Supplementary Data

MRM-based strategy for the homolog-focused detection of minor ginsenosides from Notoginseng Total Saponins by ultra-performance liquid chromatography coupled with hybrid triple quadrupole-linear ion trap mass spectrometry

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Contents of Supplementary Data

1. Characterization of the saponins in NGTS by integrating MRM-IDA-EPI and IT-TOF/MS^n analyses

Combining the MRM-IDA-EPI and IT-TOF/MS^n analyses, a total of 112 compounds were characterized, among which, peaks 66, 67, 69, 86, 88, 89, 90, 94, 95, 98, 109, and 110 were characterized by comparison with the reference compounds; peaks 19, 23, 24, and 88 were characterized in the manuscript. So, the detailed descriptions of the other components are presented here.

Peaks 1 and 21 shared the same molecular composition of $C_{47}H_{82}O_{19}$ and similar fragmentation behaviors. The identical fragment ions at *m/z* 493.38 [A−H]$^-$, 417.2 [A−H−H_2O−C_3H_6O]$^-$, and 391.4 [A−H−$C_6H_{14}O$]$^-$ were observed, suggesting their sapogenin as [PPT 16]. The prominent neutral losses of 162.05 Da × 2 and 132.04 Da indicated the possible presence of a xylosyl and two glucosyl substituents. Besides, the prominent product ions at *m/z* 817.48 [M-H-xyl]$^-$ and 787.47 [M-H-glc]$^-$ suggested peaks 1 and 21 to be bidesmosidic saponins. Thus, peaks 1 and 21 were assigned as [PPT 16]-6-glucosyl-xylosyl-20-glucoside or its isomer, respectively.[1] Peaks 2, 4, and 7 shared the same elemental composition of $C_{42}H_{74}O_{16}$ and sequential neutral losses of 162 Da × 2. In view of other fragment ions at *m/z* 415.2 [A−H−2H_2O−C_3H_6O]$^-$, 403.3 [A−H−H_2O−$C_4H_8O_2$]$^-$, and 391.4 [A−H−$C_5H_{10}O_3$]$^-$, their structures were assigned as vinaginsenoside or its isomers, respectively.[2] The HR-MS/MS spectral profiles of peaks 3 and 5 suggested they possess the identical molecular composition of $C_{47}H_{82}O_{20}$. The sequential neutral losses of 132 Da and 162 Da × 2 indicated that they were substituted by one xylosyl and two glucosyl groups. The presence of the fragment ions at *m/z* 803.4 [M-H-glc]$^-$ and 833.2 [M-H-xyl]$^-$ indicated peaks 3 and 5 were bidesmosidic saponins. Furthermore, the fragment ions at *m/z* 509.3, 415.3, and 403.3 proposed peaks 3 and 5 as [PPT 21]-6-glucosyl-xylosyl-20-glucoside or its isomer, respectively.[2] The molecular formulas of peaks 6, 9, and 11 were deduced as $C_{48}H_{84}O_{20}$ based on their HR-MS/MS data. Among them, peaks 6 and 9 shared the same successive neutral losses of 162.05 Da × 2 and 146.06 Da, along with the deprotonated aglycone ion ([A−H]$^-$) at *m/z* 509.3778. The identical fragment ion at *m/z* 415.3, originating from the 58 Da (C_3H_6O) loss from the [A−H]$^-$

ion, further assigned peaks 6 and 9 as [PPT 21]-6-rhamnosyl-20-glucosyl-glucoside or [PPT 21]-6-rutinosyl-20-glucoside, respectively.[2] Whereas peak 11 was plausibly characterized as vinaginsenoside R_{13} or its isomer with the observation of the three stepwise neutral losses of 162 Da × 3.[2] The formate anions of peaks 12, 18, and 45 were observed at *m/z* 993.52, corresponding to the elemental composition of $C_{47}H_{80}O_{19}$. In combination with the prominent product ions at *m/z* 403.2 and 391.3, peak 12 was tentatively identified as notoginsenoside H or its isomer.[4,5] As the fragment ions at *m/z* 553.3 and 415.3 were the diagnostic ions of [PPT 13], peak 18 was assigned as sanshichisaponin G or its isomer.[7] In contrast to peaks 12 and 18, the prominent ion at *m/z* 477.3828 indicated peak 45 was substituted by a glucosyl and a rutinosyl moieties.[7] Peaks 14, 66, and 79 exhibited the same molecular composition of $C_{47}H_{80}O_{18}$ and the sequential neutral losses of 132.04 Da and 162.05 Da × 2, indicating that these compounds were substituted by two glucosyl and a xylosyl/arabinosyl residues. Among them, peak 66 was confirmed as notoginsenoside R_1 by the reference compound. The product ion at *m/z* 369.2 $[A\text{-}H\text{-}2H_2O\text{-}C_4H_6O]^-$ suggested the sapogenin of peak 14 as [PPD 8].[8-11] However, the predominant product ions at *m/z* 799.4809 [M-H-xyl]$^-$, 637.4245 [M-H-xyl-glc]$^-$, 475.3741 [M-H-xyl-2glc]$^-$, and 391.3 $[A\text{-}H\text{-}C_6H_{12}]^-$ proposed the sapogenin of peak 79 is [PPT 6].[3] Peaks 15, 31, and 51 gave the same pseudo-molecular ion at *m/z* 861.48, along with a sequential neutral losses of 162.05 Da × 2. The fragment ions at *m/z* 403.4 and 391.3 suggested the sapogenins of peak 15 are [PPT 11] or [PPT 14].[5] Similarly, the unique product ions at *m/z* 421.2 and 391.3 proposed peak 51 as di-glucosidated product of [PPT 11] or [PPT 14].[5,6] However, there were no obvious fragment ions to deduce the sapogenin of peak 31, which was plausibly assigned as [PPT 11], [PPT 12], [PPT 13], [PPT 14] or [PPD 10].[3-5,12] Peaks 16, 46, 49, and 59 exhibited the same molecular composition of $C_{42}H_{74}O_{15}$, but the different mass fragmentation behaviors. The mass profile of peak 16 showed the stepwise neutral losses of 162 Da × 2, along with the aglycone ion at *m/z* 493.3832. With the additional cleavages of 58 Da and 102 Da, peak 16 was deduced as diglucosidated conjugate of [PPT 15] or [PPT 16].[1] Peaks 46, 49, and 59 displayed the sapogenin ion at *m/z* 509.37, along with a sequential neutral losses of 146 Da, 162 Da, and 118 Da. Thus, peaks 46, 49, and 59 were characterized as quinquenoside L_9 or its isomers, respectively.[2] Peaks 20 and 33 afforded the quasi-molecular ion at *m/z* 963.55, corresponding to an elemental composition of $C_{48}H_{84}O_{19}$. Their negative MS^n spectra gave the dominant signals at *m/z* 801.49, 655.43, and 493.38, suggesting the stepwise neutral cleavages of a rutinosyl (308.08 Da) and a glucosyl (162.05 Da) moieties. In addition, the fragment ion at *m/z* 417.6 $[A\text{-}H\text{-}H_2O\text{-}C_3H_6O]^-$ proposed peaks 20 and 33 as [PPT 16]-20-glucosyl-6-rutinoside or its isomer, respectively.[1] Peak 22 yielded the formate anion at *m/z* 731.3854, along with the product ion at *m/z* 553.2 and 391.4, indicating its structure as [PPT 1]-*O*-xylosyl-*O*-glucoside.[11] The elemental composition of peaks 25, 30, 40, 53, 71, and 75 were elucidated as $C_{48}H_{82}O_{19}$ according to their HR-MS/MS data. Among them, peaks 25, 30, and 40 afforded the same neutral losses of 308 Da and 162 Da, resulting from the stepwise cracking a rutinosyl and a glucosyl groups. Moreover, they shared the same deprotonated aglycone ion at *m/z* 491.3, corresponding to the aglycone of [PPT 10], [PPT 11], [PPT 12], [PPT 13], [PPT 14], or [PPD 10].[3] The sequential neutral cleavages of 18 Da proposed peak 25 as majoroside F_6 or its isomer.[5] While, peaks 30 and 40 showed a neutral loss of 58 Da (C_3H_6O), which was the typical *C*-17 side chain cleavage of [PPT 13].[3] Peaks 53, 71, and 75 exhibited the similar deprotonated aglycone ions at *m/z* 475.37, generating from three sequential neutral losses of 162.05 Da. Combining with another neutral loss of 88 Da (C_6H_{12}), peaks 53 and 71 were supposed as notoginsenoside N or its isomer, respectively.[3] While the identical fragment ion at *m/z* 387.1 $[A\text{-}H\text{-}H_2O\text{-}C_4H_6O]^-$ deduced the sapogenins of peak 75 are [PPD 8] or [PPD 9].[8-10] Peaks 26, 35, 43, and 50 exhibited a $[M–H]^-$ ion at *m/z* 813.4, along with a $[A–H]^-$ ion at *m/z* 489.5, resulting from the sequential neutral losses of 162 Da × 2. In addition, the identical fragment ion at *m/z* 391.3 $[M\text{-}H\text{-}2glc\text{-}C_6H_{10}O]^-$ proposed their structures as [PPT 8]-6,20-di-*O*-glucoside or its isomers, respectively.[9] Peak 27 showed an $[M−H]^-$ ion at *m/z* 699.3791, corresponding to a molecular formula of $C_{37}H_{62}O_{15}$. In combination of the stepwise neutral losses of 162 Da and 146 Da, it was proposed as [PPT 1]-*O*-rutinoside.[11] Peaks 28, 36, 39, 44, and 55 exhibited the same molecular composition of $C_{41}H_{72}O_{15}$ and mass profiles. The deprotonated aglycone ions at *m/z* 509.37 suggested their sapogenins could be [PPT 21], [PPT 22], or [PPT 23]. With the observation of identical neutral losses of 118.06 Da ($C_5H_{10}O_3$), 88.05 Da, and 58.04 Da, their sapogenins was determined as [PPT 21]. Finally, they were assigned as the [PPT 21]-20-xylosyl-3-glucoside or its isomers, respectively, along with the separate neutral losses of 132 Da (xylosyl) and 162 Da (glucosyl).[3] All the molecular composition of peaks 29, 32, 54, 67, 95, 96, and 108 were the same as $C_{48}H_{82}O_{18}$, calculated from their HR-MS/MS data. Among them, peaks 67 and 95 were respectively confirmed as ginsenosides Re and Rd by comparison with the reference compounds. Peak 29 exhibited a stepwise neutral loss of 146 Da and 162 Da. Besides, the product ion at *m/z* 391.3 generated from the *C*-17 side chain cleavage of a $C_6H_{10}O$ (98.07 Da) unit indicated its sapogenin is [PPT 8].[9] The product ions of peak 32 were highly consistent with those of peak 29, however, the neutral loss of 98.07 Da ($C_6H_{10}O$) was not observed. The skeleton of peak 32 was thus tentatively determined as [PPT 8] or [PPT 9] .[13] Similarly, the deprotonated aglycone ion at *m/z* 475.3726 and the product ion at *m/z* 391.3 confirmed compound 54 as ginsenoside B_2 or chikusetsusaponin FK_1 or its isomer.[3] Peaks 96 and 108 showed the similar cracking patterns and deprotonated aglycone ions at *m/z* 459.38 with peak 95. Thus peaks 96 and 108 were plausibly characterized as the isomers of ginsenoside Rd. Peaks 34 and 42 showed the same deprotonated molecular ion at *m/z* 801.46, corresponding to an elemental composition of $C_{41}H_{70}O_{15}$. Besides, they shared the similar product ions at *m/z* 593.36 and 507.3, which were in high accordance with those of [PPT 19]. With the observation of sequential losses of 132 Da and 162 Da, peaks 34 and 42 were plausibly assigned as floralginsenoside C or its isomer, respectively.[13] Similarly, peak 37 gave the deprotonate molecular ion at *m/z* 861.4829, corresponding to the formula composition of $C_{42}H_{72}O_{15}$. With the observation of neutral losses of 146 Da, 162 Da, and 58 Da, it was plausibly assigned as [PPT 19]-*O*-rhamnosyl-*O*-glucoside.[13] The molecular formulas of peaks 38 and 41 were deduced as $C_{48}H_{82}O_{20}$ based on their HR-MS/MS data (Table 1). In combination with the neutral losses of 162 Da (glucosyl), 308 Da (rutinosyl), peak 38 was plausibly determined as floralginsenoside I or floralginsenoside J or its isomer.[15,16]

