Research Article

Rapid Identification of Characteristic Chemical Constituents of Panax ginseng, Panax quinquefolius, and Panax japonicus Using UPLC-Q-TOF/MS

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Saponins are the main active components in Panax ginseng C. A. Mey. (PG), Panax quinquefolius L. (PQ), and Panax japonicus C. A. Mey. (PJ), which belong to the genus Panax in the Araliacea family. Because the chemical components in the three species are similar, they are often mixed and misused in functional foods and pharmaceuticals applications. Therefore, it is urgent to establish a method to quickly distinguish among PG, PQ, and PJ. Ultraperformance liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-Q-TOF/MS) was combined with data postprocessing to identify the main characteristic fragments (CFs) and the related neutral losses (NLs) of protopanaxadiol (PPD), protopanaxatriol (PPT), oleanolic acid (OLE), and ocottillol- (OCO-) type saponins. By comparing the mass spectral data, it was possible to rapidly classify and identify saponins in PG, PQ, and PJ. A total of twenty-three chemical components were identified in the PG samples, twenty-three components were identified in the PQ samples, and twenty-seven components were identified in the PJ samples. Among them, OCO-type saponins were characteristic of PQ and PJ. Ginsenoside Rf, which was absent from PQ, allowed for differentiation between PQ and PJ. The CFs and NLs in the mass spectra of the characteristic components of PG, PQ, and PJ allowed for the rapid classification and identification of these species. Additionally, these results provide technical support for the quality evaluation of Chinese herbal medicine and for constructing a scientific regulatory system.

1. Introduction

Panax ginseng C. A. Mey. (PG), Panax quinquefolius L. (PQ), and Panax japonicus C. A. Mey. (PJ) are three important plants of the genus Panax in the Araliacea family. Based on their morphology, these plants can be divided into two groups: the first is an upright rhizome with developed fleshy roots, mainly containing dammarane- (DAM-) type tetracyclic triterpenoid saponins, such as PG, PQ, Panax notoginseng, and so on. The other is a developed rhizome, horizontal bamboo whip or rosary, with less fleshy roots. It mainly contains oleanolic acid (OLE) pentacyclic triterpenoid saponins, such as PJ [1]. Recent investigations have shown that the main active components of PG, PQ, and PJ are saponins, polysaccharides, phenolic acids, and alkaloids. Recent pharmacological studies have shown that saponins can delay aging, improve immunity, prevent and treat Alzheimer’s disease, and regulate the nervous system. Additionally, saponins exhibit antitumor activity, along with antioxidative, antihypertensive, and antihyperglycemic...
2. Materials and Methods

2.1. Materials, Reagents, and Instruments. Nine batches of representative medicinal materials were collected or purchased from Jilin, the main area producing PG and PQ, and from different areas producing PJ. The detailed sample information is presented in Table 1. High-performance liquid chromatography-grade acetonitrile was provided by Oceanpak (Sweden), high-performance liquid chromatography-grade formic acid was provided by Thermo Fisher (USA), and distilled water was purchased from Watson Food and Beverage Company (China). A Waters Acquity (Waters, USA) UPLC instrument and a Xevo G2 (Waters, USA) Q-TOF/MS system were used in this study.

2.2. Sample Preparation. The Chinese medicinal herbs PG-1, PQ-1, and PJ-1 were, respectively, crushed, and 0.2 g of the powdered PG-1, PQ-1, and PJ-1 was placed into three separate test tubes, soaked in 10 mL of 70% ethanol, and ultrasonically extracted for 50 min. After extraction, each tube was cooled and centrifuged for 10 min. The supernatant was subsequently filtered through a 0.22 μm microporous membrane and analyzed by UPLC-Q-TOF/MS.

2.3. UPLC and MS Conditions. UPLC conditions were as follows: a Waters Acquity UPLC BEH C18 column (2.1 mm × 100 mm, 1.7 μm) was used as the chromatographic column. The column temperature was set at 40°C, the flow rate was 0.3 mL/min, the injection volume was 5 μL, the mobile phase was composed of 0.1% formic acid aqueous solution (A) and acetonitrile (B), and the chromatographic gradient sequence was as follows: 0–2 min, 5–10% B; 2–6 min, 10–30% B; 6–10 min, 30–50% B; 10–15 min, 50–80% B; 15–20 min, 80–100% B; 20–25 min, 100% B; 25–30 min, 100–5% B; and 30–35 min, 5% B.

TOF-MS conditions were as follows: mass spectrometry was performed using a Waters G2 Q-TOF mass spectrometer, equipped with a negative mode electrospray ionization source. The capillary voltage was −2.4 kV, the cone voltage was 40 V, the source temperature was 120°C, the desolvation temperature was 400°C, the desolvation gas was 800 L/h, and the cone gas was 50 L/h, using leucine enkephalin (m/z 554.2615) as an external reference. In order to ensure the accuracy of the data acquisition, the full-scan data in the range of 100–1500 Da were obtained.

2.4. Method Establishment. The main pharmacological constituents of PG, PQ, and PJ are saponins. Therefore, to accurately distinguish the three traditional Chinese medicines, it was necessary to classify and identify the saponins. However, the use of conventional methods to determine the composition of saponins is complicated and time-consuming because of their large molecular weight and similar properties [2–6]. Consequently, ginsenosides are widely used in food, healthcare products, cosmetics, and medicine. Although the three traditional Chinese medicinal herbs from the genus Panax have different pharmacological actions, indications, and clinical applications, the properties and chemical composition of these Chinese herbal species are very similar, and thus adulterated products are often passed off as genuine in the market [7–10]. For example, in order to very similar, and thus adulterated products are often passed off as genuine in the market [7–10]. For example, in order to reduce the production cost or simply via mistaken identity, PQ is added to commercial PG products [11], and narrow-leaf Panax japonicus and Panax notoginseng of the same or different families and genera are often used as adulterants intentionally or mistakenly as a substitute for genuine PJ [12]. Adulterants not only compromise the integrity of the Chinese herbal medicine market but also affect the efficacy and safety of traditional Chinese medicine. Therefore, it is urgent to establish methods for the rapid identification of the three genuses of Panax used in traditional Chinese medicines so as to improve the efficacy of quality evaluation and provide scientific regulation.

