac]⁻, 783.4893[M-H-2Ac-2Glc]⁻, 621.4373[M-H-2Ac-3Glc]⁻, 459.3841[M-H-2Ac-3Glc]⁻ | Acetyl-pseudo-ginsenoside RC₁ |
| R112     | 22.13       | C₄₆H₈₂O₁₈  | 945.5441       | 783.4899[M-H-Glc]⁻, 621.4385[M-H-2Glc]⁻, 459.3848[M-H-3Glc]⁻ | Ginsenoside Rd isomer |
| R113     | 22.13       | C₄₆H₇₈O₁₉  | 969.5059       | 807.4559[M-H-Glc]⁻, 645.4022[M-H-2Glc]⁻, 455.3533[M-H-2Glc-CH₂-Glu]⁻ | Ginsenoside Ro methyl ester⁺ |
| R114     | 22.37       | C₅₈H₈₆O₂₅  | 1191.6169      | 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 R₁ isomer |
| R115     | 22.38       | C₅₈H₉₆O₂₄  | 1175.6218      | 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 Ra₆ isomer |
| R116     | 22.53       | C₄₇H₉₈O₁₇  | 915.5324       | 783.4891[M-H-Xyl]⁻, 621.4368[M-H-Xyl-Glc]⁻, 459.3842[M-H-Xyl-2Glc]⁻ | Vina-ginsenoside R₁₆ |
| R117     | 22.55       | C₅₈H₉₄O₂₃  | 1145.6121      | 1077.5864[M-H-(E)-but-2-enoyl]⁻, 945.5388[M-H-(E)-but-2-enoyl-Ara]⁻ | Ginsenoside Ra₁/Ginsenoside Rb₁/Ginsenoside Ra₆ |
| R118 | 22.55 | C_{53}H_{96}O_{25} | 1191.6167 | 0.42 | 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]^\_\_\_\_\_\_\_\_ | R_{a9}/Ginsenoside Ra_{9} |
| R119 | 22.61 | C_{42}H_{88}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-Xyl]^\_\_\_\_\_\_\_\_, 1077.5864[M-H-(E)-but-2-enoyl-Xyl-ara(p)]^\_\_\_\_\_\_\_\_, 945.5404[M-H-(E)-but-2-enoyl-Xyl-ara(p)-Glc]^\_\_\_\_\_\_\_\_, 945.5404[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_{53}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]^\_\_\_\_\_\_\_\_, 945.5404[M-H-(E)-but-2-enoyl-Xyl-ara(p)]^\_\_\_\_\_\_\_\_, 783.4888[M-H-(E)-but-2-enoyl-Xyl-ara(p)-Glc]^\_\_\_\_\_\_\_\_, 783.4888[M-H-(E)-but-2-enoyl-Xyl-ara(p)-2Glc]^\_\_\_\_\_\_\_\_ | Acetyl-quinenoseside R_{1} isomer |
| R122 | 22.72 | C_{42}H_{88}O_{17} | 915.5332 | 1.64 | 783.4983[M-H-Ara(f)]^\_\_\_\_\_\_\_\_, 621.4365[M-H-Ara(f)-Glc]^\_\_\_\_\_\_\_\_, 459.3858[M-H-Ara(f)-2Glc]^\_\_\_\_\_\_\_\_ | Notoginsenoside Fe |
| R123 | 22.72 | C_{53}H_{96}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]^\_\_\_\_\_\_\_\_, 945.5404[M-H-(E)-but-2-enoyl-Xyl-ara(p)]^\_\_\_\_\_\_\_\_, 783.4888[M-H-(E)-but-2-enoyl-Xyl-ara(p)-Glc]^\_\_\_\_\_\_\_\_, 783.4888[M-H-(E)-but-2-enoyl-Xyl-ara(p)-2Glc]^\_\_\_\_\_\_\_\_ | Ginsenoside Rg_{2} isomer |
| R125 | 22.91 | C_{32}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-2Glc]^\_\_\_\_\_\_\_\_ | Ginsenoside R_{a9}/Ginsenoside Ra_{9} |

R120: Acetyl-quinquenoside R_{1} isomer
R121: Notoginsenoside Fe
R123: Acetyl+Malonyl+Ginsenoside Rd
R124: Ginsenoside Rg_{2} isomer
R125: Ginsenoside R_{a9}/Ginsenoside Ra_{9}
| 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], 1077.5844[M-H-Malonyl-Ginsenoside Rd] | Acetyl+Malonyl+Ginsenoside Rd |
| R127 | 23.25 | C_{53}H_{90}O_{23} | 1145.6089 | -1.66 | 1077.5844[M-H-(E)-but-2-enoyl-Ara], 945.5438[M-H-(E)-but-2-enoyl-Ara-Glc], 783.4897[M-H-(E)-but-2-enoyl-Ara-2Glc], 621.4393[M-H-(E)-but-2-enoyl-Ara-3Glc], 459.3865[M-H-(E)-but-2-enoyl-Ara-4Glc], Ginsenoside Ra7 isoemer/Ginsenoside Ra8 isoemer/Ginsenoside Ra9 isoemer |
| 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 R1 isoemer |
| R129 | 23.36 | C_{42}H_{76}O_{12} | 765.4796 | 0.91 | 619.4214[M-H-Rha], 457.3696[M-H-Rha-Glc], 631.3884[M-H-Glc], 455.3553[M-H-Glc-Glu A], Ginsenoside F4a |
| R130 | 23.38 | C_{42}H_{66}O_{14} | 793.4376 | 0.25 | 783.4911[M-H-Rha], 621.4376[M-H-Rha-Glc], 459.3846[M-H-Rha-2Glc], Zingibroside R1 isoemer |
| R131 | 23.56 | C_{44}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 R1 isoemer |
| R133 | 23.64 | C_{42}H_{76}O_{12} | 765.4795 | 0.78 | 619.4216[M-H-Rha], 457.3698[M-H-Rha-Glc], 783.4922[M-H-Glc], 621.4371[M-H-2Glc], 459.3831[M-H-3Glc], Ginsenoside Rg6a |
| R134 | 23.73 | C_{42}H_{62}O_{18} | 945.5425 | 0.21 | 783.4922[M-H-Glc], 621.4371[M-H-2Glc], 459.3831[M-H-3Glc], Zingibroside R1 isoemer |
| 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 Rg3 |
| 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 R1 isoemer |
| 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 Rg3 |
| R138 | 24.49 | C_{42}H_{66}O_{14} | 793.4380 | 0.76 | 459.3844[M-H-Ac-2Glc]^- | Zingibroside R₁ 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)-Rg₃a |
| R140 | 24.72 | C_{44}H_{72}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 Rg₃ |
| 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)-Rg₃a |
| R142 | 25.48 | C_{43}H_{76}O_{12} | 753.4779 | -1.33 | 621.4398[M-H-Ara]^-; 459.3819[M-H-Ara-Glc]^-; 621.4360[M-H-Ac-Glc]^-; 459.3793[M-H-Ac-2Glc]^- | 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)-Rh₂a |
| R148 | 27.27 | C_{36}H_{62}O_{8} | 621.4371 | 0.80 | 459.3869[M-H-Glc]^- | Ginsenoside 20(Ｒ)-Rh₂a |