While peak 41 was characterized as [PPD 12] or [PPT 16]-*O*-rhamnosyl-*O*-glucosyl-*O*- glucuronide with the [A−H]$^-$ ion at *m*/*z* 493.3.[13] Likewise, peak 47 was characterized as notoginsenoside SP_8 or its isomer. Peaks 48, 56, and 72 shared the same formula of $C_{48}H_{80}O_{19}$, while displayed the different mass cracking pathways. In combination of the prominent ions at *m*/*z* 797.3 [M-H-glc]$^-$ and 489.2 [M-H-glc-rut]$^-$, peaks 48 and 56 were tentatively assigned as [PPT 8] or [PPT 9]-*O*-rutinosyl-*O*-glucoside, respectively.[9] While peak 72 was characterized as notoginsenoside G with the identical neutral losses of 162 Da × 2 and 84 Da.[17] The chemical composition of peak 52 was calculated as $C_{41}H_{72}O_{13}$ from the quasi-molecular ion at *m*/*z* 817.4975. With the observation of product ions at *m*/*z* 639.2 [M−H−xyl]$^-$ and 477.2 [M−H−xyl−glc]$^-$, it was tentatively assigned as [PPD 10]-*O*-glucosyl-*O*-xyloside.[9] Likewise, peak 57 was plausibly assigned as notoginsenoside A or its isomer,[3] and peak 58 was plausibly characterized as [PPD 12] or [PPT 16]-*O*-glucosyl-*O*-xyloside.[1,14] Peaks 60 and 64 exhibited the similar deprotonated molecular ions at *m*/*z* 1093.57 and aglycone ions at *m*/*z* 475.38. However, the prominent fragment ions at *m*/*z* 961.3 [M−H−xyl]$^-$ and 931.4 [M−H−glc]$^-$ suggested peak 60 as [PPD 8]-3-glucosyl-glucosyl-20-glucosyl- arabinoside or [PPD 9]-3-glucosyl-glucosyl-20-glucosyl-xyloside,[9,10] whereas the sapogenin of peak 64 was determined as [PPT 6] with the observation of neutral loss 84.09 Da (C_6H_{12}).[3] Peak 61 gave the molecular composition of $C_{54}H_{92}O_{23}$, calculated from the quasi-molecular ion at *m*/*z* 1107.5947. With the prominent fragment ions at *m*/*z* 961.5221, 799.4784, 637.4220, and 475.3652, peak 61 was plausibly assigned as yesanchinoside E or its isomer.[3] The molecular composition of peak 62 was $C_{47}H_{77}O_{18}$, calculated from the HR-MS/MS data. Besides, the deprotonated aglycone ion at *m*/*z* 473.2 was yielded by sequentially cracking two glucosyls and one xylosyl units. With the observation of the additional loss of 84 Da (C_6H_{12}), peak 62 was concluded to be [PPT 5]-di-*O*-glucosyl-*O*-xyloside.[3] The molecular composition of peak 63 was calculated as $C_{54}H_{94}O_{25}$ from the [M−H]$^-$ ion at *m*/*z* 1141.6044. The prominent fragment ions at *m*/*z* 979.5341 [M−H−glc]$^-$, 817.4847 [M−H−2glc]$^-$, 655.4341 [M−H−3glc]$^-$, and 493.3827 [M−H−4glc]$^-$ suggested peak 63 as quinquenoside L_{16} or its isomer.[1,14] Peaks 65 and

82 shared the similar molecular composition of $C_{42}H_{70}O_{14}$, along with the successive neutral losses of 162 Da × 2 (glucosyl). With observation of the significant neutral loss of 84 Da (C_6H_{12}), the sapogenin of peak 65 was assigned as [PPT 4] or [PPT 5].[17,18] Whereas peak 82 was determined as diglucosidated product of [PPT 4] due to the obvious neutral loss of 28 Da (CO).[17] Compounds 68 and 73 shared the same formula composition ($C_{41}H_{70}O_{14}$) and mass fragmentation pathways. The identical fragment ions at *m/z* 491.5 $[A{-}H]^-$, 415.3 $[A{-}H{-}H_2O{-}C_3H_6O]^-$, and 391.4 $[A{-}H{-}C_6H_{12}O]^-$ confirmed their sapogenin as [PPT 12]. With the observation of stepwise neutral losses of 132 Da and 162 Da, compounds 68 and 73 were supposed as vinaginsenoside R_{11} or floraginsenoside D, respectively.[3] Peak 69 was identified as ginsenoside Rg_1, using the reference compound. As the similar mass profiles, peaks 87 and 101 were assigned as the isomers of ginsenoside Rg_1. Compounds 70, 74, 86, and 91 shared the same molecular composition of $C_{41}H_{70}O_{13}$ and mass cracking patterns. Among them, peak 86 was identified as ginsenoside F_3 by comparison with the reference component. Hence, peaks 70, 74, and 91 were determined as the notoginsenoside R_2 or its isomers, respectively. Similarly, peaks 76 and 84 were tentatively proposed as [PPT 6]-6-acetylglucosyl-20-glucoside, [PPT 6]-6-glucosyl-20-acetylglucoside or [PPT 6]-20-acetyl-6-glucosyl-glucoside, respectively.[3] Peak 77 gave the pseudo-molecular ion at *m/z* 1091.6028, corresponding to the chemical formula of $C_{54}H_{92}O_{22}$. With the observation of stepwise neutral losses of 162.05 Da × 3, it was assigned as gynosaponin V or its isomer.[19] Peak 78 gave the formula composition of $C_{36}H_{62}O_{10}$, along with the neutral loss of 162 Da. With an additional loss of 58 Da, peak 78 was characterized as glucosidated conjugate of [PPT 12].[3] The molecular composition of peaks 80 and 81 were both calculated as $C_{59}H_{100}O_{27}$ based on the $[M{-}H]^-$ ion at *m/z* 1239.64. The prominent product ions at *m/z* 945.53, 783.48, 621.44, and 459.38 suggested their structures as [PPD 7]-3-glucosyl-glucosyl-20-glucosyl-glucosyl-arabinoside/xyloside or [PPD 7]-3-glucosyl-glucosyl-glucosyl-20-glucosyl-arabinoside/xyloside, respectively.[19] The HR-MS/MS data indicated the molecular formula of peak 83 as $C_{54}H_{90}O_{23}$. Its MS^2 spectrum displayed the fragment ions at *m/z* 943.5105, 781.4640, 619.4055, and 457.3616, originating from the

sequential neutral losses of glucosyl (162.05 Da). Therefore, it was characterized as [PPD 3]-3-glucosyl-glucosyl-20-glucosyl-glucoside or epoxynotoginsenoside A or its isomer.[17,21] The molecular composition of peaks 85, 89, 92, 110, and 112 were deduced as $C_{42}H_{72}O_{13}$, calculated from the HR-MS/MS data. Peaks 89 and 110 were separately assigned as 20(*S*)-ginsenoside Rg_2 and 20(*S*)-ginsenoside Rg_3, using the reference compounds. Peaks 85 and 92 exhibited the similar fragment ions at *m*/*z* 637.43 and 475.37, suggesting the presence of a rhamnosyl and a glucosyl residues. The identical $[A–H–C_6H_{12}]^-$ fragment ion at *m*/*z* 391.28 supposed them as [PPT 6]-3(6,20)-glucosyl-rhamnoside or [PPT 6]-6-rhamnosyl/glucosyl-20-glucoside/rhamnoside, respectively.[3] On the contrary, the MS^2 spectrum of peak 112 displayed the identical product ions at *m*/*z* 637.43 and 459.38, producing from the successive losses of 162.05 Da (glucosyl residues). Another fragment ion at *m*/*z* 375.2 $[A–H–C_6H_{12}]^-$ proposed peak 112 as ginsenoside F_2 or its isomer.[19] Similarly, peak 97 was assigned as [PPT 6]-6,20-di-*O*-xyloside with the sequential neutral losses of 132 Da.[3] Peak 93 gave the deprotonated aglycone ion at *m*/*z* 443.1, resulting from three step wise neutral losses of 162 Da. Hence, it was confirmed as vinaginsenoside R_3 or its isomer.[18] Likewise, peak 103 was assigned as [PPD 7]-3-glucosyl-20-rutinoside or [PPD 7]-3-glucosyl-glucosyl-20-rhamnoside from its product ions at *m*/*z* 783.4816 $[M−H−rha]^-$, 621.4333 $[M−H−rha−glc]^-$, and 459.3828 $[M−H−rha−2glc]^-$.[19] Compounds 99 and 111 exhibited the same molecular formula of $C_{47}H_{80}O_{17}$ and the mass cracking patterns. Their MS^2 spectra gave a $[A–H]^-$ ion at *m*/*z* 459.3782, generating from the sequential losses of a xylosyl (132.04 Da) and two glucosyls (162.05 Da) units. The identical fragment ion at *m*/*z* 375.2 resulting from *C*-17 chain cleavage indicated their sapogenin are [PPD 7].[19] The molecular composition of peak 100 was $C_{41}H_{66}O_{12}$, calculated from the formic anion at *m*/*z* 795.4539. Besides, the two major product ions at *m*/*z* 617.3 and 455.3 were originated from the successive losses of a xylosyl (132 Da) and a glucosyl (162 Da) groups, which characterized peak 100 as [PPD 2]-*O*-xylosyl-*O*-glucoside. Peaks 102 and 107 displayed the same molecular composition of $C_{42}H_{70}O_{13}$ and the same successive neutral losses of 162 Da (glucosyl). The additional fragment ion at *m*/*z* 373.3 $[M−H−2glc−C_6H_{12}]^-$ further confirmed peaks 102 and 107 as ginsenoside Rg_9 or its isomer, respectively.[19] Compound 105 exhibited a $[M–H]^−$ ion at *m*/*z* 751.4620, along with a serious product ions at *m*/*z* 619.3 and 457.4, corresponding to sequential neutral loss of xylosyl (132 Da) and glucosyl (162 Da). Thus it was identified as [PPD 4]-*O*-xylosyl-*O*-glucoside. Likewise, compound 106 was tentatively assigned as chikusetsusaponin LT_8 or its isomer.