The ginsenosides found in PG can be divided into two groups according to their glycosidic structure: DAM-type and OLE-type. There are two types of DAM: protopanaxadiol-(PPD-) type saponins, for which the aglycone is 20(s)-PPD; these contain the most ginsenosides, including ginsenoside Rb1, Rb2, Rb3, Rc, Rd, Rg3, and Rh2, and protopanaxatriol-(PPT-) type saponins, for which the aglycone is 20(s)-PPT, including ginsenoside Re, Rf, Rg1, and Rh1. The aglycone of OLE-type ginsenosides, such as ginsenoside Ro, is oleanolic acid [13]. Compared to PG, PQ and PJ not only contain PPD-, PPT-, and OLE-type saponins but also contain ococtillol- (OCO-) type saponins, such as pseudoginsenoside F11 and pseudoginsenoside RT4 [14, 15]. In addition, ginsenoside Rf has not been found in PQ [16]. The types of saponins, similar to the structures of their parental nucleus, are rich and complex. Therefore, it is necessary to develop a rapid method for the qualitative analysis of saponins that allows for the accurate classification and identification of different traditional Chinese medicines from the genus Panax.

In this study, an accurate, rapid, and sensitive ultra-performance liquid chromatography quadrupole tandem time-of-flight mass spectrometry (UPLC-Q-TOF/MS) technique combined with data postprocessing is established (Figure 1). First, the characteristic fragments (CFs) and neutral losses (NLs) of various saponins are summarized. Based on the quasi-molecular ions and the fragment ions provided by high-resolution mass spectrometry, the chromatographic retention time, and related literature data, the saponin profiles of PG, PQ, and PJ are identified in order to realize accurate distinction between the three. This study aims to explore the medicinal basis of the three traditional Chinese medicinal herbs from the genus Panax and provide basic information for establishing a comprehensive system for evaluating the quality of medicinal materials. Simultaneously, this approach can provide technical support for constructing a scientifically based regulatory system.
core structure. In collision-induced MS, compounds with the same or similar parent nuclear skeletons usually fracture similarly, and this technique is used to establish fragmentation patterns. CFs are molecular compounds with the same or similar parent core structures. When exposed to the energy impact of MS, they can fragment into ions, from which the cleavage type and material can be easily inferred. CFs can be used to help to rapidly classify the target materials. In addition, molecular ions can lose neutral radicals or molecules in MS, as shown by the difference between the mass/load ratio and the molecular ion peak and the product ion peaks, respectively. ©K_ese lost free-radicals or molecules are known as NLs, which aidthescreeningandidentificationof substances [17–22]. ©K_erefore, we present the MS fragmentation of PG, PQ, and PJ and summarize their CFs and common NLs, which are based on the different core structures (DAM-, OLE-, and OCO-types). First, the different CFs were used to preliminarily classify the unknown components. The various saponins were identified by combined analysis of their molecular ions, retention time, and the fragmentation pattern of the unknown components, along with their fracture processes, which were estimated using common NLs. Based on the types of saponins in the samples, the three traditional Chinese medicinal herbs could be identified quickly and accurately.

3. Results and Discussion

Based on the summarized CF and NL data, PG, PQ, and PJ were analyzed. Twenty-three chemical constituents were identified for the PG samples, which included 10 PPD saponins, 11 PPT saponins, and 2 OLE saponins. A total of twenty-three components was identified from PQ, which included 12 PPD saponins, 4 PPT saponins, 3 OLE saponins, and 4 OCO saponins. A total of twenty-seven components was identified in the PJ samples, which included 7 PPD saponins, 6 PPT saponins, 11 OLE saponins, and 3 OCO saponins. The CFs and NLs of the different types of saponins are shown in Figure 2. The total ion chromatograms of the PG, PQ, and PJ extracts in negative ion mode are shown in Figure 3, and their compositions are shown in Tables 2–4.

3.1. Analysis of Dammarane-Type Saponins by MS

3.1.1. PPD-Type Saponins. PPD-type ginsenosides, such as ginsenosides Rb, Rb₂, Rc, and Rg₃, are saponins in the genus Panax. In 1966, Shibata et al. isolated ginsenediol from the root of ginseng for the first time and reported its chemical properties and structure [35]. Considering the structural types of PPD and the mass spectral information in the literature, it was found that two CFs were produced, with signals at m/z 621 [C₃₆H₅₁O₈]⁻ and m/z 459 [C₃₆H₃₇O₅]⁻. At the same time, the product ions observed in the MS² profiles

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**Table 1: Detailed information of the tested PG, PQ, and PJ samples.**

| Sample number | Source               | Identity               |
|---------------|----------------------|------------------------|
| PG-1          | Jilin province, China| Panax ginseng C. A. Mey.|
| PG-2          | Jilin province, China| Panax ginseng C. A. Mey.|
| PG-3          | Jilin province, China| Panax ginseng C. A. Mey.|
| PQ-1          | Jilin province, China| Panax quinquefolius L. |
| PQ-2          | Jilin province, China| Panax quinquefolius L. |
| PQ-3          | Jilin province, China| Panax quinquefolius L. |
| PJ-1          | Anhui province, China | Panax japonicus C. A. Mey. |
| PJ-2          | Sichuan province, China | Panax japonicus C. A. Mey. |
| PJ-3          | Yunnan province, China | Panax japonicus C. A. Mey. |

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**Figure 1:** The rapid identification strategy of three traditional Chinese medicines in the genus Panax.
Saponins of traditional Chinese medicines in genus Panax

CFs
569 \[C_{35}H_{54}O_6\]^−
455 \[C_{30}H_{47}O_3\]^−

CFs
621 \[C_{36}H_{61}O_8\]^−
459 \[C_{30}H_{51}O_3\]^−

CFs
637 \[C_{36}H_{61}O_9\]^−
475 \[C_{30}H_{51}O_4\]^−

CFs
653 \[C_{36}H_{61}O_{10}\]^−
491 \[C_{30}H_{51}O_5\]^−

Protopanaxadiol type
Protopanaxatriol type
Oleanane type
Ocotillol type

CO₂[44Da] H₂O[18Da]
Mal[86Da]
Ara[132Da]
Ac[42Da] Rha[146Da]
Glc[162Da] Xyl[132Da]

GlcUA[176Da]

Figure 2: Characteristic fragments and neutral losses of different types of saponins in genus *Panax*. Ac: acetyl; Mal: malonyl; Glc: glucose residue; Ara: arabinose residue; Rha: rhamnose residue; Xyl: xylose residue; GlcUA: glucuronic acid.

Figure 3: Continued.
of the PPD-type saponins generally resulted in the following NLs: CO₂ (44 Da), H₂O (18 Da), Mal (86 Da), Ara (132 Da), Glc (162 Da), Xyl (132 Da), Ac (42 Da), and Rha (146 Da). Therefore, based on the CFs and NLs, it was possible to identify the compounds and infer their fracture processes.