### Saponins from Astragalus 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_{48}H_{80}O_{20} | 987.5167 | 0.20 | 945.5074[M-H-Ac]^-; 927.4952[M-H-Ac-H₂O]^-; 783.4525[M-H-Ac-Glc]^-; 765.4435[M-H-Ac-Glc-H₂O]^-; 621.3989[M-H-Ac-2Glc]^-; 489.3623[M-H-Ac-2Glc-Xyl]^- | Agroastagaloside 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_{48}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]^- | Agroastagaloside IV isomer |
| H6  | 17.69 | C_{40}H_{80}O_{20} | 987.5159 | 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 | 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 | 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 | 783.4573 [M-H-Glc], 489.3593 [M-H-Glc-Xyl] | Astragaloside VI |
| H10 | 18.72 | C_{51}H_{82}O_{21} | 1029.5265 | 927.5116 [M-H-2Ac-H_2O], 783.4541 [M-H-2Ac-Glc], 765.4396 [M-H-2Ac-Glc-H_2O], 621.4099 [M-H-2Ac-2Glc] | Agroastragaloside III isomer |
| H11 | 18.80 | C_{43}H_{70}O_{15} | 825.4640 | 945.5061 [M-H-Ac], 927.4971 [M-H-Ac-H_2O], 783.4526 [M-H-Ac-Glc], 765.4396 [M-H-Ac-Glc-H_2O], 621.4099 [M-H-Ac-2Glc], 489.3492 [M-H-Ac-2Glc-Xyl] | Astragaloside II isomer |
| H12 | 19.48 | C_{49}H_{80}O_{20} | 987.5172 | 621.3884 [M-H-Glc], 489.3532 [M-H-Glc-Xyl] | Agroastragaloside IV isomer |
| H13 | 19.72 | C_{41}H_{68}O_{14} | 783.4535 | 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 | 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 | 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 | 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 | 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], 621.405873 [M-H-2Ac-2Glc] | Agroastragaloside III |
| H18 | 21.44 | C_{43}H_{70}O_{15} | 825.4644 | 783.4563 [M-H-Ac], 621.3985 [M-H-Ac-Glc], 489.3577 [M-H-Ac-Glc-Xyl] | Astragaloside II a |
| No. | \( t_r \) (min) | Molecular formula | Measured value \((m/z)\) | Diff (ppm) | Product ions | Compound name |
|-----|-----------------|-------------------|---------------------|------------|--------------|--------------|
| H19 | 21.62           | C_{43}H_{70}O_{15}| 825.4639            | 0.36       | 783.4533[A-H-Ac]\(^-\), 621.3995[A-H-Ac-Glc]\(^-\), 489.3585[A-H-Ac-Glc-Xyl]\(^-\) | Astragaloside II isomer |
| H20 | 22.17           | C_{44}H_{72}O_{17}| 911.5016            | 1.32       | 765.4301[A-H-Rha]\(^-\) | Astragaloside VIII |
| H21 | 22.23           | C_{48}H_{80}O_{20}| 987.5167            | 0.20       | 945.5215[A-H-Ac]\(^-\), 783.4659[A-H-Ac-Glc]\(^-\), 489.3621[A-H-Ac-2Glc-Xyl]\(^-\) | Agroastragaloside IV |
| H22 | 22.25           | C_{46}H_{78}O_{18}| 941.5106            | -0.42      | 795.4499[A-H-Rha]\(^-\) | Soyasaponin I |
| H23 | 22.96           | C_{48}H_{82}O_{16}| 867.4746            | 0.46       | 765.5357[A-H-2Ac-H_{2}O]\(^-\) | Astragaloside I |
| H24 | 23.44           | C_{47}H_{80}O_{17}| 911.5011            | 0.77       | 765.4304[A-H-Rha]\(^-\) | Astragaloside VIII isomer |
| H25 | 23.61           | C_{48}H_{78}O_{18}| 909.4855            | 0.77       | 783.4506[A-H-3Ac]\(^-\), 765.4476[A-H-3Ac-H_{2}O]\(^-\) | 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 |
|-----|-----------------|-------------------|---------------------|------------|--------------|--------------|
| H26 | 5.31            | C_{22}H_{22}O_{11}| 461.1090            | 1.30       | 299.0554[A-H-Glc]\(^-\), 284.0328[A-H-Glc-CH_{3}]\(^-\) | Kaempferol-4'-methoxy-3-O-β-D-glucopyranoside isomer |
| H27 | 6.56            | C_{23}H_{28}O_{11}| 503.1558            | 0.99       | 299.0563[A-H-(6'-acetyl)Glc]\(^-\), 284.0327[A-H-(6'-acetyl)Glc-CH_{3}]\(^-\), (-)-Methylinissol in 3-O-β-D-(6'-acetyl)-glucoside daidzein |
| H28 | 7.18            | C_{21}H_{20}O_{9} | 415.1032            | 0.72       | 253.0495[A-H-Glc]\(^-\) | 7-O-β-D-glucoside de daidzein |
| H29 | 7.39            | C_{16}H_{20}O_{11}| 461.1086            | 0.43       | 299.0565[A-H-Glc]\(^-\), 284.032354[A-H-Glc-CH_{3}]\(^-\) | Kaempferol-4'-methoxy-3-O-β-D-glucopyranoside isomer |
| H30 | 7.54            | C_{13}H_{10}O_{4} | 253.0502            | 0.40       | 201.0707[M-H-C_{2}H_{2}O]\(^-\) | Daidzein isomer daidzein |
| H31 | 7.82            | C_{13}H_{20}O_{9} | 415.1026            | -0.72      | 253.0503[M-H-Glc]\(^-\) | 7-O-β-D-glucoside de isomer calycosin-7-O-β-D-glucoside |
| H32 | 7.97            | C_{25}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 isomer |
| 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 |
|   |   |   |   |   |
|---|---|---|---|---|
| H34 | 8.58 | C_{21}H_{26}O_{12} | 463.0880 | 0.65 | 239.0355[M-H-CO\_2], 224.0489[M-H-CO\_2-CH\_3], 301.0716[M-H-Glc] | Quercetin-3-O-β-D-glucopyranoside |
| H35 | 8.74 | C_{21}H_{26}O_{12} | 463.0882 | 1.08 | 301.0715[M-H-Glc], 285.0771[M-H-Glc], 270.0541[M-H-Glc-CH\_3], 228.0424[M-H-CH\_3-C\_2H\_2O] | Isoquercitrin |
| H36 | 8.93 | C_{22}H_{24}O_{10} | 447.1297 | 1.34 | 270.0513[M-H-CH\_3], 228.0424[M-H-CH\_3-C\_2H\_2O] | Vesticarpan isomer |
| H37 | 8.94 | C_{18}H_{14}O_{5} | 285.0768 | 1.75 | 270.0513[M-H-CH\_3], 228.0424[M-H-CH\_3-C\_2H\_2O] | Daidzein isomer |
| H38 | 9.34 | C_{18}H_{16}O_{4} | 253.0505 | 1.58 | 201.0715[M-H-C\_2H\_2O] | Calycosin isomer |
| H39 | 9.67 | C_{18}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] | Rhamnocitrin isomer |
| H40 | 9.71 | C_{18}H_{12}O_{6} | 299.0562 | 2.01 | 284.0337[M-H-CH\_3], 256.0366[M-H-CH\_3-CO] | Vesticarpan isomer |
| H41 | 9.77 | C_{18}H_{14}O_{5} | 285.0768 | 1.75 | 270.0455[M-H-CH\_3] | Calycosin isomer |
| H42 | 9.89 | C_{18}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] | Rhamnocitrin isomer |
| H43 | 10.08 | C_{18}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-3-O-β-D-glucopyranoside 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] | Kumatakenin |
| H45 | 10.20 | C_{18}H_{16}O_{4} | 253.0503 | 0.79 | 201.0710[M-H-C\_2H\_2O] | Daidzein isomer |
| H46 | 10.21 | C_{18}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_{18}H_{14}O_{5} | 285.0768 | 1.75 | 270.0436[M-H-CH\_3] | Vesticarpan isomer |
| H50  | 10.40 | C_{18}H_{12}O_{6} | 299.0561 | 1.67 | 284.0326[M-H-CH₃]^+ | Rhamnocitrin isomer |
|------|-------|-------------------|----------|-----|-----------------------|----------------------|
| H51  | 11.17 | C_{13}H_{10}O_{4} | 253.0504 | 1.19 | 201.0715[M-H-C_{2}H_{2}O]^+ | Daidzein isomer |
| H52  | 11.25 | C_{14}H_{12}O_{6} | 299.0561 | 1.67 | 284.0278[M-H-CH₃]^+ | Rhamnocitrin isomer |
|      |       |                   |          |     | 269.0359[M-H-OCH₃]^+  | Vesticarpan isomer |
|      |       |                   |          |     | 270.0479[M-H-CH₃]^+  |                      |
| H53  | 11.29 | C_{13}H_{14}O_{5} | 285.0763 | 0.00 | 279.0571[M-H-Glc]^+ | Rhamnocitrin-3-O-β-D-glucopyranoside isomer |