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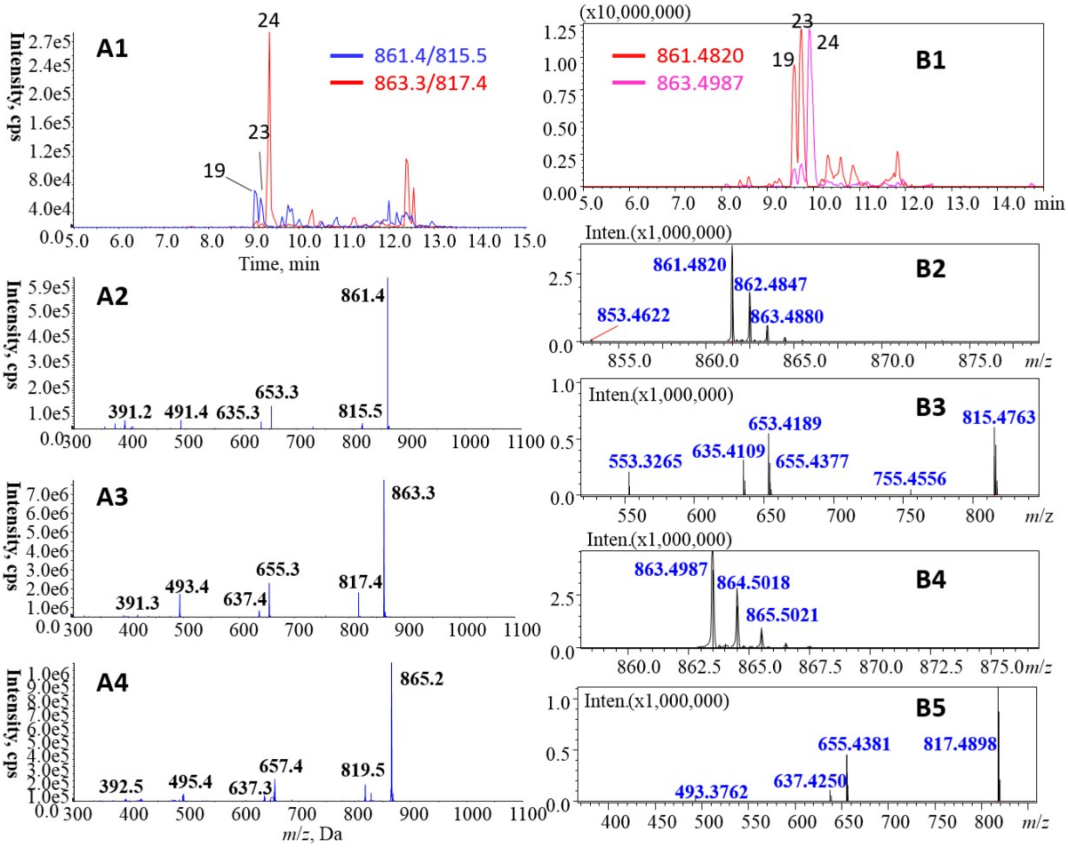

Fig. S1 The extracted ion chromatograms (EICs) of peaks 19, 23, and 24 and their corresponding mass profiles obtained by the MRM-IDA-EPI (A) and LC-IT-TOF/MS^n analyses (B); A1: EICs of *m*/*z* 861.4 > 815.5 and 863.3 > 817.4; A2: MS^2 spectrum of *m*/*z* 861.4; A3: MS^2 spectrum of *m*/*z* 863.3; A4: MS^2 spectrum of *m*/*z* 865.2; B1, EICs of *m*/*z* 861.4820 and 863.4987; B2: MS^1 spectrum of *m*/*z* 861.4820; B3: MS^2 spectrum of *m*/*z* 861.4820; B4: MS^1 spectrum of *m*/*z* 863.4987; B5: MS^2 spectrum of *m*/*z* 863.4987.

R-QC-III-015-04

附件 2

云南植物药业有限公司检验报告单

报告单编号	20110577	规　　格	20kg/件
品　　名	三七总皂苷	请检单位	原料药车间
批　　号	HB20111005	送检日期	2011 年 10 月 26 日
数　　量	200.00kg(10 件)	取样日期	2011 年 10 月 26 日
来　　源	原料药车间	报告日期	2011 年 11 月 28 日
依　　据	《中国药典》2010 年版三七总皂苷质量标准		

检验项目	标准依据	检验结果	单项结论
【性　状】	本品为类白色至淡黄色的无定形粉末，味苦、微甘	本品为淡黄色无定形粉末。	符合规定
【鉴　别】	供试品色谱图中应呈现与三七总皂苷对照提取物中三七皂苷 R_1、人参皂苷 Rg_1、人参皂苷 Re、人参皂苷 Rb_1、人参皂苷 Rd 保留时间相同的色谱峰。	供试品色谱中呈现与对照品 R_1、Rg_1、Re、Rb_1、Rd 保留时间一致的色谱峰。	符合规定
【检　查】			
干燥失重	减失重量不得过 5.0%	0.9%	符合规定
炽灼残渣	依法检查不得过 0.5%	0.4%	符合规定
溶液的颜色	不得深于黄色 4 号标准比色液。	为 4 号黄色	符合规定
重金属及有害元素	铅不得过百万分之五；镉不得过千万分之三；砷不得过百万分之二；汞不得过千万分之二；铜不得过百万分之二十	均符合规定	符合规定
【含量测定】	本品按干燥品计		
R_1%	应不得少于 5.0%	6.2%	符合规定
Rg_1%	应不得少于 25.0%	26.6%	符合规定
Re%	应不得少于 2.5%	4.1%	符合规定
Rb_1%	应不得少于 30.0%	32.5%	符合规定
Rd%	应不得少于 5.0%	6.6%	符合规定
(R_1+Rg_1+Re+Rb_1+Rd)%	应不得少于 75.0%	76.0%	符合规定
【指纹图谱】	供试品色谱图应与对照提取物的色谱图相似，5 分钟后的色谱峰，其相似度应不低于 0.95。	符合规定	符合规定
【微生物限度】			
细菌数	应不得过 1000cfu/g	小于 10cfu/g	符合规定
霉菌数	应不得过 100cfu/g	小于 10cfu/g	符合规定

总结论：本品按《中国药典》2010 年版三七总皂苷质量标准检验，结果符合规定。

QC 负责人：张洪　　复核人：杨光梅　　检验人：梁红

Table S1 Quality inspection report of NGTS.

Table S2 Translation of the quality inspection report of NGTS

Test report number	201110577	**Size**	**230 kg/piece**
Name	Notoginseng total saponins (NGTS)	Applicant	Material medica workshop
Batch number	HB20111005	Applicant data	Oct. 26, 2011
Counts	Ten	Sampling Date	Oct. 26, 2011
Source	Material medica workshop	Report date	Nov. 28, 2011
Basis	Chinese Pharmacopoeia 2010 Edition, monograph of Notoginseng total saponins		
Inspecting item	Standard basis	Test results	Individual conclusion
Description	Off-white or light-yellow amorphous powder	Light-yellow amorphous powder	Qualified
Identification	The chromatogram obtained with the test solution should contain the peaks with the same retention times corresponding to those of notoginsenoside R_1, ginsenosides Rg_1, Re, Rb_1, and Rd obtained with the reference extract of NGTS.	The chromatogram obtained with the test solution contains the peaks with the same retention times corresponding to those of the references of notoginsenoside R_1, ginsenosides Rg_1, Re, Rb_1, and Rd.	Qualified
Test			
Loss on drying	When dried to constant weight at 80 °C, loses not more than 5.0% of its weight.	0.9%	Qualified

Residue on ignition	Not more than 0.5 per cent.	0.4 per cent	Qualified
Colour of solution	Dissolve a quantity of weight with water to produce a solution containing 25 mg per mL. Not more intense than yellow reference solution No.4.	No.4 yellow	Qualified
Heavy metal and harmful elements	Not more than 5 ppm of Lead [Pb], 0.3 ppm of Carmium [Cd], 2 ppm of Arsenic [As], 0.2 ppm of Mercury [Hg] and 20 ppm of Copper [Cu]	Qualified	Qualified
Assay			
Notoginsenoside R_1	Not less than 5.0 per cent	6.2 per cent	Qualified
Ginsenoside Rg_1	Not less than 25.0 per cent	26.6 per cent	Qualified
Ginsenoside Re	Not less than 2.5 per cent	4.1 per cent	Qualified
Ginsenoside Rb_1	Not less than 30.0 per cent	32.5 per cent	Qualified
Ginsenoside Rd	Not less than 5.0 per cent	6.6 per cent	Qualified
[R_1+Rg_1+Re+Rb_1+Rd]	Not less than 75.0 per cent	76.0 per cent	Qualified
Fingerprint	According to the Similarity evaluation system for chromatography fingerprint of TCM, calculate the similarity of the retention times of the peaks after initial 5 minutes	Qualified	Qualified

	between the test solution fingerprint and the reference fingerprint, not less than 0.95.		
Microorganism limits			
Bacterial counts	Not more than 1000 cfu/g	Less than 10 cfu/g	Qualified
Mold counts	Not more than 100 cfu/g	Less than 10 cfu/g	Qualified

Conclusion: Various index accorded with the quality standard and inspection of NGTS from the Chinese pharmacopoeia [2010 edition].

QC responsible person: Zhang Hong **Checking authenticator:** Yang Guangmei **Inspector:** Liang Hong

Table S3 The exclude ions list for the full san on LC-IT-TOF/MS

Start *m*/*z*	End *m*/*z*	Start t_R	End t_R
334	334.5	12.7	12.8
427	427.5	7.7	7.8
497.3	497.5	9.79	9.82
503	503.4	8.3	8.4
503	503.5	8.3	8.4
599.2	599.32	12.6	12.75
683.4	683.5	12.9	13.02
713.4	713.5	11.3	11.4
717.4	717.5	10.45	10.52
723.4	723.5	11.3	11.4
783.4	783.5	12.8	12.9
815.4	815.5	12.4	12.5
845.4	845.5	12.2	12.3
861.2	861.5	8.9	9
863	863.5	9.1	9.2
977.5	977.6	12	12.2
991.5	991.5	12.9	13.1
1107.5	1107.5	12.8	12.9

Table S4 The preferred ions list for the full san on LC-IT-TOF/MS

No.	*m*/*z*	No.	*m*/*z*	No.	*m*/*z*	No.	*m*/*z*	No.	*m*/*z*
1	699.2	11	835.3	22	947.5	32	1025.5	42	1187.5
2	715.2	13	847.3	23	949.5	33	1059.5	43	1195.5
3	745.2	14	849.3	24	975.5	34	1109.2	44	1221.4
4	785.2	15	851.4	25	979.5	35	1123.5	45	1237.3
5	809.3	16	859.4	26	991.5	36	1137.5	46	1245.4
6	813.3	17	861.4	27	993.5	37	1139.5	47	1285.2
7	815.3	18	863.4	28	1005.5	38	1151.5	48	977.5
8	817.3	19	875.4	29	1007.5	39	1153.5	49	1315.4
9	829.3	20	879.4	30	1019.5	40	1167.5		
10	831.3	21	903.4	31	1026.5	41	1169.5		

Table S5 Detailed LC/MS data for characterization of the ginsenosides in NGTS

No.	t_R (min)	Identification	Parent ions	Product ions from IT/TOF-MS^n analysis	Product ions from MRM analysis	Ref
1	7.620	[PPT 16]-6-glucosyl-xylosyl -20-glucoside or its isomer	995.5423 [M+HCOO]$^-$	815.3825[M+HCOO-glc-H_2O]$^-$	949.3[M-H]$^-$, 769.2[M-H-glc-H_2O]$^-$, 655.3[M-H-xyl-glc]$^-$	1
2	7.680	Vinaginsenoside R_{22} or its isomer	879.4974 [M+HCOO]$^-$	833.4829[M-H]$^-$, 671.4276[M-H-glc]$^-$, 653.4185[M-H-glc-H_2O]$^-$	833.4[M-H]$^-$, 671.3[M-H-glc]$^-$, 653.3[M-H-glc-H_2O]$^-$, 509.4[M-H-2glc]$^-$, 491.4[M-H-2glc-H_2O]$^-$, 473.3[M-H-2glc-2H_2O]$^-$, 455.3[M-H-glc-3H_2O]$^-$, 415.2[M-H-2glc-2H_2O-C_3H_6O]$^-$, 403.3[M-H-2glc-H_2O-$C_4H_8O_2$]$^-$, 391.4[M-H-2glc-$C_5H_{10}O_3$]$^-$	2
3	7.803	[PPT 21]-6-glucosyl-xylosyl -20-glucoside or its isomer	1011.5334 [M+HCOO]$^-$	965.5203[M-H]$^-$, 785.4657[M-H-glc-H_2O]$^-$, 671.4221[M-H-glc-xyl]$^-$,	965.2[M-H]$^-$, 921.2, 831.2, 803.2[M-H-glc]$^-$, 785.3, 699.5, 671.3[M-H-glc-xyl]$^-$,	2