Compound 11 (Table 2) had a retention time of 8.42 min and a molecular formula of C₅₇H₉₄O₂₆. In the negative ion mode, compound 11 produced a precursor ion at m/z 1193.5938 [M-H]⁻ and seven fragment ion peaks at m/z 1149.6027, 1107.5938, 945.5364, 783.4828, 765.4836, 621.4205, and 459.3793. Based on the CF ions at m/z 621.4205 and 459.3793, compound 11 in Table 2 could be preliminarily identified as a PPD-type saponin. The product ion at m/z 1149.6027 was produced by the removal of a CO₂ molecule (44 Da) from the precursor ion. The product ion at m/z 1107.5938 was produced by the malonyl group (86 Da) of the precursor ion. The m/z 945.5364 product ion was produced by the neutral loss of malonyl and a part of the glucose residue (162 Da) from the precursor ion. When the product ions at m/z 945.5364 continued to lose glucose residues, products with m/z 783.4828 [M-H-Mal-2Glc]⁻, m/z 765.4836 [M-H-Mal-3Glc]⁻, and m/z 621.4205 [M-H-Mal-4Glc]⁻ were formed. When the product ion with a peak at m/z 783.4828 lost one H₂O molecule (18 Da), the product ion at m/z 765.4836 [M-H-Mal-2Glc-H₂O]⁻ was formed. Therefore, compound 11 (Table 2) was identified as malonyl-ginsenoside Rb₁ from its molecular ion and secondary mass spectral fracture pattern [24, 30]. The cleavage pathway of malonyl-ginsenoside Rb₁ in negative ion mode is shown in Figures 4 and 5.

Figure 3: Chromatogram BPI diagram of PG, PJ, and PQ under negative ions (a) PG, (b) PQ, and (c) PJ.
| No. | Identity                          | Formula       | Rt  | Theoretical value                  | Actual value                  | Ppm   | Main MS/MS fragments detected                                                                 | Saponin type | Ref. |
|-----|-----------------------------------|---------------|-----|-----------------------------------|------------------------------|-------|------------------------------------------------------------------------------------------------|--------------|------|
| 1   | Ginsenoside Re₅                   | C₄₂H₇₂O₁₅    | 4.65| 861.4848 [M + HCOO]⁻              | 861.4824 [M + HCOO]⁻          | -2.79 | 415.0735 [M-H-GlUA-Rha-CH₂COOH-H₂O]⁻                                                           | PPT          | [23]|
| 2   | 20-O-glucosylginsenoside Rf       | C₄₈H₈₂O₁₉    | 6.09| 1007.5427 [M + HCOO]⁻             | 1007.5408 [M + HCOO]⁻          | -1.89 | 961.5369 [M-H]⁻                                                                                  | PPT          | [24]|
|     |                                  |               |     |                                   |                              |       | 799.4875 [M-H-Glc]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 637.4326 [M-H-2Glc]⁻                                                                              |              |      |
|     |                                  |               |     |                                   |                              |       | 475.3742 [M-H-3Glc]⁻                                                                              |              |      |
| 3   | Notoginsenoside R₁                | C₄₇H₆₈O₁₈    | 6.23| 977.5321 [M + HCOO]⁻              | 977.5280 [M + HCOO]⁻          | -4.19 | 931.5211 [M-H]⁻                                                                                  | PPT          | [24]|
|     |                                  |               |     |                                   |                              |       | 799.4812 [M-H-Xyl]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 637.4296 [M-H-Xyl-Glc]⁻                                                                           |              |      |
|     |                                  |               |     |                                   |                              |       | 475.3794 [M-H-Xyl-2Glc]⁻                                                                          |              |      |
| 4   | Ginsenoside Re                    | C₄₈H₈₂O₁₈    | 6.48| 991.5478 [M + HCOO]⁻              | 991.5457 [M + HCOO]⁻          | -2.12 | 799.4819 [M-H]⁻                                                                                  | PPT          | [24–27]|
|     |                                  |               |     |                                   |                              |       | 637.4293 [M-H-Glc]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 475.3801 [M-H-2Glc-Rha]⁻                                                                          |              |      |
| 5   | Ginsenoside Rg₆                   | C₄₂H₇₂O₁₄    | 6.52| 845.4899 [M + HCOO]⁻              | 845.4871 [M + HCOO]⁻          | -3.31 | 799.4816 [M-H]⁻                                                                                  | PPT          | [27, 28]|
|     |                                  |               |     |                                   |                              |       | 637.4293 [M-H-Glc]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 475.3775 [M-H-2Glc]⁻                                                                              |              |      |
| 6   | Ginsenoside Rg₇                   | C₄₂H₇₂O₁₄    | 6.54| 845.4899 [M + HCOO]⁻              | 845.4870 [M + HCOO]⁻          | -3.43 | 799.4816 [M-H]⁻                                                                                  | PPT          | [24, 27]|
|     |                                  |               |     |                                   |                              |       | 637.4293 [M-H-Glc]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 475.3775 [M-H-2Glc]⁻                                                                              |              |      |
| 7   | Malonyl-ginsenoside Rg₁           | C₄₅H₇₄O₁₇    | 6.72| 885.4848 [M-H]⁻                   | 885.4771 [M-H]⁻               | -8.70 | 841.4857 [M-H-CO₂]⁻                                                                               | PPT          | [27–29]|
|     |                                  |               |     |                                   |                              |       | 799.4765 [M-H-Mal]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 781.4659 [M-H-Mal-H₂O]⁻                                                                            |              |      |
|     |                                  |               |     |                                   |                              |       | 637.4263 [M-H-Mal-Glc]⁻                                                                           |              |      |
|     |                                  |               |     |                                   |                              |       | 475.3755 [M-H-Mal-2Glc]⁻                                                                           |              |      |
| 8   | Yesanchinoside D (6’-O-acetyl-    | C₄₄H₇₄O₁₅    | 7.31| 887.5004 [M + HCOO]⁻              | 887.4955 [M + HCOO]⁻          | -5.52 | 841.4865 [M-H]⁻                                                                                  | PPT          | [24]|
|     | ginsenoside Rg₆)                 |               |     |                                   |                              |       | 781.4639 [M-CH₂COOH]⁻                                                                             |              |      |
| 9   | Notoginsenoside R₂                | C₄₁H₇₀O₁₃    | 7.35| 815.4793 [M + HCOO]⁻              | 815.4787 [M + HCOO]⁻          | -0.74 | 769.4833 [M-H]⁻                                                                                  | PPT          | [27, 30]|
|     |                                  |               |     |                                   |                              |       | 637.4329 [M-H-Xyl]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 475.3798 [M-H-Xyl-Glc]⁻                                                                           |              |      |
| 10  | Ginsenoside Rf                    | C₄₂H₇₂O₁₄    | 8.15| 845.4899 [M + HCOO]⁻              | 845.4879 [M + HCOO]⁻          | -2.37 | 799.4833 [M-H]⁻                                                                                  | PPT          | [24]|
|     |                                  |               |     |                                   |                              |       | 781.4752 [M-H-H₂O]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 637.4337 [M-H-Glc]⁻                                                                               |              |      |
|     |                                  |               |     |                                   |                              |       | 475.3816 [M-H-2Gk]⁻                                                                               |              |      |
| No. | Identity               | Formula | Rt   | Theoretical value | Actual value | Ppm  | Main MS/MS fragments detected                                      | Saponin type | Ref.          |
|-----|------------------------|---------|------|-------------------|--------------|------|-------------------------------------------------------------------|--------------|---------------|
| 11  | Malonyl-ginsenoside Rb₁ | C₅₇H₉₄O₂₆ | 8.42 | 1193.5955 [M-H]⁻ | 1193.5938 [M-H]⁻ | -1.42 | 1149.6027 [M-H-CO₂]⁻ | 1107.5938 [M-H-Mal]⁻ | 945.5364 [M-H-Mal-Glc]⁻ | 783.4828 [M-H-Mal-2Glc]⁻ | 765.4836 [M-H-Mal-2Glc-H₂O]⁻ | 621.4205 [M-H-Mal-3Glc]⁻ | 459.3793 [M-H-Mal-4Glc]⁻ | PPD | [24, 27, 30] |
| 12  | Malonyl-ginsenoside Rç  | C₅₆H₉₂O₂₅ | 8.60 | 1163.5849 [M-H]⁻ | 1163.5798 [M-H]⁻ | -4.38 | 1119.5902 [M-H-CO₂]⁻ | 1077.5809 [M-H-Mal]⁻ | 945.5629 [M-H-Mal-Xyl]⁻ | 783.4856 [M-H-Mal-Xyl-Glc]⁻ | 621.4377 [M-H-Mal-Xyl-2Glc]⁻ | 459.3702 [M-H-Mal-Xyl-3Glc]⁻ | PPD | [24, 26, 27, 30] |
| 13  | Ginsenoside Ro          | C₄₈H₇₆O₁₉ | 8.64 | 955.4903 [M-H]⁻  | 955.4875 [M-H]⁻ | -2.93 | 955.4875 [M-H]⁻ | 793.4306 [M-H-Glc]⁻ | 569.3799 [M-H-CO₂-H₂O-2Glc]⁻ | 455.3496 [M-H-2Glc-GlcUA]⁻ | OLE | [24, 27] |
| 14  | Ginsenoside Rç          | C₅₃H₉₀O₂₂ | 8.75 | 1123.5900 [M+HCOO]⁻ | 1123.5856 [M+HCOO]⁻ | -3.92 | 1077.5808 [M-H]⁻ | 945.5377 [M-H-Xyl]⁻ | 783.4871 [M-H-Xyl-Glc]⁻ | 621.4434 [M-H-Xyl-2Glc]⁻ | 459.3853 [M-H-Xyl-3Glc]⁻ | PPD | [24, 27, 30] |
| 15  | Ginsenoside Rb₂/ginsenoside Rb₃ | C₅₃H₉₀O₂₂ | 8.76 | 1123.5900 [M+HCOO]⁻ | 1123.5859 [M+HCOO]⁻ | -3.65 | 1077.5814 [M-H]⁻ | 945.5422 [M-H-Xyl]⁻ | 783.4926 [M-H-Xyl-Glc]⁻ | 621.4468 [M-H-Xyl-2Glc]⁻ | 459.3786 [M-H-Xyl-3Glc]⁻ | PPD | [24, 25, 27] |
| 16  | Malonyl-ginsenoside Rb₂ | C₅₆H₉₂O₂₅ | 8.81 | 1163.5849 [M-H]⁻ | 1163.5817 [M-H]⁻ | -2.75 | 1119.5912 [M-H-CO₂]⁻ | 1077.5797 [M-H-Mal]⁻ | 945.5309 [M-H-Mal-Xyl]⁻ | 783.4660 [M-H-Mal-Xyl-Glc]⁻ | 621.4481 [M-H-Mal-Xyl-2Glc]⁻ | 459.3897 [M-H-Mal-Xyl-3Glc]⁻ | PPD | [24, 30] |
| 17  | Malonyl-ginsenoside Rb₃ | C₅₆H₉₂O₂₅ | 9.06 | 1163.5849 [M-H]⁻ | 1163.5876 [M-H]⁻ | 2.32  | 1077.5974 [M-H-Mal]⁻ | 945.5316 [M-H-Mal-Xyl]⁻ | 783.5035 [M-H-Mal-Xyl-Glc]⁻ | 621.4245 [M-H-Mal-Xyl-2Glc]⁻ | 459.3838 [M-H-Mal-Xyl-3Glc]⁻ | PPD | [24] |
| 18  | Zingibroside R₁         | C₄₂H₆₆O₁₄ | 9.24 | 793.4374 [M-H]⁻  | 793.4355 [M-H]⁻ | -2.39 | 631.3826 [M-H-Glc]⁻ | 569.3931 [M-H-Glc-CO₂-H₂O]⁻ | 455.3629 [M-H-Glc-GlcUA]⁻ | OLE | [27] |
Table 2: Continued.