|      |       |                   |          |     | 284.0305[M-H-Glc-CH₃]^+ |                      |
| H54  | 11.37 | C_{23}H_{22}O_{11}| 461.1090 | 1.30 | 299.0570[M-H-Glc]^+ | 5,7,4’-Trihydroxy-isoflavonone isomer |
|      |       |                   |          |     | 284.0301[M-H-Glc-CH₃]^+ |                      |
| H55  | 11.50 | C_{13}H_{10}O_{5} | 269.0455 | 1.86 | 241.0504[M-H-CO]^+ | 5,7,4’-Trihydroxy-isoflavonone isomer |
| H56  | 11.72 | C_{23}H_{22}O_{11}| 461.1086 | 0.43 | 299.0570[M-H-Glc]^+ | 5,7,4’-Trihydroxy-isoflavonone isomer |
|      |       |                   |          |     | 284.0301[M-H-Glc-CH₃]^+ |                      |
| H57  | 11.72 | C_{23}H_{24}O_{11}| 475.1240 | 0.00 | 267.0659[M-H-Glc-OCH₃-CH₃]^+ | Rhamnocitrin-3-O-β-D-glucopyranoside isomer |
| H58  | 11.72 | C_{22}H_{22}O_{9} | 429.1190 | 0.93 | 267.0661[M-H-Glc]^+ | Ononin |
|      |       |                   |          |     | 252.0432[M-H-Glc-CH₃]^+ |                      |
| H59  | 11.77 | C_{13}H_{10}O_{4} | 253.0505 | 1.58 | 201.0712[M-H-C_{2}H_{2}O]^+ | Daidzein licoagroside D isomer |
| H60  | 11.77 | C_{23}H_{24}O_{10}| 447.1295 | 0.89 | 285.0769[M-H-Glc]^+ | Vesticarpan isomer |
|      |       |                   |          |     | 299.0570[M-H-Glc]^+ | Rhamnocitrin-3-O-β-D-glucopyranoside isomer |
|      |       |                   |          |     | 284.0301[M-H-Glc-CH₃]^+ |                      |
| H61  | 11.86 | C_{18}H_{14}O_{5} | 285.0768 | 1.75 | 270.0536[M-H-CH₃]^+ | 5,7,4’-Trihydroxy-isoflavonone isomer |
| H62  | 11.87 | C_{14}H_{12}O_{6} | 299.0561 | 1.67 | 284.0328[M-H-CH₃]^+ | Rhamnocitrin a |
|      |       |                   |          |     | 269.0454[M-H-OCH₂]^+ |                            |
|      |       |                   |          |     | 256.0379[M-H-CH₃-CH₂]^+ |                            |
|      |       |                   |          |     | 273.0411[M-H-CH₃]^+ |                            |
|      |       |                   |          |     | 257.0460[M-H-CH₂O]^+ |                            |
|      |       |                   |          |     | 245.0458[M-H-2CO]^+ |                            |
|      |       |                   |          |     | 229.0499[M-H-2CO-CH₃]^+ |                            |
| H63  | 12.61 | C_{15}H_{10}O_{7} | 301.0349 | 0.33 | 217.0507[M-H-C₂O₂]^+ | Quercetin a |
| H64  | 12.63 | C_{15}H_{10}O_{6} | 285.0405 | 2.10 | 217.0507[M-H-C₂O₂]^+ | Kaempferol (6aR, 11aR)-9,10-Dimethoxypterocarpn-3-O-β-D-glucopyranoside Calycosin |
| H65  | 12.72 | C_{23}H_{26}O_{10}| 461.1450 | 0.43 | 299.0570[M-H-Glc]^+ |                            |
|      |       |                   |          |     | 284.0692[M-H-Glc-CH₃]^+ |                            |
| H66  | 12.83 | C_{10}H_{12}O_{5} | 283.0609 | 1.06 | 268.0379[M-H-CH₃]^+ |                            |
|      |       |                   |          |     | 240.0431[M-H-CH₃-CH₂]^+ |                            |
|      |       |                   |          |     | 239.0352[M-H-2CO₂]^+ |                            |
|      |       |                   |          |     | 224.0477[M-H-2CO₂-CH₃]^+ |                            |
| H67 | 12.84 | C₁₆H₁₂O₆ | 299.0562 | 2.01 | 284.0337[M-H-CH₃]⁻ | Rhamnocitrin isomer |
| H68 | 12.84 | C₁₅H₁₀O₄ | 253.0503 | 0.79 | 201.0715[M-H-C₂H₅O]⁻ | Daidzein isomer |
| H69 | 12.94 | C₁₆H₁₄O₅ | 285.0768 | 1.75 | 270.0530[M-H-CH₃]⁻ | vesticarpan |
| H70 | 13.34 | C₁₇H₁₈O₅ | 301.1081 | 1.66 | 271.0623[M-H-OCH₃]⁻, 203.0864[M-H-OCH₂-C₂O₂]⁻ | 2',8-Dihydroxy-4',7-dimethoxyisoflavan/(3R)-7,2'-Dihydroxy-3',4'-dimethoxyisoflavone/ isomucronulatol |
| H71 | 13.34 | C₁₆H₁₂O₆ | 299.0561 | 1.67 | 284.0327[M-H-CH₃]⁻, 269.0451[M-H-OCH₃]⁻, 256.0366[M-H-CH₃-CO]⁻ | Rhamnocitrin isomer |
| H72 | 13.35 | C₂₃H₂₈O₁₀ | 463.1604 | 0.00 | 301.1074[M-H-Glc]⁻, 286.0849[M-H-Glc-CH₃]⁻, 271.0613[M-H-Glc-2CH₃]⁻, 256.0374[M-H-Glc-OCH₃]⁻, 227.0708[M-H-Glc-2CH₃-CO₂]⁻ | 3S-(−)-Mucronulitol-7-O-β-D-glucopyranoside/(3R)-7,2'-dihydroxy-3',4'-dimethoxyisoflavone/-7-O-β-D-glucoside |
| H73 | 13.36 | C₁₆H₁₂O₄ | 267.0662 | 1.87 | 252.0430[M-H-CH₃]⁻, 223.0415[M-H-CO₂]⁻ | Formononetin isomer |
| H74 | 13.44 | C₂₃H₂₈O₁₁ | 461.1087 | 0.65 | 299.0556[M-H-Glc]⁻, 284.0315[M-H-Glc-CH₃]⁻, 269.0445[M-H-Glc-OCH₃]⁻ | Rhamnocitrin-3-O-β-D-glucopyranoside |
| H75 | 13.61 | C₁₆H₁₂O₆ | 299.0562 | 2.01 | 284.0328[M-H-CH₃]⁻ | Rhamnocitrin isomer |
| H76 | 13.62 | C₂₃H₂₄O₁₀ | 471.1295 | 0.85 | 267.0671[M-H-(6″-O-acetyl)Glc]⁻, 252.0419[M-H-(6″-O-acetyl)Glc-CH₃]⁻ | 6″-O-acetyl-ononin |
| H77 | 14.12 | C₁₇H₁₈O₅ | 301.1081 | 1.66 | 271.0511[M-H-OCH₃]⁻, 203.0863[M-H-OCH₂-C₂O₂]⁻ | 2',8-Dihydroxy-4',7-dimethoxyisoflavan/(3R)-7,2'-Dihydroxy-3',4'-dimethoxyisoflavone/ isomucronulatol |
| H78 | 14.30 | C₁₅H₁₀O₅ | 269.0455 | 1.86 | 241.0520[M-H-CO₂]⁻ | 5,7,4'-Trihydroxyisoflavonone isomer |
| H79 | 14.30 | C₂₅H₂₈O₁₁ | 503.1556 | 0.60 | 299.0942[M-H-(6′-acetyl)Glc]⁻ | (−)-Methylinissol |
| H80  | 14.38 | C₁₀H₁₂O₃ | 285.0768 | 1.75 | 270.0522[M-H-CH₃]⁻ | 3-O-β-D-(6'-acetyl)-glucoside isomer |
|------|-------|-----------|----------|------|----------------------|-------------------------------------|
| H81  | 14.58 | C₁₃H₁₀O₅ | 269.0455 | 1.86 | 241.0516[M-H-CO]⁻   | 5,7,4'-Trihydroxy-iso-flavanone isomer |
| H82  | 14.96 | C₁₇H₁₈O₅ | 301.1081 | 1.66 | 286.0861[M-H-CH₃]⁻, 271.0627[M-H-OCH₂]⁻, 203.0861[M-H-OCH₂-C₆H₃]⁻ | 2',8-Dihydroxy-4',7-dimethoxyiso-flavan/(3R), 7,2'-Dihydroxy-3',4'-dimethoxy iso-flavan/ isomucronulatol |
| H83  | 15.17 | C₁₈H₁₂O₆ | 299.0560 | 1.34 | 284.0331[M-H-CH₃]⁻, 269.0455[M-H-OCH₂]⁻ | Rhamnocitrin isomer |
| H84  | 15.25 | C₁₇H₁₆O₆ | 315.0873 | 1.27 | 285.0409[M-H-OCH₂]⁻, 257.0464[M-H-OCH₂-CO]⁻, 241.0522[M-H-OCH₂-CO₂]⁻, 211.1346[M-H-OCH₂-CO₂]⁻ | 2',4'-Dihydroxy-5,6-Dimethoxy iso-flavanone |
| H85  | 15.51 | C₁₈H₁₄O₅ | 285.0768 | 1.75 | 270.0480[M-H-CH₃]⁻ | Vesticarpan isomer |
| H86  | 15.74 | C₁₈H₁₂O₆ | 299.0561 | 1.67 | 284.0329[M-H-CH₃]⁻ | Rhamnocitrin isomer |
| H87  | 16.42 | C₁₈H₁₂O₅ | 283.0611 | 1.77 | 268.0377[M-H-CH₃]⁻, 240.0429[M-H-CH₃-CO]⁻, 239.0350[M-H-CO₂]⁻, 224.0482[M-H-CO₂-CH₂]⁻ | Wogonin/Oroxylin A |
| H88  | 17.60 | C₁₈H₁₂O₄ | 267.0660 | 1.12 | 252.0429[M-H-CH₃]⁻, 223.0405[M-H-CO₂]⁻ | Formononetin |
| H89  | 17.78 | C₁₈H₁₂O₆ | 299.0556 | 0.00 | 284.0340[M-H-CH₃]⁻, 269.0455[M-H-OCH₂]⁻ | Rhamnocitrin isomer |
| H90  | 17.90 | C₁₈H₁₄O₅ | 285.0766 | 1.05 | 270.0450[M-H-CH₃]⁻ | Vesticarpan isomer |
| H91  | 18.45 | C₁₈H₁₂O₆ | 299.0560 | 1.34 | 284.0325[M-H-CH₃]⁻, 269.0457[M-H-OCH₂]⁻ | Rhamnocitrin isomer |
| H92  |       |           |          |      |                      |                                     |