				653.4085[M-H-glc-H_2O-xyl]$^-$, 491.3678[M-H-glc-H_2O-xyl-glc]$^-$ 415.3109[M-H-glc-H_2O-xyl-glc-H_2O-C_3H_6O]$^-$	653.2[M-H-glc-H_2O-xyl]$^-$, 635.1[M-H-glc-2H_2O-xyl]$^-$, 509.3[M-H-glc-xyl-glc]$^-$, 491.3[M-H-2glc-H_2O]$^-$, 455.4[M-H-glc-3H_2O]$^-$, 415.2[M-H-glc-H_2O-xyl-glc-H_2O-C_3H_6O]$^-$, 403.3[M-H-2glc-H_2O-$C_4H_8O_2$]$^-$	
4	7.937	Vinaginsenoside R_{22} or its isomer	879.4921 [M+HCOO]$^-$	833.4816[M-H]$^-$, 699.3728, 671.4298[M-H-glc]$^-$, 653.4214[M-H-glc-H_2O]$^-$, 509.3802[M-H-2glc]$^-$	833.3[M-H]$^-$, 671.2[M-H-glc]$^-$, 653.2[M-H-glc-H_2O]$^-$, 509.3[M-H-2glc]$^-$, 391.3[M-H-2glc-$C_5H_{10}O_3$]$^-$	2
5	8.157	[PPT 21]-6-glucosyl-xylosyl -20-glucoside or its isomer	1011.5357 [M+HCOO]$^-$	965.5282[M-H]$^-$, 803.4738[M-H-glc]$^-$, 785.4626[M-H-glc-H_2O]$^-$, 671.4315[M-H-glc-xyl]$^-$, 653.4202[M-H-glc-xyl-H_2O]$^-$, 491.3678[M-H-glc-xyl-H_2O-glc]$^-$	965.2[M-H]$^-$, 833.2[M-H-xyl]$^-$, 785.3[M-H-glc-H_2O]$^-$, 699.5, 509.3[M-H-glc-glc-xyl]$^-$, 491.3[M-H-2glc-H_2O]$^-$, 455.4[M-H-2glc-3H_2O]$^-$,	2

				415.3109[M-H-glc-xyl-H_2O-glc-H_2O-C_3H_6O]$^-$	415.2[M-H-glc-H_2O-xyl-glc-H_2O-C_3H_6O]$^-$, 403.3[M-H-2glc-H_2O-$C_4H_8O_2$]$^-$	
6	8.220	[PPT 21]-6-rutinosyl-20-glucoside /[PPT 21]-6-rhamnosyl-20-glucosyl-glucoside	1025.5493 [M+HCOO]$^-$	979.5442[M-H]$^-$, 845.4330[M+COOH-glc-H_2O]$^-$, 799.4819[M-H-glc-H_2O]$^-$, 671.4352[M-H-rut]$^-$, 509.3778[M-H-rut-glc]$^-$	979.3[M-H]$^-$, 845.3[M+COOH-glc-H_2O]$^-$, 817.4[M-H-glc]$^-$, 799.1[M-H-glc-H_2O]$^-$, 751.4, 671.4[M-H-glc-rha]$^-$, 653.2[M-H-glc-H_2O-rha]$^-$, 565.3[M-H-glc-H_2O-rha-$C_4H_8O_2$]$^-$, 509.2[M-H-rha-2glc]$^-$, 455.3[M-H-2glc-3H_2O]$^-$, 415.3[M-H-glc-H_2O-xyl-glc-H_2O-C_3H_6O]$^-$	2
7	8.377	Vinaginsenoside R_{22} or its isomer	879.4921 [M+HCOO]$^-$	833.4866[M-H]$^-$, 671.4298[M-H-glc]$^-$, 653.4198[M-H-glc-H_2O]$^-$,	833.4[M-H]$^-$	2

				509.3797[M-H-2glc]$^-$, 491.3570[M-H-glc-H_2O-glc]$^-$		
8#	8.390	[PPD 11]-3-glucosyl-glucoside/ [PPT 12]-6,20-di-*O*-glucoside/ [PPT 13]-di-*O*-glucoside	861.4821 [M+HCOO]$^-$	681.4092[M+HCOO-glc-H_2O]$^-$, 623.3697[M+HCOO-glc-H_2O-C_3H_6O]$^-$		3, 4
9	8.470	[PPT 21]-6-rutinosyl-20-glucoside /[PPT 21]-6-rhamnosyl-20- glucosyl-glucoside	1025.5510 [M+HCOO]$^-$	979.5485[M-H]$^-$, 845.4268[M+HCOO-glc-H_2O]$^-$, 817.4961[M-H-glc]$^-$, 799.4753[M-H-glc-H_2O]$^-$, 699.3697[M-H-glc-$C_5H_{10}O_3$]$^-$, 653.4085[M-H-glc-H_2O-rha]$^-$	979.3[M-H]$^-$, 845.3, 817.4[M-H-glc]$^-$, 799.3[M-H-glc-H_2O]$^-$, 671.2[M-H-glc-rha]$^-$, 653.3[M-H-glc-H_2O-rha]$^-$, 565.3[M-H-glc-H_2O-rha-$C_4H_8O_2$]$^-$ 509.2[M-H-2glc-rha]$^-$, 491.0, 455.3[M-H-2glc-rha-3H_2O]$^-$, 415.3[M-H-2glc-rha-2H_2O-C_3H_6O]$^-$	2
10#	8.580	[PPD 11]-3-glucosyl-glucoside/ [PPT 12]-6,20-di-*O*-glucoside /[PPT 13]-di-*O*-glucoside	861.4869 [M+HCOO]$^-$	681.4130[M+HCOO-H_2O-glc]$^-$, 623.3775[M+HCOO-H_2O-glc-C_3H_6O]$^-$		3, 4

11	8.733	Vinaginsenoside R_{13} or its isomer	1025.5497 $[M+HCOO]^-$	817.4849[M-H-glc]$^-$, 799.4739[M-H-glc-H_2O]$^-$	979.3[M-H]$^-$, 817.3[M-H-glc]$^-$, 654.9[M-H-2glc]$^-$,493.4[M-H-3glc]$^-$, 417.3[M-H-3glc-H_2O-C_3H_6O]$^-$	2
12	8.907	Notoginsenoside H or its isomer	993.5226 $[M+HCOO]^-$	947.5119[M-H]$^-$, 815.4722[M-H-xyl]$^-$, 653.4202[M-H-xyl-glc]$^-$, 635.4115[M-H-xyl-glc-H_2O]$^-$	947.3[M-H]$^-$, 815.3[M-H-xyl]$^-$, 785.4[M-H-glc]$^-$, 767.3[M-H-glc-H_2O]$^-$, 635.3[M-H-glc-H_2O-xyl]$^-$, 473.3[M-H-glc-H_2O-xyl-glc]$^-$ 403.2 [M-H-glc-H_2O-xyl-glc-C_4H_6O]$^-$, 391.3[M-H-glc-H_2O-xyl-glc-C_6H_{10}]$^-$	4, 5
13[$, Ψ]	8.910	Dicaffeoyl-[PPD 10]	847.4654 $[M+HCOO]^-$	801.4559[M-H]$^-$, 639.4099[M-H-caffeoyl]$^-$, 621.3948[M-H-caffeoyl-H_2O]$^-$	801.4[M-H]$^-$, 639.2[M-H-caffeoyl]$^-$, 621.4[M-H-caffeoyl-H_2O]$^-$, 477.2[M-H-2caffeoyl]$^-$	7
14	8.967	Ginsenoside Re_4 or its isomer	977.5329 $[M+HCOO]^-$		931.3[M-H]$^-$, 799.5[M-H-xyl]$^-$, 751.4[M-H-H_2O-glc]$^-$, 619.3[M-H-xyl-H_2O-glc]$^-$,	8-11

					601.3[M-H-xyl-H_2O-glc-H_2O]$^-$, 457.2[M-H-xyl-H_2O-2glc]$^-$, 439.1[M-H-xyl-2H_2O-2glc]$^-$	
15	9.158	Floaginsenoside B or its isomer	861.4854 [M+COOH]$^-$	815.4679[M-H]$^-$, 653.4176[M-H-glc]$^-$, 635.4078[M-H-glc-H_2O]$^-$, 553.3243[M-H-glc-$C_6H_{12}O$]$^-$	815.4[M-H]$^-$, 653.4[M-H-glc]$^-$, 635.3[M-H-glc-H_2O]$^-$, 553.2, 491.3[M-H-2glc]$^-$, 473.2[M-H-2glc-H_2O]$^-$, 403.4[M-H-2glc-C_4H_6O]$^-$, 391.3[M-H-2glc-$C_6H_{12}O$]$^-$	5
16	9.23	[PPT 16]-3(6),20-di-*O*-glucoside /[PPD 12]-6(20)-glucosyl-glucoside	863.5006 [M+HCOO]$^-$	817.4888[M-H]$^-$, 655.4356[M-H-glc]$^-$, 637.4332[M-H-glc-H_2O]$^-$, 493.3832[M-H-2glc]$^-$, 417.3364 [M-H-2glc-H_2O-C_3H_6O]$^-$	817.3[M-H]$^-$, 655.4[M-H-glc]$^-$, 637.4[M-H-glc-H_2O]$^-$, 493.4[M-H-2glc]$^-$, 417.5[M-H-2glc-H_2O-C_3H_6O]$^-$, 391.3[M-H-2glc-$C_6H_{14}O$]$^-$	1
17[$,Ψ]	9.415	Dicaffeoyl-[PPD 10]	847.4641 [M+HCOO]$^-$	801.4519[M-H]$^-$, 639.4094[M-H-caffeoyl]$^-$,	801.4[M-H]$^-$, 639.2[M-H-caffeoyl]$^-$, 621.4, 477.2[M-H-2caffeoyl]$^-$	7
18	9.477	Sanshichisaponin G or its isomer	993.5297	947.5178[M-H]$^-$, 785.4687[M-H-glc]$^-$,	947.3[M-H]$^-$, 815.3[M-H-xyl]$^-$,	3

			[M+HCOO]$^-$	767.4469[M-H-glc-H$_2$O]$^-$, 653.4068[M-H-glc-xyl]$^-$, 635.4099[M-H-glc-xyl-H$_2$O]$^-$, 553.3236[M-H-glc-xyl-C$_6$H$_{12}$O]$^-$	785.2[M-H-glc]$^-$, 653.2[M-H-glc-xyl]$^-$, 635.2[M-H-glc-xyl-H$_2$O]$^-$, 491.4[M-H-glc-xyl-glc]$^-$, 415.3 [M-H-glc-xyl-glc-H$_2$O-C$_3$H$_6$O]$^-$	
19	9.520	Floaginsenoside B or its isomer	861.4833 [M+HCOO]$^-$	815.4742[M-H]$^-$, 653.4222[M-H-glc]$^-$, 491.3786[M-H-2glc]$^-$, 391.2732[M-H-2glc-C$_6$H$_{12}$O]$^-$	815.2[M-H]$^-$, 653.3[M-H-glc]$^-$, 635.2[M-H-glc-H$_2$O]$^-$, 491.4[M-H-2glc]$^-$, 455.2[M-H-2glc-2H$_2$O]$^-$, 403.3[M-H-glc-H$_2$O-C$_4$H$_6$O-glc]$^-$ 391.3[M-H-2glc-C$_6$H$_{12}$O]$^-$	5
20	9.640	[PPT 16]-20-glucosyl-6-rutinoside or its isomer	1009.5555 [M+HCOO]$^-$	963.5382[M-H]$^-$	963.4[M-H]$^-$, 817.3[M-H-rha]$^-$, 801.2[M-H-glc]$^-$, 783.5[M-H-glc-H$_2$O]$^-$, 655.4[M-H-rha-glc]$^-$, 619.1, 493.5[M-H-rha-2glc]$^-$,	1

					475.3[M-H-rha-2glc-H_2O]⁻, 417.6[M-H-rha-2glc-H_2O-C_3H_6O]⁻	
21	9.650	[PPT 16]-6-glucosyl-xylosyl -20-glucoside or its isomer	949.5365 [M-H]⁻	817.4864[M-H-xyl]⁻, 787.4757[M-H-glc]⁻, 769.4692[M-H-glc-H_2O]⁻, 655.4338[M-H-xyl-glc]⁻, 637.4243[M-H-xyl-glc-H_2O]⁻, 493.3843[M-H-xyl-2glc]⁻	949.3, 817.3[M-H-xyl]⁻, 787.4[M-H-glc]⁻, 769.4[M-H-glc-H_2O]⁻, 655.3[M-H-xyl-glc]⁻, 493.3[M-H-xyl-2glc]⁻, 417.2[M-H-xyl-2glc-H_2O-C_3H_6O]⁻, 391.4[M-H-xyl-2glc-$C_6H_{14}O$]⁻	1
22$^{\Psi}$	9.744	[PPT 1]-*O*-xylosyl-*O*-glucoside	731.3854 [M+HCOO]⁻	685.3726[M-H]⁻, 553.3348[M-H-xyl]⁻	685.1[M-H]⁻, 553.2[M-H-xyl]⁻, 535.1[M-H-xyl-H_2O]⁻, 391.4[M-H-xyl-glc]⁻	11
23	9.757	Floaginsenoside B or its isomer	861.4842 [M+HCOO]⁻	815.4695[M-H]⁻, 653.4198[M-H-glc]⁻, 635.3992[M-H-glc-H_2O]⁻	815.5[M-H]⁻, 653.3[M-H-glc]⁻, 635.2[M-H-glc-H_2O]⁻, 491.4[M-H-2glc]⁻, 403.2[M-H-2glc-H_2O-C_4H_6O]⁻ 391.4[M-H-2glc-$C_6H_{12}O$]⁻	5, 6