| No. | Identity                        | Formula | Rt  | Theoretical value | Actual value | Ppm  | Main MS/MS fragments detected                      | Saponin type   | Ref.     |
|-----|---------------------------------|---------|-----|-------------------|--------------|------|---------------------------------------------------|----------------|----------|
| 19  | Ginsenoside Rd                  | C_{48}H_{82}O_{18} | 9.29| 991.5478 [M + HCOO]^− | 991.5463 [M + HCOO]^− | −1.51| 945.5413 [M-H]^−, 783.4880 [M-H-Glc]^−, 621.4258 [M-H-2Glc]^−, 459.3817 [M-H-3Glc]^−, 161.0483 [Glc-H]^− | PPD            | [24, 26, 27]|
| 20  | Malonyl-ginsenoside Re          | C_{51}H_{84}O_{21} | 9.35| 1031.5427 [M-H]^− | 1031.5428 [M-H]^− | 0.10 | 1031.5460 [M-H]^−, 987.5533 [M-H-CO₂]^−, 945.4340 [M-H-Mal]^−, 783.4849 [M-H-Mal-Glc]^−, 637.4373 [M-H-Mal-Rha-Glc]^−, 475.3859 [M-H-Mal-Rha-2Glc]^− | PPT            | [24, 27] |
| 21  | Notoginsenoside Fe/vina-ginsenoside R_{16} | C_{47}H_{80}O_{17} | 10.09| 961.5372 [M + HCOO]^− | 961.5469 [M + HCOO]^− | 10.09| 915.5186 [M-H]^−, 783.5407 [M-H-Xyl]^−, 753.5070 [M-H-Glc]^−, 621.4315 [M-H-Xyl-Glc]^−, 459.3875 [M-H-Xyl-2Glc]^− | PPD            | [27]     |
| 22  | Malonyl-notoginsenoside Fe      | C_{50}H_{82}O_{20} | 10.14| 1001.5321 [M-H]^− | 1001.5320 [M-H]^− | −0.10| 783.4836 [M-H-Xyl-Mal]^−, 459.3748 [M-H-Xyl-Mal-2Glc]^− | PPD            | [27]     |
| 23  | Ginsenoside F_{2}/ginsenoside R_{83} | C_{42}H_{72}O_{13} | 11.62| 829.4949 [M + HCOO]^− | 829.4916 [M + HCOO]^− | −3.98| 783.4875 [M-H]^−, 621.4391 [M-H-Glc]^−, 459.3772 [M-H-2Glc]^− | PPD            | [27, 31, 32]|