**Flavonoids from Corni officinalis**

| Flavonoids | Retention Time (min) | Molecular Formula | Molecular Weight | Exact Mass | Isotope Mass Difference | Exact Mass (Ppm) | Mass Range |
|------------|-----------------------|-------------------|------------------|-----------|------------------------|-----------------|-----------|
| S64        | 5.77                  | C₂₇H₃₀O₁₅        | 593.1504         | -0.34     | 285.0387[M-H-Gal-Rha]⁻ | -0.34           | 593.1504  | 29   |

284.0690[M-H-(6'-acetyl)Glc-CH₃]⁻ in 3-O-β-D-(6'-acetyl)-glucoside isomer Vesticarpan isomer

5,7,4'-Trihydroxy-iso-flavanone 2',8-Dihydroxy-4',7-dimethoxyiso-flavan/(3R), 7,2'-Dihydroxy-3',4'-dimethoxyiso-flavan/ isomucronulatol

Rhamnocitrin isomer 2',4'-Dihydroxy-5,6-Dimethoxy iso-flavanone

Vesticarpan isomer

Wogonin/Oroxylin A

Formononetin

Rhamnocitrin isomer

Vesticarpan isomer

Rhamnocitrin isomer

Rhamnocitrin isomer

Kaempferol-3-O-α-L-rhamnosyl(1-6)-β-D-galactosi
| Isomer | RRT  | Formula | M.Wt | Molar Abs. | Mass Fragments |
|--------|------|---------|------|------------|----------------|
| S65    | 6.03 | C_{21}H_{22}O_{11} | 449.1091 | 1.56 | 287.0569[M-H-Glc], 269.0457[M-H-C_{6}H_{12}O_{6}], |
|        |      |         |      |            | 431.0997[M-H-Gal], 285.0405[M-H-Gal-Rha], |
| S66    | 6.21 | C_{27}H_{30}O_{15} | 593.1508 | 0.34 | Aromadendrin 7-O-β-D-glucoside de isomer |
|        |      |         |      |            | 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_{6}H_{12}O_{6}], 259.0613[M-H-Glc-CO] |
|        |      |         |      |            | Aromadendrin 7-O-β-D-glucoside de isomer |
| S68    | 7.10 | C_{21}H_{22}O_{11} | 449.1091 | 1.56 | 259.0637[M-H-Glc-CO], 243.0672[M-H-CO], |
|        |      |         |      |            | 2R,3R-Trans-aromadendrin |
| S69    | 7.40 | C_{15}H_{12}O_{6}  | 287.0558 | 0.70 | 259.0606[M-H-CO], 243.0672[M-H-CO], |
|        |      |         |      |            | Kaempferol-3-O-α-L-rhamnosyl(1-6)-β-D-galactosi de isomer |
| S70    | 7.77 | C_{21}H_{22}O_{11} | 449.1089 | 1.11 | 287.0569[M-H-Glc], 269.0455[M-H-C_{6}H_{12}O_{6}], 259.0633[M-H-Glc-CO] |
|        |      |         |      |            | Aromadendrin 7-O-β-D-glucoside de isomer |
| S71    | 7.77 | C_{27}H_{30}O_{15} | 593.1497 | -1.52 | 285.0407[M-H-Gal-Rha], 267.0315[M-H-Gal-Rha-H_{2}O], 241.0507[M-H-Gal-Rha-CO] |
|        |      |         |      |            | Kaempferol-3-O-α-L-rhamnosyl(1-6)-β-D-galactosi de isomer |
| S72    | 8.24 | C_{21}H_{18}O_{13} | 477.0670 | 0.21 | 301.0374[M-H-GluA], |
|        |      |         |      |            | Quercetin 3-O-β-D-glucuronide de 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-rhamnosyl(1-6)-β-D-galactoside |
| 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-rhamnosyl(1-6)-β-D-galactoside |
| 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_{2}H_{2}O], |
|        |      |         |      |            | Quercetin-3-O-β-D-galactopyranoside 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 |
| No. | Rf  | C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> | M.Wt | RSD  | MSH-| MSH-| Compound |
|-----|-----|-------------------------------|------|------|-----|-----|-----------|
| S78 | 8.74| C<sub>21</sub>H<sub>20</sub>O<sub>12</sub> | 463.0881 | 0.86 | 301.0361[M-H-Glc/Gal]<sup>-</sup> | 3-O-β-D-glucuronide |
| S79 | 8.80| C<sub>21</sub>H<sub>22</sub>O<sub>11</sub> | 449.1090 | 1.34 | 287.0561[M-H-Glc]<sup>-</sup>, 269.0466[M-H-C<sub>4</sub>H<sub>12</sub>O<sub>3</sub>]<sup>-</sup> | Quercetin-3-O-β-D-galactopyranoside |
| S80 | 8.92| C<sub>27</sub>H<sub>30</sub>O<sub>15</sub> | 593.1508 | 0.34 | 285.0410[M-H-Gal]<sup>-</sup>, 267.0302[M-H-Gal-Rha-H<sub>2</sub>O]<sup>-</sup>, 241.0510[M-H-Gal-Rha-CO<sub>2</sub>]<sup>-</sup> | Aromadendrin 7-O-β-D-glucoside |
| S81 | 9.07| C<sub>20</sub>H<sub>18</sub>O<sub>11</sub> | 433.0775 | 0.92 | 301.0346[M-H-Xyl]<sup>-</sup> | Quercetin 3-O-β-D-Xylopyranoside |
| S82 | 9.25| C<sub>20</sub>H<sub>18</sub>O<sub>11</sub> | 433.0773 | 0.46 | 301.0346[M-H-Xyl]<sup>-</sup> | Quercetin 3-O-β-D-Xylopyranoside isomer |
| S83 | 9.28| C<sub>27</sub>H<sub>30</sub>O<sub>15</sub> | 593.1506 | 0.00 | 285.0407[M-H-Gal]<sup>-</sup>, 267.0302[M-H-Gal-Rha-H<sub>2</sub>O]<sup>-</sup>, 241.0510[M-H-Gal-Rha-CO<sub>2</sub>]<sup>-</sup> | Kaempferol-3-O-α-L-Rhamnosyl(1-6)-β-D-galactoside |
| S84 | 10.18| C<sub>15</sub>H<sub>12</sub>O<sub>6</sub> | 287.0560 | 1.39 | 243.0652[M-H-CO<sub>2</sub>]<sup>-</sup> | 2R,3R-Trans-aromadendrin isomer |
| S85 | 11.66| C<sub>15</sub>H<sub>12</sub>O<sub>6</sub> | 287.0561 | 1.74 | 259.0605[M-H-CO]<sup>-</sup> | 2R,3R-Trans-aromadendrin isomer |
| S86 | 11.82| C<sub>16</sub>H<sub>14</sub>O<sub>5</sub> | 285.0767 | 1.40 | 270.0539[M-H-CH<sub>3</sub>]<sup>-</sup>, 217.0523[M-H-C<sub>2</sub>O<sub>2</sub>]<sup>-</sup> | Naringenin-7-O-methylether |
| S87 | 14.65| C<sub>15</sub>H<sub>12</sub>O<sub>5</sub> | 271.0612 | 2.21 | 229.0507[M-H-C<sub>4</sub>H<sub>2</sub>O]<sup>-</sup>, 227.0726[M-H-CO<sub>2</sub>]<sup>-</sup>, 203.0862[M-H-C<sub>3</sub>O<sub>2</sub>]<sup>-</sup> | Naringenin<sup>a</sup> |

Flavonoid from *Chinese yam*

| No. | Rf  | C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> | M.Wt | RSD  | MSH-| MSH-| Compound |
|-----|-----|-------------------------------|------|------|-----|-----|-----------|
| SY8 | 19.45| C<sub>16</sub>H<sub>14</sub>O<sub>4</sub> | 269.0818 | 1.49 | 254.0583[M-H-CH<sub>3</sub>]<sup>-</sup>, 239.0348[M-H-OCH<sub>2</sub>H]<sup>-</sup>, 211.0399[M-H-OCH<sub>2</sub>-CO]<sup>-</sup> | 3,5-Dimethoxy-2,7-phenanthrenedione |