24	9.857	[PPT 16]-3,20-di-*O*-glucoside/ [PPT 16]-6,20-di-*O*-glucoside/ [PPT 16]-6(20)-glucosyl-glucoside	863.4997 $[M+HCOO]^-$	817.4892$[M-H]^-$, 655.4344$[M-H-glc]^-$, 637.4219$[M-H-glc-H_2O]^-$, 493.3858$[M-H-2glc]^-$, 417.3364$[M-H-2glc-H_2O-C_3H_6O]^-$	817.4$[M-H]^-$, 655.2$[M-H-glc]^-$, 637.2$[M-H-glc-H_2O]^-$, 493.2$[M-H-2glc]^-$	12
25	9.885	Majoroside F_6 or its isomer	1007.5424 $[M+HCOO]^-$	961.5183$[M-H]^-$, 799.4693$[M-H-glc]^-$, 781.4621$[M-H-glc-H_2O]^-$, 635.4123$[M-H-glc-H_2O-rha]^-$	961.2$[M-H]^-$, 799.5$[M-H-glc]^-$, 781.2$[M-H-glc-H_2O]^-$, 635.1$[M-H-glc-H_2O-rha]^-$, 491.4$[M-H-glc-glc-rha]^-$ 455.4$[M-H-glc-glc-rha-2H_2O]^-$, 437.5$[M-H-glc-glc-rha-3H_2O]^-$	5
26	9.992	[PPT 8]-6,20-di-*O*-glucoside or its isomer	859.4655 $[M+HCOO]^-$	813.4636$[M-H]^-$, 633.3891$[M-H-glc-H_2O]^-$	813.4$[M-H]^-$, 651.2$[M-H-glc]^-$, 633.4$[M-H-glc-H_2O]^-$, 553.2$[M-H-glc-C_6H_{10}O]^-$, 489.2$[M-H-2glc]^-$, 471.4$[M-H-glc-H_2O-glc]^-$, 453.2$[M-H-glc-H_2O-glc-H_2O]^-$,	9

					391.3[M-H-2glc-$C_6H_{10}O$]$^-$	
27$^{\Psi}$	10.011	[PPT 1]-*O*-rutinoside	745.4028 [M+HCOO]$^-$	699.3791[M-H]$^-$	699.2[M-H]$^-$, 553.2[M-H-rha]$^-$, 535.3, 391.4[M-H-rha-glc]$^-$	11
28	10.020	[PPT 21]-20-xylosyl-3-glucoside or its isomer	849.4866 [M+HCOO]$^-$	803.4652[M-H]$^-$, 671.4319[M-H-xyl]$^-$, 509.3842[M-H-xyl-glc]$^-$, 391.2835[M-H-xyl-glc-$C_5H_{10}O_3$]$^-$	803.3[M-H]$^-$, 671.4[M-H-xyl]$^-$, 509.4[M-H-xyl-glc]$^-$, 421.3[M-H-xyl-glc-$C_4H_8O_2$]$^-$, 391.2[M-H-xyl-glc-$C_5H_{10}O_3$]$^-$	3
29$^{\Psi}$	10.037	[PPT 8]-*O*-xylosyl-di-*O*-glucoside	991.5159 [M+HCOO]$^-$		945.4[M-H]$^-$, 783.2[M-H-glc]$^-$, 765.4[M-H-glc-H_2O]$^-$, 633.1[M-H-glc-H_2O-xyl]$^-$, 471.2[M-H-glc-H_2O-xyl-glc]$^-$, 453.1[M-H-glc-2H_2O-xyl-glc]$^-$, 391.3[M-H-glc-xyl-glc-$C_6H_{10}O$]$^-$	9
30	10.243	Ginsenoside Re_8 or its isomer	961.5362 [M-H]$^-$	799.4693[M-H-glc]$^-$, 781.4640[M-H-glc-H_2O]$^-$, 635.4123[M-H-glc-H_2O-rha]$^-$	961.4[M-H]$^-$, 799.3[M-H-glc]$^-$, 653.3[M-H-glc-rha]$^-$, 491.3[M-H-glc-rha-glc]$^-$ 415.3[M-H-glc-rha-glc-C_3H_6O-H_2O]$^-$	3

					403.2[M-H-glc-rha-glc-$C_4H_8O_2$]$^-$	
31	10.362	[PPT 11]-6-glucosyl-glucoside/ [PPT 11]-3(6),20-di-*O*-glucoside/ [PPT 14]-6,20-di-*O*-glucoside/ [PPD 10]-3-glucosyl-glucoside/ [PPT 12]-6,20-di-*O*-glucoside/ [PPT 13]-di-*O*-glucoside	861.4850 [M+HCOO]$^-$	815.4648[M-H]$^-$, 653.4117[M-H-glc]$^-$, 635.4017, 491.3714[M-H-glc-glc]$^-$	815.3[M-H]$^-$, 653.3[M-H-rha]$^-$, 491.4[M-H-glc-glc]$^-$	3-5, 12
32$^{\Psi}$	10.369	[PPT 8]/[PPT 9]-*O*-xylosyl -di-*O*-glucoside	945.4997 [M-H]$^-$		945.2[M-H]$^-$, 813.2[M-H-xyl]$^-$, 783.2[M-H-glc]$^-$, 765.4[M-H-glc-H_2O]$^-$, 633.4[M-H-glc-H_2O-xyl]$^-$, 471.2[M-H-xyl-H_2O-2glc]$^-$,	13
33	10.372	[PPT 16]-20-glucosyl-6-rutinoside or its isomer	963.5488 [M-H]$^-$	801.4933[M-H-glc]$^-$, 783.4803, 655.4280[M-H-glc-rha]$^-$, 637.4233, 493.3828[M-H-glc-rha-glc]$^-$	963.2[M-H]$^-$, 817.3[M-H-rha]$^-$, 783.5[M-H-glc-H_2O]$^-$, 655.4[M-H-rha-glc]$^-$, 493.4[M-H-rha-2glc]$^-$, 417.6[M-H-rha-2glc-H_2O-C_3H_6O]$^-$	1, 14

34	10.402	Floralginsenoside C or its isomer	801.4657 [M-H]$^-$	685.3804[M-H-$C_6H_{12}O_2$]$^-$, 669.4280[M-H-xyl]$^-$, 593.3551[M-H-xyl-H_2O-C_3H_6O]$^-$, 553.3236[M-H-$C_6H_{12}O_2$-xyl]$^-$, 391.2732[M-H-$C_6H_{12}O_2$-xyl-glc]$^-$	801.2[M-H]$^-$, 685.2[M-H-$C_6H_{12}O_2$]$^-$ 669.5[M-H-xyl]$^-$, 593.3[M-H-xyl-H_2O-C_3H_6O]$^-$, 575.4, 507.3[M-H-xyl-glc]$^-$,	13
35	10.498	[PPT 8]-6,20-di-*O*-glucoside or its isomer	859.4668 [M+HCOO]$^-$	813.4548 [M-H]$^-$	813.2[M-H]$^-$, 651.4[M-H-glc]$^-$, 633.4[M-H-glc-H_2O]$^-$, 489.5[M-H-2glc]$^-$, 471.4[M-H-glc-H_2O-glc]$^-$ 391.3[M-H-2glc-$C_6H_{10}O$]$^-$	9
36	10.520	[PPT 21]-20-xylosyl-3-glucoside or its isomer	849.4835 [M+HCOO]$^-$	803.4786[M-H]$^-$, 671.4215[M-H-xyl]$^-$, 509.3738[M-H-xyl-glc]$^-$, 391.2854 [M-H-xyl-glc-$C_5H_{10}O_3$]$^-$	803.3[M-H]$^-$, 671.3[M-H-xyl]$^-$, 653.3[M-H-xyl-H_2O]$^-$, 509.4[M-H-xyl-glc]$^-$, 391.3[M-H-xyl-glc-$C_5H_{10}O_3$]$^-$	2
37	10.550	[PPT 19]-*O*-rhamnosyl-*O*-glucoside	861.4829 [M+HCOO]$^-$	815.4786[M-H]$^-$, 669.4122[M-H-rha]$^-$, 653.4177[M-H-glc]$^-$, 611.3656[M-H-rha-C_3H_6O]$^-$,	815.3[M-H]$^-$, 669.2[M-H-rha]$^-$, 653.5, 611.5, 507.3[M-H-rha-glc]$^-$, 431.3[M-H-rha-glc-H_2O-C_3H_6O]$^-$,	13

				593.3551[M-H-rha-C_3H_6O-H_2O]$^-$ 507.3638[M-H-rha-glc]$^-$, 449.3122[M-H-rha-glc-C_3H_6O]$^-$	391.2[M-H-rha-glc-$C_6H_{12}O_2$]$^-$	
38[Ψ]	10.592	Floralginsenoside I or floralginsenoside J	1023.5367 [M+HCOO]$^-$		977.3[M-H]$^-$, 959.3, 815.4[M-H-glc]$^-$, 797.3[M-H-glc-H_2O]$^-$, 779.2, 651.3[M-H-glc-H_2O-rha]$^-$, 619.3[M-H-glc-H_2O-rha-O_2]$^-$, 457.2[M-H-glc-H_2O-rha-O_2-glc]$^-$	15, 16
39	10.650	[PPT 21]-20-xylosyl-3-glucoside or its isomer	849.4822 [M+HCOO]$^-$	803.4705[M-H]$^-$, 671.4285[M-H-xyl]$^-$, 509.3805[M-H-xyl-glc]$^-$	803.2[M-H]$^-$, 671.4[M-H-xyl]$^-$, 509.3[M-H-xyl-glc]$^-$, 421.2[M-H-xyl-glc-$C_4H_8O_2$]$^-$, 391.4[M-H-xyl-glc-$C_5H_{10}O_3$]$^-$	2
40	10.725	Ginsenoside Re_8 or its isomer	1007.5373 [M+HCOO]$^-$		961.2[M-H]$^-$, 799.2[M-H-glc]$^-$, 781.2[M-H-glc-H_2O]$^-$, 723.2[M-H-glc-H_2O-C_3H_6O]$^-$ 653.3[M-H-glc-rha]$^-$,	3

					491.4[M-H-glc-rha-glc]$^-$	
41	10.840	[PPD 12]/[PPT 16]-*O*-rhamnosyl -*O*-glucosyl-*O*-glucuronide	1023.5384 [M+HCOO]$^-$	977.5193[M-H]$^-$	1023.2, 976.9, 493.3[M-H-glc-glcA-rha]$^-$	1, 14
42	10.860	Floralginsenoside C or its isomer	801.4633 [M-H]$^-$	669.4168[M-H-xyl]$^-$, 593.3551[M-H-xyl-H_2O-C_3H_6O]$^-$		1
43	10.905	[PPT 8]-6,20-di-*O*-glucoside or its isomer	859.4673 [M+HCOO]$^-$	813.4409[M-H]$^-$	813.5[M-H]$^-$, 651.2[M-H-glc]$^-$, 633.1[M-H-glc-H_2O]$^-$, 489.5[M-H-2glc]$^-$, 471.1[M-H-glc-H_2O-glc]$^-$ 391.3[M-H-2glc-$C_6H_{10}O$]$^-$	9
44	11.088	[PPT 21]-20-xylosyl-3-glucoside or its isomer	849.4837 [M+HCOO]$^-$	803.4644[M-H]$^-$, 671.4333[M-H-xyl]$^-$, 509.3607[M-H-xyl-glc]$^-$, 415.3109[M-H-xyl-glc-2H_2O-C_3H_6O]$^-$, 391.2732 [M-H-xyl-glc-$C_5H_{10}O_3$]$^-$	803.4[M-H]$^-$, 671.4[M-H-xyl]$^-$, 653.3[M-H-xyl-H_2O]$^-$, 509.4[M-H-xyl-glc]$^-$, 493.3, 403.4, 391.3[M-H-xyl-glc-$C_5H_{10}O_3$]$^-$,	2
45$^{\Psi}$	11.145	[PPD 10]-*O*-glucosyl-*O*-rutinoside	993.5297 [M+HCOO]$^-$	477.3828[M-H-2glc-rha]$^-$	947.5, 461.4,	7
46	11.205	Quinquenoside L_9 or its isomer	863.4995	817.4761[M-H]$^-$, 671.4315[M-H-rha]$^-$,	817.3[M-H]$^-$, 671.3[M-H-rha]$^-$,	2