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| No. | Identity         | Formula    | Rt  | Theoretical value | Actual value | Ppm  | Main MS/MS fragments detected                  | Saponin type | Ref. |
|-----|------------------|------------|-----|-------------------|--------------|------|-----------------------------------------------|--------------|------|
| 1   | Ginsenoside Re   | C_{48}H_{82}O_{18} | 6.47| 991.5478 [M + HCOO]^- | 991.5468 [M + HCOO]^- | -1.01 | 945.5403 [M-H]^-, 799.4841 [M-H-Rha]^-, 783.4899 [M-H-Glc]^-, 637.4333 [M-H-Glc-Rha]^-, 475.3792 [M-H-2Glc-Rha]^-, 945.5408 [M-H]^-, 783.4871 [M-H-Glc]^-, 621.4116 [M-H-2Glc]^-, 459.7427 [M-H-3Glc]^-, 161.0451 [Glc-H]^-, 1119.4801 [M-H-CO2]^-, 1077.7046 [M-H-Mal]^-, 783.4866 [M-H-Mal-Xyl-Glc]^-, | PPT          | [28] |
| 2   | Gypenoside X VII | C_{48}H_{82}O_{18} | 6.50| 991.5478 [M + HCOO]^- | 991.5472 [M + HCOO]^- | -0.61 | 945.5408 [M-H]^-, 783.4871 [M-H-Glc]^-, 621.4116 [M-H-2Glc]^-, 459.7427 [M-H-3Glc]^-, 161.0451 [Glc-H]^-, 1119.4801 [M-H-CO2]^-, 1077.7046 [M-H-Mal]^-, 783.4866 [M-H-Mal-Xyl-Glc]^-, | PPD          | [28] |
| 3   | Malonyl-ginsenoside Re | C_{56}H_{92}O_{25} | 6.87| 1209.5904 [M + HCOO]^- | 1209.5897 [M + HCOO]^- | -0.58 | 799.4836 [M-H]-, 637.4357 [M-H-Glc]-, 475.3795 [M-H-2Glc]-, 841.4931 [M-H]^-, 799.4761 [M-H-Ac]^-, 781.4734 [M-H-Ac-H_2O]^-, 679.4437 [M-H-Glc]^-, 637.4263 [M-H-Ac-Glc]^-, 619.4208 [M-H-Ac-Glc-H_2O]^-, 475.3736 [M-H-Ac-2Glc]^-, 1119.4801 [M-H-CO2]^-, 1077.7046 [M-H-Mal]^-, 783.4866 [M-H-Mal-Xyl-Glc]^-, | PPD          | [28] |
| 4   | Ginsenoside Rg1  | C_{42}H_{72}O_{14} | 6.93| 845.4899 [M + HCOO]^- | 845.4886 [M + HCOO]^- | -1.54 | 799.4836 [M-H]-, 637.4357 [M-H-Glc]-, 475.3795 [M-H-2Glc]-, 841.4931 [M-H]^-, 799.4761 [M-H-Ac]^-, 781.4734 [M-H-Ac-H_2O]^-, 679.4437 [M-H-Glc]^-, 637.4263 [M-H-Ac-Glc]^-, 619.4208 [M-H-Ac-Glc-H_2O]^-, 475.3736 [M-H-Ac-2Glc]^-, 1119.4801 [M-H-CO2]^-, 1077.7046 [M-H-Mal]^-, 783.4866 [M-H-Mal-Xyl-Glc]^-, | PPT          | [28] |
| 5   | Acetyl-ginsenoside Rg1 | C_{44}H_{74}O_{15}| 7.31| 887.5004 [M + HCOO]^- | 887.4990 [M + HCOO]^- | -1.58 | 799.4686 [M-H-Ac]^-, 653.3508 [M-H-Ac-Rha]^-, 491.3585 [M-H-Ac-Rha-Glc]^-, 987.5534 [M-H]^-, 945.5455 [M-H-Ac]^-, 783.4812 [M-H-Ac-Glc]^-, 621.4262 [M-H-Ac-2Glc]^-, 459.1374 [M-H-Ac-Glc]^-, 161.0461 [Glc-H]^-, | PPT          | [28, 31, 32] |
| 6   | Vina-ginsenoside R1 | C_{44}H_{74}O_{15} | 7.32| 887.5004 [M + HCOO]^- | 887.4999 [M + HCOO]^- | -0.56 | 799.4686 [M-H-Ac]^-, 653.3508 [M-H-Ac-Rha]^-, 491.3585 [M-H-Ac-Rha-Glc]^-, 987.5534 [M-H]^-, 945.5455 [M-H-Ac]^-, 783.4812 [M-H-Ac-Glc]^-, 621.4262 [M-H-Ac-2Glc]^-, 459.1374 [M-H-Ac-Glc]^-, 161.0461 [Glc-H]^-, | OCO          | [28] |
| 7   | Pseudoginsenoside RC1 | C_{50}H_{84}O_{19} | 7.35| 1033.5583 [M + HCOO]^- | 1033.5575 [M + HCOO]^- | -0.77 | 945.5403 [M-H]^-, 799.4841 [M-H-Rha]^-, 783.4899 [M-H-Glc]^-, 475.3792 [M-H-2Glc-Rha]^-, 459.1374 [M-H-Ac-Glc]^-, 161.0461 [Glc-H]^-, | PPD          | [28] |

Table 3: Cracking information of chemical components in PQ under negative ion mode.
Table 3: Continued.