<sup>a</sup>: Compound identified by comparison with the standard reference.
| No. | $t_R$ (min) | Molecular formula | Measured value (m/z) | Diff (ppm) | Product ions | Compound name |
|-----|-------------|-------------------|---------------------|------------|--------------|---------------|
| D1  | 1.40        | C₁₅H₂₂O₁₀         | 361.1136            | 0.28       | 199.0604[M-H-Glc]⁻, 169.0508[M-H-Glc-CH₂O]⁻ | Catalpol⁻ |
| D2  | 2.03        | C₁₅H₂₂O₁₅         | 523.1665            | 0.38       | 199.0614[M-H-2Glc]⁻, 169.0507[M-H-2Glc-OCH₂]⁻ | Rehmannioside A |
| D3  | 2.72        | C₁₅H₂₂O₁₀         | 361.1137            | 0.55       | 199.0617[M-H-Glc]⁻, 169.0511[M-H-Glc-CH₂O]⁻ | Monomelittoside |
| D4  | 3.12        | C₁₅H₂₂O₂₀         | 685.2192            | 0.15       | 505.1195[M-H-Glc-H₂O]⁻, 361.0782[M-H-2Glc], 343.0674[M-H-2Glc-H₂O]⁻, 181.0503[M-H-3Glc-H₂O]⁻ | Rehmannioside D |
| D5  | 3.17        | C₁₅H₂₄O₁₀         | 363.1295            | 1.10       | 201.0711[M-H-Glc]⁻ | Dihydrocatalpol isomer |
| D6  | 3.19        | C₉H₁₂O₃           | 167.0712            | 2.39       | 152.0117[M-H-CH₃]⁻, 123.0455[M-H-CO₂]⁻, 108.0218[M-H-CH₂-CO₂]⁻ | 6β-hydroxy-2-oxabicyclo[4.3.0]△8-9-nonen-1-one |
| D7  | 3.22        | C₁₅H₂₂O₁₀         | 373.1140            | 1.34       | 329.0873[M-H-CO₂]⁻, 167.0346[M-H-CO₂-Glc]⁻ | Gardoside |
| D8  | 3.27        | C₁₅H₂₂O₁₅         | 523.1666            | 0.57       | 361.1154[M-H-Glc]⁻, 199.0609[M-H-2Glc]⁻ | Melittoside |
| D9  | 3.30        | C₁₅H₂₂O₁₀         | 361.1138            | 0.83       | 199.0605[M-H-Glc]⁻, 169.0511[M-H-Glc-CH₂O]⁻ | Catalpol isomer/Monomelittoside isomer |
| D10 | 3.72        | C₁₅H₂₂O₁₀         | 363.1295            | 1.10       | 201.0714[M-H-Glc]⁻ | Dihydrocatalpol |
| D11 | 3.80        | C₁₅H₂₂O₁₀         | 373.1138            | 0.80       | 329.0871[M-H-CO₂]⁻, 167.0349[M-H-CO₂-Glc]⁻ | Geniposidic acid a |
| D12 | 3.81        | C₁₅H₂₄O₁₄         | 509.1872            | 0.39       | 185.049213.0776[M-H-2Glc]⁻ | Rehmannioside C |
| D13 | 4.46        | C₁₅H₂₂O₉          | 347.1345            | 0.86       | 167.0468[M-H-Glc-H₂O]⁻ | Ajugol |
| D14 | 4.47        | C₁₅H₂₂O₁₀         | 375.1294            | 0.80       | 213.0773[M-H-Glc]⁻, 169.0866[M-H-Glc-CO₂]⁻ | Mussaenosidic acid |
| D15 | 4.84        | C₁₅H₂₂O₉          | 345.1189            | 0.87       | 183.0661[M-H-Glc]⁻ | Aucubin |
| D16 | 5.17        | C₁₅H₂₂O₁₀         | 375.1291            | 0.00       | 213.0776[M-H-Glc]⁻, 169.0872[M-H-Glc-CO₂]⁻ | 8-Epiloganic acid a |
| D17 | 5.45        | C₁₇H₂₆O₁₀         | 389.1450            | 0.51       | 227.0942[M-H-Glc]⁻, 169.0143[M-H-Glc-COCH₂]⁻ | Ajugoside |
| D18 | 6.03        | C₁₅H₂₄O₁₅         | 549.1824            | 0.91       | 387.1440[M-H-Glc]⁻, 225.0766[M-H-2Glc]⁻ | Genipin |
| D19 | 6.73        | C₁₅H₂₆O₁₀         | 401.1451            | 0.75       | 167.0716[M-H-Glc-Ac-OCH₂]⁻, 225.0782[M-H-Glc]⁻, 181.0503[M-H-Glc-CO₂]⁻ | 1-gentiobioside a |
| D20 | 6.93        | C₁₅H₂₄O₁₀         | 387.1296            | 1.29       |  | Acetylcatalpol Geniposide a |
|    |     |                         |                      |                        |                        |
|----|-----|------------------------|----------------------|------------------------|------------------------|
| D21| 6.94| C_{31}H_{48}O_{18}     | 707.2766             | 0.57                   | 163.0401[M-H-Glc-CO_{2}-H_{2}O]⁺ |
|    |     |                        |                      |                        | 545.1743[M-H-Glc]⁺,     |
|    |     |                        |                      |                        | 383.1188[M-H-2Glc]⁺     |
|    |     |                        |                      |                        | Frehmaglutoside          |
|    |     |                        |                      |                        | G/Frehmaglutoside de 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}]⁺ |
| D23| 6.97| C_{16}H_{25}O_{8}      | 345.1553             | 1.16                   | 139.1123[M-H-CO_{2}-Glc]⁺ |
| 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_{2}O_{3}]⁺ |
|    |     |                        |                      |                        | 193.0508[C_{10}H_{16}O_{4}-H]⁺ |
|    |     |                        |                      |                        | 175.0405[C_{10}H_{16}O_{4}-H-Glc]⁺ |
| D25| 8.69| C_{26}H_{30}O_{13}     | 525.1613             | 0.95                   | 201.0719[M-H-C_{9}H_{18}O_{3}-Glc]⁺ |
|    |     |                        |                      |                        | 6-O-E-caffeoylajugol isomer |
| D26| 9.28| C_{25}H_{28}O_{11}     | 467.1558             | 1.07                   | 287.0901[M-H-Glc-H_{2}O]⁺ |
|    |     |                        |                      |                        | 137.0246[C_{9}H_{4}O_{2}-H]⁻ |
| D27| 9.30| C_{26}H_{30}O_{13}     | 525.1613             | 0.95                   | 201.0703[M-H-C_{9}H_{18}O_{3}-Glc]⁺ |
|    |     |                        |                      |                        | 6-O-E-caffeoylajugol isomer |
| D28| 9.61| C_{25}H_{32}O_{12}     | 523.1821             | 0.96                   | 361.1662[M-H-Glc]⁺,     |
|    |     |                        |                      |                        | 193.0509[C_{10}H_{16}O_{4}-H]⁺ |
|    |     |                        |                      |                        | 175.0401[C_{10}H_{16}O_{4}-H-Glc]⁺ |
| D29| 11.10| C_{26}H_{30}O_{10}    | 477.1765             | 0.84                   | 315.0876[M-H-Glc]⁻       |
|    |     |                        |                      |                        | Frehmaglutoside A        |
| D30| 11.17| C_{26}H_{32}O_{12}    | 523.1816             | 0.00                   | 193.0508[C_{10}H_{16}O_{4}-H]⁺ |
|    |     |                        |                      |                        | 175.0765[C_{10}H_{16}O_{4}-H-Glc]⁺ |
| D31| 11.72| C_{26}H_{30}O_{13}    | 525.1613             | 0.95                   | 201.0713[M-H-C_{9}H_{18}O_{3}-Glc]⁺ |
|    |     |                        |                      |                        | 6-O-E-Feruloylajugol isomer |
| D32| 14.22| C_{25}H_{32}O_{12}    | 523.1819             | 0.57                   | 193.0507[C_{10}H_{16}O_{4}-H]⁺ |
|    |     |                        |                      |                        | 175.0401[C_{10}H_{16}O_{4}-H-Glc]⁺ |