			$[M+HCOO]^-$	509.3797$[M-H-rha-glc]^-$, 391.2732$[M-H-rha-glc-C_5H_{10}O_3]^-$	653.0$[M-H-rha-H_2O]^-$, 509.3$[M-H-rha-glc]^-$	
47	11.260	Notoginsenoside SP_8 or its isomer	669.4230 $[M-H]^-$	593.3630$[M-H-C_3H_8O_2]^-$, 507.3661$[M-H-glc]^-$ 449.3214$[M-H-glc-C_3H_6O]^-$		13
48	11.367	[PPT 9]-3-rutinosyl-20-glucoside or its isomer	1005.5278 $[M+HCOO]^-$		959.3$[M-H]^-$, 797.3$[M-H-glc]^-$, 779.3$[M-H-glc-H_2O]^-$, 697$[M-H-glc-C_5H_8O_2]^-$, 489.2$[M-H-glc-rutinosyl]^-$, 471.2$[M-H-glc-rutinosyl-H_2O]^-$	13
49	11.474	Quinquenoside L_9 or its isomer	863.5003 $[M+HCOO]^-$	817.4850$[M-H]^-$, 671.4441$[M-H-rha]^-$, 653.4210$[M-H-rha-H_2O]^-$, 509.3717$[M-H-rha-glc]^-$, 391.2862$[M-H-rha-glc-C_5H_{10}O_3]^-$	817.3$[M-H]^-$, 671.3$[M-H-rha]^-$, 509.3$[M-H-rha-glc]^-$, 391.3$[M-H-rha-glc-C_5H_{10}O_3]^-$	2
50	11.717	[PPT 8]-6,20-di-*O*-glucoside or its isomer	859.4673 $[M+HCOO]^-$	813.4409$[M-H]^-$	813.5$[M-H]^-$, 651.2$[M-H-glc]^-$, 633.1$[M-H-glc-H_2O]^-$, 489.5$[M-H-2glc]^-$,	9

					471.1[M-H-glc-H_2O-glc]$^-$ 391.3[M-H-2glc-$C_6H_{10}O$]$^-$	
51	11.752	Floaginsenoside B or its isomer	861.4808 [M+HCOO]$^-$	815.4745[M-H]$^-$, 653.4192[M-H-glc]$^-$, 635.4099[M-H-glc-H_2O]$^-$	815.4[M-H]$^-$, 653.3[M-H-glc]$^-$, 491.5[M-H-2glc]$^-$, 421.2[M-H-2glc-C_4H_6O]$^-$, 391.3[M-H-2glc-$C_6H_{12}O$]$^-$	5, 6
52$^{\Psi}$	11.457	[PPD 10]-*O*-glucosyl-*O*-xyloside	817.4975 [M+HCOO]$^-$		771.2[M-H]$^-$, 687.4, 655.4, 639.2[M-H-xyl]$^-$, 477.2[M-H-xyl-glc]$^-$, 459.6[M-H-xyl-glc-H_2O]$^-$	7
53	11.780	Notoginsenoside N or its isomer	1007.5402 [M+HCOO]$^-$	961.5400[M-H]$^-$, 799.4730[M-H-glc]$^-$, 637.4204[M-H-2glc]$^-$, 619.4015[M-H-2glc-H_2O]$^-$, 475.3722[M-H-3glc]$^-$	961.1[M-H]$^-$, 799.4[M-H-glc]$^-$, 637.3[M-H-2glc]$^-$, 553.3[M-H-2glc-C_6H_{12}]$^-$, 475.3[M-H-3glc]$^-$, 391.2[M-H-3glc-C_6H_{12}]$^-$	3
54	11.848	Ginsenoside B_2 or chikusetsusaponin FK_1	945.5423 [M-H]$^-$	799.4808[M-H-rha]$^-$, 783.4762[M-H-glc]$^-$,	945.4, 799.3[M-H-rha]$^-$, 783.5[M-H-glc]$^-$,	3

				637.4228[M-H-rha-glc]⁻, 619.4167[M-H-rha-glc-H_2O]⁻, 475.3726[M-H-rha-2glc]⁻	637.4[M-H-rha-glc]⁻, 619.6, 475.3[M-H-rha-2glc]⁻, 391.3[M-H-rha-2glc-C_6H_{12}]⁻	
55	11.860	[PPT 21]-20-xylosyl-3-glucoside or its isomer	803.4769 [M-H]⁻	671.4311[M-H-xyl]⁻, 653.4085[M-H-xyl-H_2O]⁻, 509.3827[M-H-xyl-glc]⁻, 415.3239[M-H-xyl-glc-2H_2O-C_3H_6O]⁻, 403.3191[M-H-xyl-glc-H_2O-$C_4H_8O_2$]⁻, 391.2820[M-H-xyl-glc-$C_5H_{10}O_3$]⁻	849.4, 803.4	2
56$^{\Psi}$	11.888	[PPT 8]/[PPT 9]-*O*-rutinosyl -*O*-glucoside	1005.5302 [M+HCOO]⁻	959.5145[M-H]⁻, 779.4519[M-H-glc-H_2O]⁻	959.3[M-H]⁻, 797.3[M-H-glc]⁻, 779.3[M-H-glc-H_2O]⁻, 633.2[M-H-glc-H_2O-rha]⁻, 471.2[M-H-glc-H_2O-rha-glc]⁻	9
57	11.908	Notoginsenoside A or its isomer	1123.5916 [M-H]⁻	961.5320[M-H-glc]⁻, 637.4233[M-H-3glc]⁻, 475.3734[M-H-4glc]⁻	961.3[M-H-glc]⁻, 799.3[M-H-2glc]⁻, 637.3[M-H-3glc]⁻, 475.1[M-H-4glc]⁻, 391.2[M-H-4glc-C_6H_{12}]⁻	3

58^Ψ	11.933	[PPD 12]/[PPT 16]-*O*-glucosyl-*O*-xyloside	833.4912 $[M+HCOO]^-$		833.3, 787.4$[M-H]^-$, 655.3$[M-H-xyl]^-$, 637.3$[M-H-xyl-H_2O]^-$, 493.4$[M-H-xyl-glc]^-$, 417.4$[M-H-xyl-glc-H_2O-C_3H_6O]^-$, 391.4$[M-H-xyl-glc-C_6H_{14}O]^-$	1, 14
59	11.965	Quinquenoside L_9 or its isomer	863.5000 $[M+HCOO]^-$	817.4907$[M-H]^-$, 671.4363$[M-H-rha]^-$, 509.3732$[M-H-rha-glc]^-$ 391.2809$[M-H-glc-C_5H_{10}O_3]^-$	817.4, 763.2, 697.4, 659.3, 655.2$[M-H-glc]^-$, 637.2, 535.3, 509.3$[M-H-rha-glc]^-$, 493.3, 417.3, 391.3$[M-H-glc-C_5H_{10}O_3]^-$	2
60	11.968	[PPD 8]-3-glucosyl-glucosyl -20-glucosyl-arabinoside/ [PPD 9]-3-glucosyl-glucosyl -20-glucosyl-xyloside	1093.5794 $[M-H]^-$	961.5315$[M-H-xyl]^-$, 931.5268$[M-H-glc]^-$, 799.4792$[M-H-xyl-glc]^-$, 769.4573$[M-H-glc-glc]^-$, 637.4259$[M-H-xyl-2glc]^-$, 619.4055$[M-H-xyl-2glc-H_2O]^-$, 475.3742$[M-H-xyl-3glc]^-$, 323.2758	961.3$[M-H-xyl]^-$, 931.4$[M-H-glc]^-$, 799.3$[M-H-xyl-glc]^-$, 637.3$[M-H-2glc]^-$, 475.3$[M-H-xyl-3glc]^-$	9, 10

61	12.088	Yesanchinoside E or its isomer	1107.5947 [M-H]⁻	961.5221[M-H-rha]⁻, 945.5313[M-H-glc]⁻, 799.4784[M-H-rha-glc]⁻, 783.4514[M-H-2glc]⁻, 637.4220[M-H-rha-2glc]⁻, 619.4055, 475.3652[M-H-rha-3glc]⁻ 391.2732[M-H-rha-3glc-C_6H_{12}]⁻	961.3[M-H-rha]⁻, 945.5[M-H-glc]⁻, 783.2[M-H-rha-glc]⁻, 637.3[M-H-rha-2glc]⁻, 475.4[M-H-rha-3glc]⁻	3
62[Ψ]	12.137	[PPT 5]-di-*O*-glucosyl-*O*-xyloside	975.5163 [M+HCOO]⁻		929.4[M-H]⁻, 767.4[M-H-glc]⁻, 749.4[M-H-glc-H_2O]⁻, 617.3[M-H-glc-H_2O-xyl]⁻, 473.2[M-H-2glc-xyl]⁻, 455.3[M-H-glc-H_2O-xyl-glc]⁻ 389.4[M-H-2glc-xyl-C_6H_{12}]⁻	3
63	12.148	Quinquenoside L_{16} or its isomer	1141.6044 [M-H]⁻	979.5341[M-H-glc]⁻, 817.4847[M-H-2glc]⁻, 799.4747[M-H-2glc-H_2O]⁻, 655.4341[M-H-3glc]⁻,	979.3[M-H-glc]⁻, 817.4[M-H-2glc]⁻, 799.3[M-H-2glc-H_2O]⁻, 655.2[M-H-3glc]⁻, 493.2[M-H-4glc]⁻	1, 14

				637.4233[M-H-3glc-H_2O]⁻, 589.3315, 493.3827[M-H-4glc]⁻		
64	12.160	[PPT 6]-6-glucosyl-xylosyl -20-glucosyl-glucoside/ [PPT 6]-3-glucosyl-glucosyl -20-glucosyl-arabinoside (xyloside)	1093.5814 [M-H]⁻	961.5329[M-H-xyl]⁻, 799.4745[M-H-xyl-glc]⁻, 637.4200[M-H-xyl-2glc]⁻, 619.4195[M-H-xyl-2glc-H_2O]⁻, 475.3749[M-H-xyl-3glc]⁻, 391.2758[M-H-xyl-3glc-C_6H_{12}]⁻,	961.3[M-H-xyl]⁻, 799.3[M-H-xyl-glc]⁻, 781.2[M-H-xyl-glc-H_2O]⁻, 637.3[M-H-xyl-2glc]⁻, 475.4[M-H-xyl-3glc]⁻ 391.2[M-H-xyl-3glc-C_6H_{12}]⁻	3
65	12.190	[PPT 4]-6,20-di-*O*-glucoside/ [PPT 5]-3,20-di-*O*-glucoside	843.4725 [M+HCOO]⁻		797.4[M-H]⁻, 635.3[M-H-glc]⁻, 473.2[M-H-2glc]⁻, 457.3, 437.2, 419.3, 389.5[M-H-2glc-C_6H_{12}]⁻	17, 18
66*	12.208	Notoginsenoside R_1	931.5277 [M-H]⁻	799.4793[M-H-xyl]⁻, 781.4763[M-H-xyl-H_2O]⁻, 769.4742[M-H-glc]⁻, 751.4750[M-H-glc-H_2O]⁻, 637.4264[M-H-xyl-glc]⁻, 619.4164[M-H-xyl-glc-H_2O]⁻,	931.3, 799.3[M-H-xyl]⁻, 769.3[M-H-glc]⁻, 637.3[M-H-xyl-glc]⁻, 475.4[M-H-xyl-2glc]⁻, 457.3[M-H-xyl-2glc-H_2O]⁻, 391.3[M-H-xyl-2glc-C_6H_{12}]⁻	