| No. | Identity          | Formula | Rt | Theoretical value | Actual value | Ppm  | Main MS/MS fragments detected | Saponin type | Ref. |
|-----|-------------------|---------|----|-------------------|--------------|------|-------------------------------|--------------|------|
| 8   | Pseudoginsenoside RT₂ | C₄₁H₇₀O₁₄ | 8.13 | 831.4742 [M + HCOO]⁻ | 831.4772 [M + HCOO]⁻ | 3.61 | 785.4709 [M-H]⁻, 653.4288 [M-H-Xyl]⁻ | OCO          | [28] |
| 9   | Majonoside R₂     | C₄₁H₇₀O₁₄ | 8.14 | 831.4742 [M + HCOO]⁻ | 831.4769 [M + HCOO]⁻ | 3.25 | 785.4690 [M-H]⁻, 653.4274 [M-H-Xyl]⁻ | OCO          | [28] |
| 10  | Pseudoginsenoside F₁₁ | C₄₂H₇₄O₁₄ | 8.25 | 845.4899 [M + HCOO]⁻ | 845.4912 [M + HCOO]⁻ | 1.54 | 785.4709 [M-H]⁻, 653.4288 [M-H-Xyl]⁻, 1193.5955 [M-H]⁻, 1193.5978 [M-H]⁻ | OCO          | [28, 33, 34] |
| 11  | Malonyl-ginsenoside Rb₁ | C₅₇H₉₄O₂₆ | 8.39 | 1193.5955 [M-H]⁻ | 1193.5978 [M-H]⁻ | 1.93 | 783.4980 [M-H-Mal-2Glc]⁻, 621.4172 [M-H-Mal-3Glc]⁻, 459.3224 [M-H-Mal-4Glc]⁻ | PPD          | [28] |
| 12  | Malonyl-ginsenoside Rb₂ | C₅₆H₉₂O₂₅ | 8.60 | 1163.5849 [M-H]⁻ | 1163.5861 [M-H]⁻ | 1.03 | 783.4878 [M-H-Mal-Xyl-Glc]⁻, 621.4401 [M-H-Mal-Xyl-2Glc]⁻, 459.2655 [M-H-Mal-Xyl-3Glc]⁻ | PPD          | [28] |
| 13  | Ginsenoside Ro    | C₄₈H₇₆O₁₉ | 8.65 | 955.4903 [M-H]⁻ | 955.4913 [M-H]⁻ | 1.05 | 955.4924 [M-H]⁻, 793.4407 [M-H-Glc]⁻, 569.3823 [M-H-CO₂-H₂O-2Glc]⁻, 455.3648 [M-H-2Gk-GlcUA]⁻ | OLE          | [28] |
| No. | Identity               | Formula         | Rt  | Theoretical value | Actual value | Ppm  | Main MS/MS fragments detected                                                                 | Saponin type | Ref. |
|-----|------------------------|-----------------|-----|-------------------|--------------|------|------------------------------------------------------------------------------------------------|--------------|------|
| 14  | Malonyl-ginsenoside Rb₃ | C₅₆H₉₂O₂₅      | 8.85| 1163.5849 [M-H]⁻ | 1163.5825 [M-H]⁻ | −2.06| 1077.5806 [M-H-Mal]− 945.5403 [M-H-Mal-Xyl]− 783.4883 [M-H-Mal-Xyl-Glc]− 621.4357 [M-H-Mal-Xyl-2Glc]− 459.3861 [M-H-Mal-Xyl-3Glc]− | PPD          | [28] |
| 15  | Zingibroside R₁        | C₄₂H₆₆O₁₄      | 9.25| 793.4374 [M-H]⁻ | 793.4337 [M-H]⁻ | −4.66| 793.4332 [M-H]⁻ 631.3823 [M-H-Glc]⁻ 569.3790 [M-H-Glc-CO₂-H₂O]⁻ 455.3538 [M-H-Glc-GlcUA]⁻ | OLE          | [28] |
| 16  | Ginsenoside Rd         | C₄₈H₈₂O₁₈      | 9.52| 991.5478 [M + HCOO]⁻ | 991.5460 [M + HCOO]⁻ | −1.82| 945.5386 [M-H]⁻ 783.4875 [M-H-Glc]⁻ 621.4283 [M-H-2Glc]⁻ 459.3574 [M-H-3Glc]⁻ | PPD          | [28] |
| 17  | Quinquefolium III      | C₅₀H₇₆O₁₉      | 10.04| 1033.5583 [M + HCOO]⁻ | 1033.5500 [M + HCOO]⁻ | −8.03| 945.5333 [M-H-Ac]⁻ 783.4835 [M-H-Ac-Glc]⁻ 621.4166 [M-H-Ac-2Glc]⁻ 459.3737 [M-H-Ac-3Glc]⁻ 161.0451 [Glc-H]⁻ | PPD          | [28] |
| 18  | Malonyl-ginsenoside Rd | C₅₀H₇₆O₁₉      | 10.41| 1033.5583 [M + HCOO]⁻ | 1033.5500 [M + HCOO]⁻ | −8.03| 987.5585 [M-H]⁻ 945.5641 [M-H-Ac]⁻ 783.4999 [M-H-Ac-Glc]⁻ 621.4255 [M-H-Ac-2Glc]⁻ | PPD          | [28] |
| 19  | Quinquefolium I        | C₅₂H₈₆O₁₉      | 10.70| 1059.5740 [M + HCOO]⁻ | 1059.5701 [M + HCOO]⁻ | −3.68| 945.5345 [M-H-C₄H₈O]⁻ 783.4911 [M-H-C₄H₈O-Glc]⁻ 621.4280 [M-H-C₄H₈O-2Glc]⁻ 161.0440 [Glc-H]⁻ | PPD          | [28, 29] |
| No. | Identity | Rt | Formula | Identity | Rt | Formula |
|-----|----------|----|---------|----------|----|---------|
| 20  | Ginsenoside Rg3/ginsenoside Rg5/ginsenoside Rk1/ginsenoside Rg4 | 10.91 | C_{42}H_{70}O_{12} | [M+HCOO]^- & 811.4844 | 10.95 | C_{42}H_{72}O_{13} | [M+HCOO]^- & 829.4949 | 11.02 | C_{42}H_{66}O_{14} | [M-H]^- & 793.4374 | 11.62 | C_{42}H_{72}O_{13} | [M+HCOO]^- & 829.4949 |
|     |          |    |         |          |    |         |          |          |          |          |          |          |

Main MS/MS fragments detected: 765.4565 [M-H]^-; 619.4848 [M-H-Rha]^-; 693.2623 [M-H-Glc]^-; 457.2162 [M-H-Rha-Glc]^-; 161.9476 [Glc-H]^-; 783.4891 [M-H-Glc]^-; 621.4318 [M-H-Glc]^-; 459.3699 [M-H-2Glc]^-; 631.3883 [M-H-Glc-CO_2-H_2O]^-; 569.3820 [M-H-Glc-GlcUA]^-; 799.4536 [M-H]^-; 793.4574 [M-H]^-; 793.4336 [M-H-Glc]^-; 609.3820 [M-H-Glc-CO_2-H_2O]^-; 455.3252 [M-H-Glc-GlcUA]^-; 829.4918 [M+HCOO]^-; 829.4918 [M+HCOO]^-; 637.6862 [M-H-Rha]^-; 783.4839 [M-H]^-; 783.4839 [M-H]^-.