**Iridoids from Corni officinalis**

|    |     |                         |                      |                        |                        |
|----|-----|------------------------|----------------------|------------------------|------------------------|
| S1 | 2.26| C_{18}H_{22}O_{5}      | 357.1188             | 0.56                   | 195.0679[M-H-Glc]⁺,     |
|    |     |                        |                      |                        | 177.0551[M-H-Glc-H_{2}O]⁺ |
|    |     |                        |                      |                        | Secoxyloganinin        |
|    |     |                        |                      |                        | isomer                 |
| S2 | 3.22| C_{18}H_{22}O_{10}     | 373.1138             | 0.80                   | 211.0613[M-H-Glc]⁺,     |
|    |     |                        |                      |                        | 167.0346[M-H-Glc-CO_{2}]⁺ |
|    |     |                        |                      |                        | Secoxyloganinin        |
|    |     |                        |                      |                        | isomer                 |
| S3 | 4.11| C_{18}H_{22}O_{10}     | 373.1137             | 0.54                   | 211.0613[M-H-Glc]⁺,     |
|    |     |                        |                      |                        | 167.0350[M-H-Glc-CO_{2}]⁺ |
|    |     |                        |                      |                        | Secologanoside isomer  |
| S4 | 4.36| C_{18}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]⁻ |
| S5 | 4.37| C_{25}H_{30}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            |
| S7  | 4.71 | C_{23}H_{36}O_{16} | 567.1924 | -0.18 | 405.1410[M-H-Glc]\(^{\ddagger}\), 243.0878[M-H-2Glc] \(\ddagger\), 213.0775[M-H-Glc]\(^{\ddagger}\), 169.0874[M-H-Glc-CO\(_2\)]\(^{\ddagger}\), 151.0770[M-H-Glc-CO\(_2\)-H\(_2\)O]\(^{\ddagger}\), cornusglucoside D/E/G/isomer Loganic acid\(^a\) |
| S8  | 4.81 | C_{16}H_{24}O_{10} | 375.1292 | 0.27 | 213.0775[M-H-Glc]\(^{\ddagger}\), cornusglucoside Loganic acid\(^a\) |
| S9  | 4.86 | C_{16}H_{22}O_{9} | 357.1189 | 0.84 | 195.0681[M-H-Glc]\(^{\ddagger}\), 177.0569[M-H-Glc-H\(_2\)O]\(^{\ddagger}\), Sweroside isomer |
| S10 | 4.86 | C_{23}H_{36}O_{16} | 567.1925 | 0.00 | 243.0878[M-H-2Glc] \(\ddagger\), cornusglucoside D/E/G/isomer |
| S11 | 5.01 | C_{23}H_{36}O_{16} | 567.1924 | -0.18 | 405.1410[M-H-Glc]\(^{\ddagger}\), 243.0880[M-H-2Glc] \(\ddagger\), cornusglucoside D/E/G/isomer |
| S12 | 5.10 | C_{23}H_{36}O_{16} | 567.1923 | -0.35 | 405.1394[M-H-Glc]\(^{\ddagger}\), 243.0880[M-H-2Glc] \(\ddagger\), cornusglucoside D/E/G/isomer |
| S13 | 5.25 | C_{23}H_{36}O_{16} | 567.1927 | 0.35 | 405.1410[M-H-Glc]\(^{\ddagger}\), 243.0872[M-H-2Glc] \(\ddagger\), D/E,G/isomer β-dihydrocorin |
| S14 | 5.38 | C_{17}H_{28}O_{10} | 389.1450 | 0.51 | 227.0928[M-H-Glc]\(^{\ddagger}\), 209.0821[M-H-C\(_6\)H\(_{12}\)O\(_2\)]\(^{\ddagger}\), cornusglucoside D/E/G/isomer |
| S15 | 5.43 | C_{23}H_{36}O_{16} | 567.1927 | 0.35 | 405.1416[M-H-Glc]\(^{\ddagger}\), 243.0885[M-H-2Glc] \(\ddagger\), cornusglucoside D/E/G/isomer |
| S16 | 5.56 | C_{17}H_{28}O_{11} | 405.1398 | 0.25 | 243.0885[M-H-Glc]\(^{\ddagger}\), 225.0701[M-H-C\(_6\)H\(_{12}\)O\(_2\)]\(^{\ddagger}\), Morroniside\(^a\) |
| S17 | 5.82 | C_{16}H_{24}O_{10} | 375.1293 | 0.53 | 213.0771[M-H-Glc]\(^{\ddagger}\), 169.0871[M-H-Glc-CO\(_2\)]\(^{\ddagger}\), 151.0765[M-H-Glc-CO\(_2\)-H\(_2\)O]\(^{\ddagger}\), Loganic acid isomer |
| S18 | 5.91 | C_{16}H_{22}O_{11} | 389.1087 | 0.77 | 345.1190[M-H-CO\(_2\)]\(^{\ddagger}\), 227.1403[M-H-Glc]\(^{\ddagger}\), 183.0663[M-H-Glc-CO\(_2\)]\(^{\ddagger}\), 139.0770[M-H-2CO\(_2\)-Glc], Secologanoside |
| S19 | 5.94 | C_{16}H_{23}O_{11} | 419.1557 | 0.95 | 239.0653[M-H-C\(_6\)H\(_{12}\)O\(_2\)]\(^{\ddagger}\), 7R-O-methylmor | 
| S20 | 6.15 | C_{17}H_{24}O_{10} | 387.1291 | 0.00 | 225.0739[M-H-Glc]\(^{\ddagger}\), 165.0513[M-H-Glc-COCH\(_3\)]\(^{\ddagger}\), Cornine isomer |
| S21 | 6.38 | C_{17}H_{24}O_{10} | 387.1295 | 1.03 | 225.0768[M-H-Glc]\(^{\ddagger}\), 165.0558[M-H-Glc-COCH\(_3\)]\(^{\ddagger}\), Cornine isomer |
| S22 | 6.50 | C_{23}H_{36}O_{14} | 505.1561 | 0.79 | 459.1069[M-H-HCOOH]\(^{\ddagger}\), 429.0970[M-H-HCOOH-OCH\(_2\)]\(^{\ddagger}\), 399.0876[M-H-HCOOH-2OCH\(_2\)]\(^{\ddagger}\), 371.0912[M-H-HCOOH-2OCH\(_2\)-CO\(_2\)]\(^{\ddagger}\), Logmalicid A isomer/Logmalicid B isomer |
| S23 | 6.72 | C_{16}H_{28}O_{11} | 419.1556 | 0.72 | 257.0820[M-H-Glc]\(^{\ddagger}\), 239.0720[M-H-C\(_6\)H\(_{12}\)O\(_2\)]\(^{\ddagger}\), 7S-O-methylmor | 
| S24 | 6.81 | C_{17}H_{24}O_{10} | 387.1292 | 0.26 | 225.0780[M-H-Glc]\(^{\ddagger}\), Cornine \(^a\) |
| No. | Rf  | Molecule Formula | M/z Value | % Int. | Compound Description |
|-----|-----|------------------|-----------|--------|----------------------|
| S25 | 6.83| C₁₁H₁₄O₅        | 225.0767  | 1.78   | 165.0530[M-H-Glc-COCH₃]⁻  |
| S26 | 6.85| C₁₂H₂₀O₁₀       | 389.1453  | 1.28   | 195.0652[M-H-CH₂]⁻, 181.0772[M-H-CO₂]⁻  |
| S27 | 7.01| C₁₆H₂₂O₉        | 357.1188  | 0.56   | 227.0941[M-H-Glc]⁻, 209.0812[M-H-C₆H₁₂O₆]⁻  |
| S28 | 7.42| C₁₇H₂₆O₁₀       | 389.1451  | 0.77   | 195.0663[M-H-Glc]⁻, 177.0559[M-H-Glc-H₂O]⁻  |
| S29 | 7.42| C₂₁H₃₀O₁₄      | 505.1557  | 0.00   | 227.0919[M-H-Glc]⁻, 209.0822[M-H-C₆H₁₂O₆]⁻  |
| S30 | 7.50| C₂₁H₃₀O₁₄      | 505.1556  | -0.20  | 487.1445[M-H-H₂O]⁻, 389.1441[M-H-HCOOH-HCOOCH₃]⁻, 227.0928[M-H-HCOOH-HCOOCH₃-Glc]⁻, 209.0825[M-H-HCOOH-HCOOCH₃-Glc-H₂O]⁻  |
| S31 | 7.73| C₂₁H₃₀O₁₄      | 505.1561  | 0.79   | 487.1473[M-H-H₂O]⁻, 389.1416[M-H-HCOOH-HCOOCH₃]⁻, 227.0927[M-H-HCOOH-HCOOCH₃-Glc]⁻, 209.0804[M-H-HCOOH-HCOOCH₃-Glc-H₂O]⁻  |
| S32 | 7.73| C₁₇H₂₄O₁₁      | 403.1242  | 0.25   | 241.1088[M-H-Glc]⁻, 197.1183[M-H-Glc-CO₂]⁻  |
| S33 | 7.86| C₂₁H₃₀O₁₄      | 505.1557  | 0.00   | 487.1474[M-H-H₂O]⁻, 227.0930[M-H-HCOOH-HCOOCH₃-Glc]⁻, 209.0832[M-H-HCOOH-HCOOCH₃-Glc-H₂O]⁻  |
| S34 | 7.91| C₁₇H₂₆O₁₀      | 389.1452  | 1.03   | 227.0950[M-H-Glc]⁻  |
| S35 | 8.11| C₂₁H₃₀O₁₄      | 505.1562  | 0.99   | 227.0927[M-H-HCOOH-HCOOCH₃-Glc]⁻, 209.0833[M-H-HCOOH-HCOOCH₃-Glc-H₂O]⁻  |
| S36 | 8.96| C₁₇H₂₆O₁₁      | 433.1714  | 0.92   | 271.0627[M-H-Glc]⁻, 253.0869[M-H-C₆H₁₂O₆]⁻, 225.0770[M-H-C₆H₁₂O₆-CO]⁻  |
| S37 | 9.61| C₁₆H₂₂O₉        | 357.1188  | 0.56   | 195.0664[M-H-Glc]⁻, 177.0567[M-H-Glc-H₂O]⁻  |
| S38 | 9.61| C₂₁H₂₄O₇        | 387.1447  | 0.77   | 372.1206[M-H-CH₃]⁻, 357.0978[M-H-2CH₃]⁻, 341.1096[M-H-CH₃-OCH₃]⁻  |
| S39 | 9.66| C₂₀H₂₂O₆        | 357.1337  | -0.28  | 342.1125[M-H-CH₃]⁻, 311.0929[M-H-CH₃-OCH₃]⁻  |