				475.3739[M-H-xyl-2glc]$^-$, 391.2845[M-H-xyl-2glc-C_6H_{12}]$^-$		
67*	12.229	Ginsenoside Re	945.5420 [M-H]$^-$	799.4725[M-H-rha]$^-$, 783.4801[M-H-glc]$^-$, 637.4225[M-H-rha-glc]$^-$, 619.4121[M-H-rha-glc-H_2O]$^-$, 475.3735[M-H-rha-2glc]$^-$	945.4[M-H]$^-$, 799.3[M-H-rha]$^-$, 783.5[M-H-glc]$^-$, 637.4[M-H-rha-glc]$^-$, 619.4[M-H-rha-glc-H_2O]$^-$, 475.3[M-H-rha-2glc]$^-$ 391.3[M-H-rha-2glc-C_6H_{12}]$^-$	
68	12.240	Vinaginsenoside R_{11} or floraginsenoside D	831.4705 [M+HCOO]$^-$		785.4[M-H]$^-$, 653.3[M-H-xyl]$^-$, 491.5[M-H-xyl-glc]$^-$ 415.3[M-H-xyl-glc-H_2O-C_3H_6O]$^-$ 391.2[M-H-xyl-glc-$C_6H_{12}O$]$^-$	3
69*	12.350	Ginsenoside Rg_1	845.4898 [M+HCOO]$^-$	799.4813[M-H]$^-$, 637.4305[M-H-glc]$^-$	799.6[M-H]$^-$, 637.4[M-H-glc]$^-$, 619.3[M-H-glc-H_2O]$^-$, 475.6, 391.3	
70	12.403	Notoginsenoside R_2 or its isomer	815.4810 [M+HCOO]$^-$	769.4673[M-H]$^-$, 637.4166[M-H-xyl]$^-$, 619.4195[M-H-xyl-H_2O]$^-$, 607.4127[M-H-glc]$^-$,	769.4[M-H]$^-$, 637.3[M-H-xyl]$^-$, 475.4[M-H-xyl-glc]$^-$ 391.3[M-H-xyl-glc-C_6H_{12}]$^-$	

				475.3664[M-H-xyl-glc]⁻		
71	12.432	Notoginsenoside N or its isomer	1007.5427 [M+HCOO]⁻	961.5332[M-H]⁻, 799.4753[M-H-glc]⁻, 781.4651[M-H-glc-H_2O]⁻, 637.4306[M-H-2glc]⁻, 619.4055[M-H-2glc-H_2O]⁻, 475.3734[M-H-3glc]⁻	961.3[M-H]⁻, 799.2[M-H-glc]⁻, 781.3[M-H-glc-H_2O]⁻, 637.4[M-H-2glc]⁻,475.2[M-H-3glc]⁻ 391.3[M-H-3glc-C_6H_{12}]⁻, 375.2, 349.3	3
72	12.448	Notoginsenoside G or its isomer	959.5213 [M-H]⁻	797.4637[M-H-glc]⁻, 779.4247[M-H-glc-H_2O]⁻, 635.4099[M-H-2glc]⁻, 473.3573[M-H-3glc]⁻	797.3[M-H-glc]⁻, 779.3, 635.2[M-H-2glc]⁻, 617.3, 473.2[M-H-3glc]⁻, 455.4, 389.1[M-H-3glc-C_6H_{12}]⁻	3
73	12.502	Vinaginsenoside R_{11} or floraginsenoside D	785.4693 [M-H]⁻	653.4210[M-H-xyl]⁻	785.2[M-H]⁻, 653.3[M-H-xyl]⁻, 491.5[M-H-xyl-glc]⁻, 415.3[M-H-xyl-glc-H_2O-C_3H_6O]⁻, 391.8[M-H-xyl-glc-$C_6H_{12}O$]⁻	17
74	12.51	Notoginsenoside R_2 or its isomer	815.4773 [M+HCOO]⁻	769.4601[M-H]⁻	769.3[M-H]⁻, 607.3[M-H-glc]⁻, 475.3[M-H-glc-xyl]⁻ 391.3[M-H-glc-xyl-C_6H_{12}]⁻	3

75	12.528	[PPD 8]-tri-*O*-glucoside/ [PPD 9]-3-glucosyl-glucosyl-20-glucoside	961.5359 [M-H]$^-$	799.4715[M-H-glc]$^-$, 781.4640[M-H-glc-H_2O]$^-$, 637.4356[M-H-2glc]$^-$	1007.3, 961.3[M-H]$^-$, 799.3[M-H-glc]$^-$, 637.2[M-H-2glc]$^-$, 475.4[M-H-3glc]$^-$, 387.1[M-H-3glc-H_2O-C_4H_6O]$^-$	3
76	12.547	[PPT 6]-6-acetylglucosyl -20-glucoside/[PPT 6]-6-glucosyl-20-acetylglucoside /[PPT 6]-20-acetyl-6-glucosyl-glucoside	887.4997 [M+HCOO]$^-$	841.4835[M-H]$^-$, 799.4820[M-H-Ac]$^-$, 781.4597[M-H-Ac-H_2O]$^-$, 637.4254[M-H-Ac-glc]$^-$, 619.4195[M-H-Ac-glc-H_2O]$^-$ 475.3734[M-H-Ac-2glc]$^-$	841.3[M-H]$^-$, 799.4[M-H-Ac]$^-$, 781.4[M-H-Ac-H_2O]$^-$, 637.3[M-H-Ac-glc]$^-$, 619.3[M-H-Ac-H_2O-glc]$^-$, 475.4[M-H-Ac-2glc]$^-$, 457.4[M-H-Ac-2glc-H_2O]$^-$, 391.3[M-H-Ac-2glc-C_6H_{12}]$^-$	8-10
77	12.548	Gynosaponin V or its isomer	1091.6028 [M-H]$^-$	929.5376[M-H-glc]$^-$, 767.4769[M-H-2glc]$^-$, 605.4359[M-H-3glc]$^-$	1091.3[M-H]$^-$, 929.3[M-H-glc]$^-$, 767.2[M-H-2glc]$^-$, 605.4[M-H-3glc]$^-$	3
78	12.583	[PPT 12]-6(12, 20)-*O*-glucoside	699.4329 [M+HCOO]$^-$		653.3[M-H]$^-$, 577.3[M-H-H_2O-C_3H_6O]$^-$ 491.3[M-H-glc]$^-$, 455.2, 429.2,	19

					389.2, 343.2	
79	12.588	Isomer of notoginsenoside R_1	977.5308 [M+HCOO]⁻	931.5245[M-H]⁻, 799.4809[M-H-xyl]⁻, 637.4245[M-H-xyl-glc]⁻, 475.3741[M-H-xyl-2glc]⁻	931.4[M-H]⁻, 799.3[M-H-xyl]⁻, 637.3[M-H-xyl-glc]⁻, 475.3[M-H-xyl-2glc]⁻, 391.3[M-H-xyl-2glc-C_6H_{12}]⁻, 353.2	3
80	12.607	[PPD 7]-3-glucosyl-glucosyl -20-glucosyl-glucosyl-arabinoside (xyloside)/[PPD 7] -3-glucosyl-glucosyl-glucosyl -20-glucosyl-xyloside	1239.6369 [M-H]⁻	1107.5868[M-H-xyl]⁻, 945.5333[M-H-xyl-glc]⁻, 783.4821[M-H-xyl-2glc]⁻, 621.4351[M-H-xyl-3glc]⁻, 459.3828[M-H-xyl-4glc]⁻	1239.2[M-H]⁻, 1107.4[M-H-xyl]⁻, 1077.4[M-H-glc]⁻, 945.5[M-H-xyl-glc]⁻, 783.5[M-H-xyl-2glc]⁻, 621.6[M-H-xyl-3glc]⁻, 459.3[M-H-xyl-4glc]⁻	3
81	12.630	[PPD 7]-3-glucosyl-glucosyl -20-glucosyl-glucosyl-arabinoside (xyloside)/[PPD 7] -3-glucosyl-glucosyl-glucosyl -20-glucosyl-xyloside	1239.6396 [M-H]⁻	1107.5919[M-H-xyl]⁻, 945.5337[M-H-xyl-glc]⁻, 783.4840[M-H-xyl-2glc]⁻, 621.4289[M-H-xyl-3glc]⁻, 459.3749[M-H-xyl-4glc]⁻	1239.2[M-H]⁻, 1107.4[M-H-xyl]⁻, 1077.4[M-H-glc]⁻, 945.5[M-H-xyl-glc]⁻, 783.5[M-H-xyl-2glc]⁻, 621.6[M-H-xyl-3glc]⁻, 458.9[M-H-xyl-4glc]⁻	19

82	12.652	[PPT 4]-6,20-di-*O*-glucoside or its isomer	843.4703 [M+HCOO]$^-$		797.3[M-H]$^-$, 635.3[M-H-glc]$^-$, 617.3[M-H-glc-H_2O]$^-$, 607.2[M-H-glc-CO]$^-$, 473.2[M-H-2glc]$^-$	19
83	12.668	[PPD 3]-3-glucosyl-glucosyl -20-glucosyl-glucoside or epoxynotoginsenoside A or its isomer	1105.5802 [M-H]$^-$	943.5105[M-H-glc]$^-$, 781.4640[M-H-2glc]$^-$, 619.4055[M-H-3glc]$^-$, 457.3616[M-H-4glc]$^-$	1105.3[M-H]$^-$, 943.5[M-H-glc]$^-$, 781.2[M-H-2glc]$^-$, 619.4[M-H-3glc]$^-$, 543.2, 457.2[M-H-4glc]$^-$,	17, 21
84	12.683	[PPT 6]-6-acetylglucosyl -20-glucoside/[PPT 6]-6-glucosyl-20-acetylglucoside /[PPT 6]-20-acetyl-6-glucosyl-glucoside	887.5021	781.4734[M-H-Ac-H_2O]$^-$, 619.4176[M-H-Ac-glc-H_2O]$^-$	887.4, 841.3[M-H]$^-$, 799.4[M-H-Ac]$^-$ 781.4[M-H-Ac-H_2O]$^-$, 679.2[M-H-glc]$^-$ 637.3[M-H-Ac-glc]$^-$, 619.3, 475.4[M-H-Ac-2glc]$^-$, 457.4, 391.2[M-H-Ac-2glc-C_6H_{12}]$^-$	17, 19
85	12.688	[PPT 6]-3(6,20)-glucosyl-rhamnoside /[PPT 6]-6-rhamnosyl (glucosyl)	783.4897 [M-H]$^-$	637.4259[M-H-rha]$^-$, 475.3756[M-H-rha-glc]$^-$,	783.4[M-H]$^-$, 637.3[M-H-rha]$^-$, 619.3[M-H-rha-H_2O]$^-$,	3

		-20-glucoside (rhamnoside)		457.3651[M-H-rha-glc-H_2O]$^-$, 391.2828[M-H-rha-glc-C_6H_{12}]$^-$	475.2[M-H-rha-glc]$^-$ 391.2[M-H-rha-glc-C_6H_{12}]$^-$	
86*	12.756	Ginsenoside F_3	815.4772 [M+HCOO]$^-$	769.4654[M-H]$^-$, 637.4245[M-H-xyl]$^-$, 619.4172[M-H-xyl-H_2O]$^-$, 475.3739[M-H-xyl-glc]$^-$, 391.2662[M-H-xyl-glc-C_6H_{12}]$^-$	769.4[M-H]$^-$, 637.4[M-H-xyl]$^-$, 619.3[M-H-xyl-H_2O]$^-$, 475.4[M-H-xyl-glc]$^-$, 457.3[M-H-xyl-glc-H_2O]$^-$	3
87	12.758	[PPT 6]-6(20)-glucosyl-glucoside/ [PPT 6]-3,6-di-*O*-glucoside	799.4844 [M-H]$^-$	637.4356[M-H-glc]$^-$, 475.3734[M-H-glc]$^-$, 391.2820[M-H-2glc-C_6H_{12}]$^-$	799.4[M-H]$^-$, 637.2[M-H-glc]$^-$, 619.6[M-H-glc-H_2O]$^-$, 475.3[M-H-2glc]$^-$, 459.4, 391.3[M-H-2glc-C_6H_{12}]$^-$	
88*	12.787	Ginsenoside Rb_1	1107.5959 [M-H]$^-$	945.5439[M-H-glc]$^-$, 783.4911[M-H-2glc]$^-$, 621.4316[M-H-3glc]$^-$, 459.3767[M-H-4glc]$^-$, 323.0983	1107.2[M-H]$^-$, 945.2[M-H-glc]$^-$, 783.2[M-H-2glc]$^-$, 765.5[M-H-2glc-H_2O]$^-$, 621.2[M-H-3glc]$^-$,459.4[M-H-4glc]$^-$ 375.2[M-H-4glc-C_6H_{12}]$^-$	
89*	12.824	20(S)-ginsenoside Rg_2	829.4928	783.4896[M-H]$^-$, 637.4259[M-H-rha]$^-$,	783.4[M-H]$^-$, 637.4[M-H-rha]$^-$,	