Saponin type: PPD, PP T, OLE.
| No. | Identity | Formula | Rt  | Theoretical value | Actual value | Ppm  | Main MS/MS fragments detected | Saponin type | Ref. |
|-----|----------|---------|-----|-------------------|--------------|------|-------------------------------|-------------|------|
| 1   | Notoginsenoside N/M/R3/R4/20-glucoside-Rf | C_{48}H_{82}O_{19} | 6.08 | 1007.5427 [M + HCOO]^{-} | 1007.5358 [M + HCOO]^{-} | -6.85 | 799.4779 [M-H-Glc]^{-}, 637.4254 [M-H-2Glc]^{-} | PPT | [31] |
| 2   | Ginsenoside Re1/Re2/Re3 | C_{48}H_{82}O_{19} | 6.10 | 1007.5427 [M + HCOO]^{-} | 1007.5357 [M + HCOO]^{-} | -6.95 | 799.4781 [M-H-Glc]^{-}, 637.4270 [M-H-2Glc]^{-} | PPT | [31, 32] |
| 3   | Vina-ginsenoside R7 | C_{53}H_{90}O_{22} | 6.13 | 1123.5900 [M + HCOO]^{-} | 1123.5768 [M + HCOO]^{-} | -1.75 | 945.5393 [M-H-Glc]^{-}, 637.4254 [M-H-2Glc]^{-} | PPD | [31, 32] |
| 4   | Ginsenoside Rb3/ginsenoside Rc | C_{53}H_{90}O_{22} | 6.14 | 1123.5900 [M + HCOO]^{-} | 1123.5845 [M + HCOO]^{-} | -4.90 | 783.4982 [M-H-Xyl/Ara-Glc]^{-}, 765.4770 [M-H-Xyl/Ara-Glc-H_2O]^{-}, 621.3179 [M-H-Xyl/Ara-2Glc]^{-} | PPD | [31] |
| 5   | Notoginsenoside R1/ginsenoside Re4/quinquenoside L17 | C_{47}H_{80}O_{18} | 6.23 | 977.5321 [M + HCOO]^{-} | 977.5490 [M + HCOO]^{-} | 17.29 | 931.5217 [M-H]^{-}, 799.4762 [M-H-Glc]^{-}, 475.3714 [M-H-2Glc]^{-} | PPT | [31] |
| 6   | Yesanchinoside B | C_{48}H_{82}O_{20} | 6.23 | 977.5321 [M-H]^{-} | 977.5203 [M-H]^{-} | -12.07 | 931.5415 [M-H-Glc]^{-}, 653.3294 [M-H-2Glc]^{-} | OCO | [31, 32] |
| 7   | Ginsenoside Re | C_{48}H_{82}O_{18} | 6.48 | 991.5478 [M + HCOO]^{-} | 991.5399 [M + HCOO]^{-} | -7.97 | 783.4836 [M-H-Glc]^{-}, 637.4283 [M-H-Rha-Glc]^{-}, 475.3784 [M-H-2Glc-Rha]^{-} | PPT | [31, 32] |
| 8   | Notoginsenoside K | C_{48}H_{82}O_{18} | 6.50 | 991.5478 [M + HCOO]^{-} | 991.5387 [M + HCOO]^{-} | -9.18 | 783.4836 [M-H-Glc]^{-}, 637.4272 [M-H-2Glc]^{-} | PPD | [31, 32] |
| 9   | Ginsenoside Rg1 | C_{42}H_{72}O_{14} | 6.53 | 845.4899 [M + HCOO]^{-} | 845.4824 [M + HCOO]^{-} | -8.87 | 799.4767 [M-H]^{-}, 637.4272 [M-H-Glc]^{-}, 491.3711 [M-H-2Glc]^{-} | PPT | [31, 32] |
| 10  | Majonoside R1 | C_{42}H_{72}O_{14} | 7.77 | 861.4848 [M + HCOO]^{-} | 861.4969 [M + HCOO]^{-} | 14.05 | 815.4773 [M-H]^{-}, 653.4257 [M-H-2Glc]^{-}, 491.3711 [M-H-2Glc]^{-} | OCO | [31, 32] |
| 11  | Ginsenoside Rf | C_{42}H_{72}O_{14} | 8.15 | 845.4899 [M + HCOO]^{-} | 845.4889 [M + HCOO]^{-} | -1.18 | 799.4830 [M-H]^{-}, 637.4339 [M-H-Glc]^{-}, 491.3711 [M-H-2Glc]^{-} | PPT | [31, 32] |
| 12  | Tuberoside A | C_{48}H_{76}O_{19} | 8.23 | 955.4903 [M-H]^{-} | 955.4896 [M-H]^{-} | -0.73 | 793.4327 [M-H-Glc]^{-}, 569.3922 [M-H-CO_2-H_2O-2Glc]^{-} | OLE | [31, 32] |
| 13  | Pseudoginsenoside P11 | C_{42}H_{72}O_{14} | 8.24 | 845.4899 [M + HCOO]^{-} | 845.4893 [M + HCOO]^{-} | -0.71 | 799.4825 [M-H]^{-}, 653.4245 [M-H-Rha]^{-} | OCO | [32] |
| No. | Identity | Formula     | Rt  | Theoretical value | Actual value | Ppm     | Main MS/MS fragments detected                                      | Saponin type | Ref. |
|-----|----------|-------------|-----|-------------------|--------------|---------|-------------------------------------------------------------------|--------------|------|
| 14  | Ginsenoside Ro | C_{48}H_{76}O_{19} | 8.66 | 955.4903 [M-H]^- | 955.4905 [M-H]^- | 0.21    | 793.4402 [M-H-Glc]- 613.3748 [M-H-H_2O-Glc]- 569.3944 [M-H-2Glc-H_2O-CO_2]- 455.3560 [M-H-2Glc-GlcUA]- | OLE          | [31, 32] |
| 15  | Hemsgiganoside B | C_{48}H_{76}O_{19} | 8.75 | 955.4903 [M-H]^- | 955.4906 [M-H]^- | 0.31    | 793.4359 [M-H-Glc]- 569.3929 [M-H-2Glc-H_2O-CO_2]- | OLE          | [31, 32] |
| 16  | Stipuleanoside R / chikusetsusaponin Ib | C_{47}H_{74}O_{18} | 8.92 | 925.4797 [M-H]^- | 925.4800 [M-H]^- | 0.32    | 763.3628 [M-H-Glc]- 569.3837 [M-H-Glc-Ara-H_2O-CO_2]- | OLE          | [31, 32] |
| 17  | Pseudoginsenoside RT_{1} | C_{47}H_{74}O_{18} | 8.94 | 925.4797 [M-H]^- | 925.4786 [M-H]^- | -1.19   | 613.3701 [M-H-Glc-Xyl-H_2O]- 569.3853 [M-H-Glc-Ara-H_2O-CO_2]- | OLE          | [31, 32] |
| 18  | Chikusetsusaponin IV | C_{47}H_{74}O_{18} | 9.04 | 925.4797 [M-H]^- | 925.4793 [M-H]^- | -0.43   | 793.4355 [M-H]- 631.3818 [M-H-Glc]- 569.3826 [M-H-Glc-CO_2-H_2O]- 455.3538 [M-H-Glc-GlcUA]- | OLE          | [31, 32] |
| 19  | Zingibroside R_{1} | C_{42}H_{66}O_{14} | 9.28 | 793.4374 [M-H]^- | 793.4355 [M-H]^- | -2.39   | 495.5435 [M-H]- 783.4866 [M-H-Glc]- 621.4390 [M-H-2Glc]- 459.3862 [M-H-3Glc]- 161.0467 [Glucose-H]- | OLE          | [31, 32] |
| 20  | Ginsenoside Rd | C_{48}H_{82}O_{18} | 9.65 | 991.5478 [M+HCOO]^- | 991.5479 [M+HCOO]^- | 0.10    | 945.5435 [M-H]- 783.4866 [M-H-Glc]- 621.4390 [M-H-2Glc]- 459.3862 [M-H-3Glc]- 161.0467 [Glucose-H]- | PPD         | [31, 32] |
| 21  | Ginsenoside R_{g_{3}}/ginsenoside F_{2} | C_{42}H_{72}O_{13} | 10.95 | 829.4949 [M+HCOO]^- | 829.4946 [M+HCOO]^- | -0.36   | 783.4850 [M-H]- 621.4301 [M-H-Glc]- 459.3812 [M-H-2Glc]- | PPD         | [31, 32] |
| 22  | Chikusetsusaponin IVa | C_{42}H_{66}O_{14} | 11.03 | 793.4374 [M-H]^- | 793.4355 [M-H]^- | -2.39   | 793.4348 [M-H]- 631.3970 [M-H-Glc]- 569.3805 [M-H-Glc-CO_2-H_2O]- | OLE          | [31, 32] |
| 23  | Cynarasaponin C | C_{42}H_{66}O_{14} | 11.05 | 793.4374 [M-H]^- | 793.4331 [M-H]^- | -5.42   | 793.4326 [M-H]- 631.3818 [M-H-Glc]- 569.3826 [M-H-Glc-CO_2-H_2O]- | OLE          | [31, 32] |
| No. | Identity                   | Formula      | Rt  | Theoretical value | Actual value | Ppm  | Main MS/MS fragments detected | Saponin type | Ref.  |
|-----|----------------------------|--------------|-----|-------------------|--------------|------|-------------------------------|--------------|-------|
| 24  | Ginsenoside Rg5            | C_{42}H_{70}O_{12} | 11.61 | 811.4844 [M + HCOO]− | 811.4778 [M + HCOO]− | −8.13 | 765.4724 [M-H]− 603.4313 [M-H-Glc]− | PPD          | [31, 32] |
| 25  | Pseudoginsenoside Rp1      | C_{40}H_{64}O_{13} | 11.77 | 763.4269 [M-H]−    | 763.4222 [M-H]−    | −6.16 | 613.3658 [M-H-Xyl-H_{2}O]− 569.3800 [M-H-Xyl-H_{2}O-CO_{2}]− | OLE          | [31, 32] |
| 26  | Ginsenoside Rk1            | C_{42}H_{70}O_{12} | 11.81 | 811.4844 [M + HCOO]− | 811.4800 [M + HCOO]− | −5.42 | 765.4821 [M-H]− 603.4160 [M-H-Glc]− 161.0470 [Glc-H]− | PPD          | [31, 32] |
| 27  | Oleanolic acid-28-O-β-D-glucopyranose(PJS-1) | C_{36}H_{58}O_{8} | 12.62 | 663.4108 [M + HCOO]− | 663.4067 [M + HCOO]− | −6.18 | 617.4132 [M-H]− 455.3546 [M-H-Glc]− | OLE          | [31, 32] |