- Dehydromorronide aglycone
- Loganin
- Sweroside*  
- Loganin isomer
- Logmalicid A isomer/Logmalicid B isomer
- Logmalicid A isomer/Logmalicid B isomer
- Kingside/8-epikingside
- Logmalicid A isomer/Logmalicid B isomer
- Loganin isomer
- Logmalicid A isomer/Logmalicid B isomer
- 7-O-ethylmorronide
- Sweroside isomer
- (-)-medioresinol
- (+)-pinoresinol/(+)-epipinoresinol
| No. | \( t_R \) (min) | Molecular formula | Measured value (m/z) | Diff (ppm) | Product ions | Compound name |
|-----|----------------|-------------------|---------------------|-----------|--------------|--------------|
| D42 | 4.65           | C_{20}H_{20}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_{20}O_{13} | 487.1456            | 0.82      | 179.0353[M-H-Rha-Glc]^−, 161.0247[C_6H_5O_2-H]^− | Cistanoside F |
| D44 | 6.56           | C_{21}H_{22}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/Deacetyl-martynoside |
| D45 | 7.66           | C_{33}H_{46}O_{20} | 785.2508            | 0.51      | 623.2194[M-H-C_6H_5O_3]^−, 605.2052[M-H-C_6H_5O_3-H_2O]^−, 477.1617[M-H-C_6H_5O_3-Rha]^−, 461.1667[M-H-C_6H_5O_3-Glc]^−, 443.1577[M-H-C_6H_5O_3-Glc-H_2O]^−, 161.0244[C_6H_5O_2-H]^− | Purpureaside C |
| D46 | 8.06           | C_{33}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_{33}H_{48}O_{20} | 799.2662            | 0.13      | 637.2330[M-H-Glc]^−, 623.2192[M-H-C_10H_6O_3]^−, 605.2079[M-H-C_10H_6O_3-H_2O]^−, 477.1617[M-H-C_10H_6O_3-Rha]^−, 175.0401[C_6H_5O_2-H]^− | Jionoside A1/Jionoside A2 |
| D48 | 8.68           | C_{33}H_{46}O_{20} | 785.2508            | 0.51      | 623.2120[M-H-C_6H_5O_3]^−, 477.1508[M-H-C_6H_5O_3-Rha]^−, 461.1667[M-H-C_6H_5O_3-Glc]^−, 443.1560[M-H-C_6H_5O_3-Glc-H_2O]^−, 161.0245[C_6H_5O_2-H]^− | Dihoside B |
| D49 | 9.11           | C_{20}H_{20}O_{15} | 623.1969            | -1.12     | 461.1664[M-H-C_6H_5O_3]^−, 315.1078[M-H-C_6H_5O_3-Rha]^− | Verbascoside |

*Compound identified by comparison with the standard reference.*
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_6H_8O_4          | 179.0345            | 0.56       | 135.0453[M-H-CO_2]^+           | Caffeic acid isomer |
| S46 | 4.53      | C_6H_8O_3          | 163.0396            | 0.61       | 119.0504[M-H-CO_2]^+           | p-Hydroxycinnamic acid isomer |
| S47 | 5.27      | C_6H_8O_3          | 163.0396            | 0.61       | 119.0504[M-H-CO_2]^+           | p-Hydroxycinnamic acid isomer |
| S48 | 5.33      | C_6H_8O_4          | 179.0345            | 0.56       | 135.0453[M-H-CO_2]^+           | Caffeic acid |
| S49 | 5.78      | C_6H_8O_3          | 163.0396            | 0.61       | 119.0504[M-H-CO_2]^+           | p-Hydroxycinnamic acid isomer |
| S50 | 5.95      | C_6H_8O_4          | 179.0345            | 0.56       | 135.0453[M-H-CO_2]^+           | Caffeic acid isomer |
| S51 | 6.55      | C_6H_8O_3          | 163.0396            | 0.61       | 119.0504[M-H-CO_2]^+           | p-Hydroxycinnamic acid |
| S52 | 7.47      | C_2H_2O_12         | 477.1036            | 0.63       | 313.0566[M-H-C_6H_8O_3]^+      | 4-O-(6'-O-Galloyl-β-D-glucopyranosyl)-cis-p-coumaric acid isomer |
| S53 | 7.51      | C_6H_8O_3          | 163.0396            | 0.61       | 119.0502[M-H-CO_2]^+           | p-Hydroxycinnamic acid isomer |
| No. | R | Molecular Formula | Exact Mass | Charge | MRM Peaks | Compound Name |
|-----|---|------------------|------------|--------|-----------|---------------|
| 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_6H_5O_3]^+, 169.0143[C_6H_5O_5]^+, 163.0403[C_6H_5O_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-C_2H_5-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]^+, 331.1383[M-H-Glc-H_2O]^+, 311.0921[M-H-Glc-H_2O-2CH_3]^+ | (7S,8R)-Urolignoside/Glochidioboside/(7S,8R)-Dihydrodehydrodiconiferyl alcohol |
| 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]^+, 326.1163[M-H-Glc-H_2O-CH_3]^+, 311.0921[M-H-Glc-H_2O-2CH_3]^+ | (7S,8R)-Urolignoside/Glochidioboside/(7S,8R)-Dihydrodehydrodiconiferyl alcohol |
| 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]^+ | (7S,8R)-Urolignoside/Glochidioboside/(7S,8R)-Dihydrodehydrodiconiferyl alcohol |
| 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-glucopyranosyl 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-C_2H_5-OCH_3]^+ | (-)-Secoisolariciresinol-9′-O-β-D-glucopyranosyl isomer |
| 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_3]^+ | (-)Episyringaresinol/Syringaresinol |
| S63 | 10.07 | C_{26}H_{34}O_{11} | 521.2028 | 0.96 | 341.1403[M-H-Glc-H_2O]^+ | (-)-Isolariciresinol |
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$_2$O-Glc$]^{-}$; 311.0928[M-H-Glc-H$_2$O-OCH$_3$]$^{-}$ | 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$_2$O-Glc$]^{-}$, 235.1345[M-H-H$_2$O-Glc-CH$_3$]$^{-}$, 191.1447[M-H-H$_2$O-CO$_2$]$^{-}$ | Frehmaglutoside E |
| D36 | 7.22        | C$_{10}$H$_{16}$O$_8$  | 405.2128            | 0.74      | 213.1499[M-H-Glc-2CH$_3$]$^{-}$, 195.1400[M-H-Glc-2CH$_3$-H$_2$O]$^{-}$ | Oxyrehmanionoside B |
| D37 | 8.04        | C$_{10}$H$_{10}$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$_2$O]$^{-}$, 231.1394[M-H-Glc-2H$_2$O]$^{-}$, 223.1719[M-H-Glc-CO$_2$]$^{-}$, 205.1616[M-H-Glc-H$_2$O-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$_3$H$_6$O]$^{-}$, 163.0404[C$_5$H$_{10}$O$_2$-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$_2$O]$^{-}$, 409.3488[M-H-H$_2$O-CO]$^{-}$ | Betulinic acid |
| H93 | 29.87       | C$_{30}$H$_{48}$O$_3$  | 455.3531            | 1.32      | 409.3483[M-H-H$_2$O-CO]$^{-}$ | Oleanolic acid a |
| H94 | 29.95       | C$_{30}$H$_{48}$O$_3$  | 455.3528            | 0.66      | 409.3474[M-H-H$_2$O-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$_{47}$O$_{7}$ | 519.3325 | 0.58 | 501.3213[M-H$_2$O]$^-$, 459.3167[M-H-C$_3$H$_6$O]$^-$, 387.2559[M-H-C$_3$H$_6$O-4H$_2$O]$^-$ | Cucurbitacin P isomer |
| T2  | 13.46 | C$_{30}$H$_{47}$O$_{7}$ | 517.3171 | 1.16 | 499.3054[M-H$_2$O]$^-$, 457.2955[M-H-C$_3$H$_6$O]$^-$, 439.2862[M-H-C$_3$H$_6$O-2H$_2$O]$^-$, 385.2399[M-H-C$_3$H$_6$O-C$_2$H$_4$O-6H$_2$O]$^-$ | 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$_2$O]$^-$, 459.3122[M-H-C$_3$H$_6$O]$^-$, 441.3003[M-H-C$_3$H$_6$O-4H$_2$O]$^-$, 359.2242[M-H-C$_3$H$_6$O-4H$_2$O-CO]$^-$ | Cucurbitacin P |
| T4  | 14.72 | C$_{30}$H$_{44}$O$_{7}$ | 515.3013 | 0.78 | 479.2794[M-H$_2$H$_2$O]$^-$, 437.2691[M-H-C$_3$H$_6$O-C$_2$H$_4$O]$^-$, 341.2123[M-H-C$_3$H$_6$O-C$_2$H$_4$O-C$_2$H$_4$O]$^-$ | Cucurbitacin D |
| T5  | 14.72 | C$_{30}$H$_{46}$O$_{8}$ | 533.3116 | 0.38 | 497.2876[M-H$_2$H$_2$O]$^-$, 479.2806[M-H$_2$H$_2$O]$^-$, 464.2560[M-H$_2$H$_2$O-C$_2$H$_4$]$^-$, 437.2689[M-H$_2$H$_2$O-C$_3$H$_6$O]$^-$, 427.2495[M-H$_2$H$_2$O-C$_3$H$_6$O]$^-$, 409.2382[M-H$_2$H$_2$O-C$_3$H$_6$O]$^-$, 385.2419[M-H$_2$H$_2$O-C$_3$H$_6$O-C$_2$H$_4$O]$^-$, 341.2124[M-H$_2$H$_2$O-C$_3$H$_6$O-C$_3$H$_5$O-C$_2$H$_4$O]$^-$ | Cucurbitacin H |
| T6  | 14.96 | C$_{30}$H$_{46}$O$_{8}$ | 533.3118 | 0.75 | 497.2751[M-H$_2$H$_2$O]$^-$, 427.2480[M-H$_2$H$_2$O-C$_3$H$_6$O]$^-$, 385.2428[M-H$_2$H$_2$O-C$_3$H$_6$O-C$_2$H$_4$O]$^-$, 341.2119[M-H$_2$H$_2$O-C$_3$H$_6$O-C$_2$H$_4$O-C$_2$H$_4$O]$^-$ | Cucurbitacin H isomer |
| T7  | 16.70 | C$_{30}$H$_{46}$O$_{7}$ | 517.3171 | 1.16 | 499.3082[M-H$_2$H$_2$O]$^-$, 457.2949[M-H$_2$H$_2$O]$^-$, 455.2816[M-H$_2$H$_2$O-C$_3$H$_6$O]$^-$, 439.2861[M-H$_2$H$_2$O-C$_3$H$_6$O]$^-$ | Cucurbitacin R/dihydrocucurbitacin D/cucurbitacin O |
| No. | t_R  | Molecular formula | Measured value (m/z) | Diff (ppm) | Product ions | Compound name |
|-----|------|-------------------|----------------------|------------|--------------|---------------|
| T8  | 16.70| C_{30}H_{40}O_7   | 515.3007             | -0.39      | 385.2377[M-H-H_2O-C_2H_4O-C_2H_6O]^−, 367.2302[M-H-2H_2O-C_2H_4O-C_2H_6O]^− | Cucurbitacin D isomer |
| T9  | 16.94| C_{30}H_{40}O_7   | 517.3170             | 0.97       | 499.3068[M-H-H_2O]^−, 457.2982[M-H-C_2H_4O]^−, 385.2389[M-H-H_2O-C_2H_4O-C_2H_6O]^−, 367.2295[M-H-2H_2O-C_2H_4O-C_2H_6O]^− | Cucurbitacin R/dihydrocucurbitacin D/cucurbitacin O |
| T10 | 17.62| C_{30}H_{40}O_7   | 517.3166             | 0.19       | 497.2771[M-H-H_2O]^−, 461.2759[M-H-3H_2O]^−, 385.2295[M-H-2H_2O-C_2H_4O-C_2H_6O]^− | Cucurbitacin R/dihydrocucurbitacin D/cucurbitacin O |
| T11 | 18.61| C_{30}H_{40}O_7   | 515.3014             | 0.97       | 437.2743[M-H-H_2O-C_2H_4O]^− | Cucurbitacin D isomer |