			[M+HCOO]⁻	475.3756[M-H-rha-glc]⁻, 391.2790[M-H-rha-glc-C_6H_{12}]⁻	619.2[M-H-rha-H_2O]⁻, 475.4[M-H-rha-glc]⁻, 457.3[M-H-rha-glc-H_2O]⁻	
90*	12.848	Ginsenoside Rc	1077.5804 [M-H]⁻	945.5398[M-H-ara]⁻, 783.4787[M-H-ara-glc]⁻, 459.3828[M-H-ara-3glc]⁻	1077.4[M-H]⁻, 945.4[M-H-ara]⁻, 783.4[M-H-ara-glc]⁻, 621.4[M-H-ara-2glc]⁻, 459.2[M-H-ara-3glc]⁻	
91	12.860	Notoginsenoside R_2 or its isomer	769.4733 [M-H]⁻	637.4272[M-H-xyl]⁻, 475.3741[M-H-xyl-glc]⁻, 391.2732[M-H-xyl-glc-C_6H_{12}]⁻	475.3[M-H-xyl-glc]⁻	
92	12.932	[PPT 6]-3(6,20)-glucosyl-rhamnoside /[PPT 6]-6-rhamnosyl (glucosyl) -20-glucoside (rhamnoside)	783.4910 [M-H]⁻	637.4235[M-H-rha]⁻, 619.4128[M-H-rha-H_2O]⁻, 475.3725[M-H-rha-glc]⁻, 457.3709[M-H-rha-glc-H_2O]⁻, 391.2826[M-H-rha-glc-C_6H_{12}]⁻	783.4[M-H]⁻, 637.4[M-H-rha]⁻, 619.4[M-H-rha-H_2O]⁻, 475.3[M-H-rha-glc]⁻, 459.5, 391.3[M-H-rha-glc-C_6H_{12}]⁻	3
93	12.850	Vinaginsenoside R_3 or its isomer	929.5481 [M-H]⁻	767.4878[M-H-glc]⁻, 605.4380[M-H-2glc]⁻	929.4[M-H]⁻, 767.4[M-H-glc]⁻, 605.3[M-H-2glc]⁻, 443.1[M-H-3glc]⁻	3

					339.3[M-H-3glc-C_6H_{14}-H_2O]$^-$	
94*	13.007	Ginsenoside Rh_1	683.4348 [M+HCOO]$^-$	637.4256[M-H]$^-$, 475.3766[M-H-glc]$^-$, 391.2832[M-H-glc-C_6H_{12}]$^-$	637.8, 553.3, 475.9[M-H-glc]$^-$, 391.3[M-H-glc-C_6H_{12}]$^-$	18
95*	13.008	Ginsenoside Rd	991.5484 [M+HCOO]$^-$	945.5431[M-H]$^-$, 783.4825[M-H-glc]$^-$, 621.4278[M-H-2glc]$^-$, 603.4161[M-H-2glc-H_2O]$^-$, 459.3798[M-H-3glc]$^-$, 375.2827[M-H-3glc-C_6H_{12}]$^-$	945.5[M-H]$^-$, 783.6[M-H-glc]$^-$, 621.6[M-H-2glc]$^-$,459.6[M-H-3glc]$^-$ 375.5[M-H-3glc-C_6H_{12}]$^-$	
96	13.068	Isomer of ginsenoside Rd	991.5479 [M+HCOO]$^-$	945.5434[M-H]$^-$ 783.4860[M-H-glc]$^-$, 765.4786[M-H-glc-H_2O]$^-$, 621.4323[M-H-2glc]$^-$, 603.4020[M-H-2glc-H_2O]$^-$, 459.3805[M-H-3glc]$^-$, 375.2877[M-H-3glc-C_6H_{12}]$^-$	945.4[M-H]$^-$, 783.4[M-H-glc]$^-$, 621.4[M-H-2glc]$^-$, 537.2, 459.4[M-H-3glc]$^-$ 375.5[M-H-3glc-C_6H_{12}]$^-$	
97	13.108	[PPT 6]-6,20-di-*O*-xyloside or its isomer	739.4637 [M-H]$^-$	607.4225[M-H-xyl]$^-$, 475.3710[M-H-2xyl]$^-$	739.3[M-H]$^-$, 607.2[M-H-xyl]$^-$, 475.3[M-H-2xyl]$^-$, 459.4,	19

					391.3[M-H-2xyl-C_6H_{12}]$^-$	
98*	13.148	Ginsenoside F_1	683.4352 [M+HCOO]$^-$	637.4259[M-H]$^-$, 475.3730[M-H-glc]$^-$		3
99$^\Psi$	13.208	[PPD 7]-*O*-xylosyl-di-*O*-glucoside	961.5365 [M+HCOO]$^-$	915.5333[M-H]$^-$, 783.4910[M-H-xyl]$^-$, 621.4268[M-H-glc-xyl]$^-$, 603.4054[M-H-glc-xyl-H_2O]$^-$, 459.3771[M-H-2glc-xyl]$^-$	915.2[M-H]$^-$, 783.5[M-H-xyl]$^-$, 753.2[M-H-glc]$^-$, 621.1[M-H-glc-xyl]$^-$, 537.4[M-H-glc-xyl-C_6H_{12}]$^-$, 459.4[M-H-glc-xyl-glc]$^-$ 375.5[M-H-glc-xyl-glc-C_6H_{12}]$^-$	
100 $^\Psi$	13.218	[PPD 2]-*O*-xylosyl-*O*-glucoside	795.4539 [M+HCOO]$^-$		749.4[M-H]$^-$, 633.1, 617.3[M-H-xyl]$^-$, 455.3[M-H-xyl-glc]$^-$	19
101	13.228	Isomer of ginsenoside Rg_1	845.4913 [M+HCOO]$^-$	683.4339[M+HCOO-glc]$^-$, 637.4233[M-H-glc]$^-$, 475.3744[M-H-glc]$^-$	799.3[M-H]$^-$, 637.3[M-H-glc]$^-$, 475.4[M-H-2glc]$^-$, 391.3[M-H-2glc-C_6H_{12}]$^-$	19
102	13.237	Ginsenoside Rg_9 or its isomer	827.4773 [M+HCOO]$^-$	781.4606[M-H]$^-$	781.3[M-H]$^-$, 745.1, 619.4[M-H-glc]$^-$, 457.3[M-H-2glc]$^-$,	3

					407.4, 399.3,	
103	13.301	[PPD 7]-3-glucosyl-20-rutinoside /[PPD 7]-3-glucosyl-glucosyl -20-rhamnoside	975.5553 $[M+HCOO]^-$	$783.4816[M-H-rha]^-$, $621.4333[M-H-rha-glc]^-$, $459.3828[M-H-rha-2glc]^-$	$929.3[M-H]^-$, $783.4[M-H-rha]^-$, $621.5[M-H-rha-glc]^-$, $537.1[M-H-rha-glc-C_6H_{12}]^-$, $459.4[M-H-rha-2glc]^-$, $375.3[M-H-rha-2glc-C_6H_{12}]^-$	19
104#, Ψ	13.308	[PPD 3]/[PPD 4]/[PPT 2]/[PPT 3]-decadianoyl-nonenoyl-acetyl-di -*O*-glucoside	1111.6967 $[M–H]^-$	$781.4710[M-H-deca-non-ace]^-$, 619.4152 $[M-H-deca-non-ace-glc]^-$		19
105 Ψ	13.326	[PPD 4]-*O*-xylosyl-*O*-glucoside	797.4685 $[M+HCOO]^-$	$751.4620[M-H]^-$, $619.4135[M-H-xyl]^-$, $601.4084[M-H-xyl-H_2O]^-$	$751.3[M-H]^-$, $619.3[M-H-xyl]^-$, 601.3, $457.4[M-H-xyl-glc]^-$ 423.5, $387.1[M-H-xyl-glc-C_4H_6O]^-$	17, 19, 20
106	13.348	Chikusetsusaponin LT_8 or its isomer	763.4633 $[M-H]^-$	$617.3966[M-H-rha]^-$	$763.2[M-H]^-$, $617.3[M-H-rha]^-$, 503.3, $455.6[M-H-rha-glc]^-$	20
107	13.378	Ginsenoside Rg_9 or its isomer	827.4763 $[M+HCOO]^-$	$781.4606[M-H]^-$, $619.4127[M-H-glc]^-$	$781.3[M-H]^-$, 745.1, $619.4[M-H-glc]^-$, $457.3[M-H-2glc]^-$ $373.3[M-H-2glc-C_6H_{12}]^-$	19

108	13.388	Isomer of ginsenoside Rd	991.5460 [M+HCOO]$^-$	945.5365[M-H]$^-$, 783.4795[M-H-glc]$^-$, 621.4283[M-H-2glc]$^-$, 459.3828[M-H-3glc]$^-$ 375.2877[M-H-3glc-C_6H_{12}]$^-$	945.4[M-H]$^-$, 783.4[M-H-glc]$^-$, 621.4[M-H-2glc]$^-$, 537.2[M-H-2glc-C_6H_{12}]$^-$, 459.4[M-H-3glc]$^-$	20
109*	13.467	Ginsenoside Rg_6	765.4800 [M-H]$^-$	619.4160[M-H-rha]$^-$, 601.4074[M-H-rha-H_2O]$^-$	765.4[M-H]$^-$, 619.4[M-H-rha]$^-$, 601.2, 457.3[M-H-rha-glc]$^-$	19
110*	13.502	20(S)-ginsenoside Rg_3	829.4932 [M+HCOO]$^-$	783.4807[M-H]$^-$, 621.4283[M-H-glc]$^-$, 459.3759[M-H-2glc]$^-$	783.5[M-H]$^-$, 621.4[M-H-glc]$^-$, 459.4[M-H-2glc]$^-$ 375.4[M-H-2glc-C_6H_{12}]$^-$	
111 Ψ	13.508	[PPD 7]-*O*-xylosyl-di-*O*-glucoside	961.5334 [M+HCOO]$^-$	915.4997[M-H]$^-$, 783.4815[M-H-xyl]$^-$, 621.4302[M-H-xyl-glc]$^-$, 459.3782[M-H-xyl-2glc]$^-$	915.4[M-H]$^-$, 783.6[M-H-xyl]$^-$, 663.5, 621.2[M-H-xyl-glc]$^-$, 459.2[M-H-xyl-2glc]$^-$ 375.2[M-H-xyl-2glc-C_6H_{12}]$^-$	
112	13.612	Ginsenoside F_2 or its isomer	829.4939 [M+HCOO]$^-$	783.4774[M-H]$^-$, 621.4308[M-H-glc]$^-$, 537.3370[M-H-glc-C_6H_{12}]$^-$, 459.3828[M-H-2glc]$^-$	783.4[M-H]$^-$, 621.4[M-H-glc]$^-$, 459.4[M-H-2glc]$^-$	19

*: The compound identified by comparing with the reference compound. #: The compound additionally detected by the full scan along with the excluded and

preferred ions list.

[$]: The compound revised by the LC-IT-TOF/MS analysis. [Ψ]: The potential new compound.

Here, xyl was used to represent all possible pentose moieties, including ara and xyl, which could not be discriminated by mass data. Likewise, glc was applied to collectively name the hexosyl, include glucosyl and galactosyl.