a: Compound identified by comparison with the standard reference.

Table S8  Other compounds from ZKYY

| No. | t_R  | Molecular formula | Measured value (m/z) | Diff (ppm) | Product ions | Compound name |
|-----|------|-------------------|----------------------|------------|--------------|---------------|
| 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 de isomer |
| S95 | 1.84 | C_7H_6O_5         | 169.0141             | 2.37       | 125.0246[M-H-CO_2]^− | Gallic acid 3,5-Dihydroxybenzoic acid isomer |
| S96 | 2.50 | C_7H_6O_4         | 153.0189             | 0.65       | 109.0298[M-H-CO_2]^− | Gallic acid 4-O-β-D-glucoside |
| 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-glucoside |
| S100 | 3.90 | C_{13}H_{16}O_{10} | 331.0671 | 1.81 | 169.0145[M-H-Glc]-, 125.0250[M-H-Glc-CO₂]- |
| S110 | 7.04 | C_{16}H_{18}O_{9} | 353.0874 | 0.28 | 191.0555[M-H-C₆H₄O₃]-, 161.0242[C₆H₄O₃-H]-, 147.0452[M-H-C₆H₅O₃-CO₂]-, 129.0195[M-H-C₆H₅O₃-CO₂-H₂O]-, 111.0089[M-H-C₆H₅O₃-CO₂-2H₂O]- |
| S111 | 7.83 | C_{16}H_{18}O_{9} | 353.0879 | 1.70 | 191.0560[M-H-C₆H₄O₃]-, 111.0093[M-H-C₆H₅O₃-CO₂-H₂O]-, 111.0088[M-H-C₆H₅O₃-CO₂-2H₂O]- |
| S112 | 8.59 | C_{16}H_{18}O_{9} | 353.0876 | 0.85 | 111.0088[M-H-C₆H₅O₃-CO₂-2H₂O]- |
| S113 | 9.14 | C₆H₅O₅ | 183.0297 | 2.19 | 168.0065[M-H-CH₃]-, 139.0401[M-H-CO₂]- |
| S104 | 5.37 | C₆H₅O₅ | 183.0297 | 2.19 | 168.0065[M-H-CH₃]-, 139.0401[M-H-CO₂]- |
| S101 | 4.28 | C₆H₅O₅ | 183.0297 | 2.19 | 168.0065[M-H-CH₃]-, 139.0401[M-H-CO₂]- |
| S102 | 4.84 | C₆H₅O₅ | 183.0297 | 2.19 | 168.0065[M-H-CH₃]-, 139.0401[M-H-CO₂]- |
| S105 | 5.47 | C_{16}H_{18}O_{9} | 353.0875 | 0.57 | 191.0565[M-H-C₆H₄O₃]-, 173.0456[M-H-C₆H₄O₃-H₂O]-, 161.0249[C₆H₄O₃-H]-, 147.0303[M-H-C₆H₅O₃-CO₂]-, 129.0195[M-H-C₆H₅O₃-CO₂-H₂O]-, 111.0095[M-H-C₆H₅O₃-CO₂-2H₂O]- |
| S106 | 5.82 | C_{16}H_{18}O_{9} | 353.0875 | 0.57 | 191.0562[M-H-C₆H₄O₃]-, 173.0458[M-H-C₆H₄O₃-H₂O]-, 161.0245[C₆H₄O₃-H]-, 129.0191[M-H-C₆H₅O₃-CO₂-H₂O]-, 111.0088[M-H-C₆H₅O₃-CO₂-2H₂O]- |
| S107 | 5.84 | C₆H₅O₃ | 151.0397 | 1.32 | 123.0452[M-H-CO]-, 108.0454[M-H-CO-CH₃]-, 109.0296[M-H-CO₂]- |
| S108 | 6.13 | C₆H₅O₄ | 153.0191 | 1.96 | 109.0296[M-H-CO₂]- |
| S109 | 6.63 | C_{16}H_{18}O_{9} | 353.0877 | 1.13 | 111.0090[M-H-C₆H₅O₃-CO₂-2H₂O]- |
| S111 | 7.83 | C_{16}H_{18}O_{9} | 353.0879 | 1.70 | 191.0560[M-H-C₆H₄O₃]-, 111.0093[M-H-C₆H₅O₃-CO₂-H₂O]-, 111.0088[M-H-C₆H₅O₃-CO₂-2H₂O]- |

- **Gallic acid isomer**
- **3,5-Dihydroxybenzoic acid isomer**
- **Chlorogenic acid isomer**
- **Methyl gallate isomer**
- **Vanillin isomer**
- **3,5-Dihydroxybenzoic acid isomer**
- **Methyl gallate isomer**
- **Vanillin**
- **Chlorogenic acid isomer**
- **Chlorogenic acid isomer**
- **Chlorogenic acid isomer**
- **Methyl gallate**
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| Polyphenols from *Chinese yam* |   |   |   |   |   |
| SY1 | 11.64 | C$_{14}$H$_{13}$O$_3$ | 229.0870 | 2.18 | 123.0459[M-H-C$_2$H$_2$O]$_-$ 2', 3', 5-Trihydroxybibenzyl isomer  |
| SY2 | 12.22 | C$_{19}$H$_{24}$O$_4$ | 315.1600 | 1.27 | 297.1503[M-H-H$_2$O]$_-$, 279.1394[M-H-2H$_2$O]$_-$, 191.1079[M-H-H$_2$O-C$_2$H$_4$O]$_-$, 173.0979[M-H-2H$_2$O-C$_2$H$_4$O]$_-$, 149.0610[M-H-C$_3$H$_5$O$_2$]$_-$ (3R,5R)-3,5-Dihydroxy-1,7-bis(4-hydroxyphenyl)-3,5-heptanediol |
| SY3 | 12.40 | C$_{14}$H$_{13}$O$_3$ | 229.0870 | 2.18 | 123.0453[M-H-C$_2$H$_2$O]$_-$ 2',3,5-Trihydroxybibenzyl isomer  |
| SY4 | 13.15 | C$_{21}$H$_{26}$O$_6$ | 375.1811 | 0.80 | 360.1581[M-H-CH$_3$]$_-$, 203.0865[M-H-2H$_2$O-C$_4$H$_8$O$_2$]$_-$, 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$_6$H$_5$O$_2$-H]$_-$ (3R,5R)-1,7-Bis(4-hydroxy-3-methoxyphenyl)-3,5-heptanediol |
| SY5 | 13.39 | C$_{21}$H$_{26}$O$_6$ | 375.1811 | 0.80 | 360.1573[M-H-CH$_3$]$_-$, 203.0860[M-H-2H$_2$O-C$_4$H$_8$O$_2$]$_-$, 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$_6$H$_5$O$_2$-H]$_-$ (3R,5R)-1,7-Bis(4-hydroxy-3-methoxyphenyl)-3,5-heptanediol isomer  |
| SY6 | 13.47 | C$_{16}$H$_{12}$O$_3$ | 229.0870 | 2.18 | 123.0453[M-H-C$_2$H$_2$O]$_-$ 2',3,5-Trihydroxybibenzyl isomer  |
| SY7 | 18.97 | C$_{25}$H$_{16}$O$_3$ | 243.1026 | 2.06 | 137.0609[M-H-C$_2$H$_2$O]$_-$, 122.0374[M-H-C$_2$H$_2$O-CH$_3$]$_-$, 106.0425[M-H-C$_2$H$_2$O-OCH$_3$]$_-$ Batatasin III/Batatasin 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.