Ac: acetyl; Mal: malonyl; Glc: glucose residue; Ara: arabinose residue; Rha: rhamnose residue; Xyl: xylose residue; GkUA: glucuronic acid; PPD: protopanaxadiol type; PPT: protopanaxatriol type; OLE: oleanane type; OCO: ocoillol type.
3.1.2. PPT-Type Saponins. Thus far, PPT-type saponins, such as ginsenoside Re and ginsenoside Rg1, have been found in ginseng plants. Notably, PQ did not contain ginsenoside Rf. The CFs of these saponins occurred at m/z 637 [C_{36}H_{51}O_{13}] and m/z 475 [C_{28}H_{35}O_{8}] and include GlcUA (176 Da), Rha (146 Da), CH_{3}COOH (60 Da), H_{2}O (18 Da), CO_{2} (44 Da), Glc (162 Da), Xyl (132 Da), Mal (86 Da), and Ac (42 Da). Therefore, the PPT saponins could be preliminarily identified by these product ions. This was further supported by the different NLs, which were caused by the breaking of different substituents at the C-6 and C-20 positions.

Compound 4 (Table 2) had a retention time of 6.48 min and a molecular formula of C_{48}H_{72}O_{18}. In negative ion mode, this compound had a molecular ion peak at m/z 991.5457 [M+HCOO]^− and product ion peaks at m/z 945.5381 [M-H]^−, 799.4808 [M-H-Rha]^−, 783.4891 [M-H-Glc]^−, 637.4294 [M-H-Glc-Rha]^−, and 475.3801 [M-H-2Glc-Rha]^−. Based on the CFs at m/z 637.4294 and 475.3801, the compound was identified as a PPT-type saponin. Based on the molecular ion, fragments, and reference information, compound 4 was identified as ginsenoside Re [24–27, 30]. The cleavage pathway was as follows: the molecular ion at m/z 945.5381 [M-H]^− lost one glucose residue (162 Da) at C-20 to generate the product ion at m/z 783.4891 [M-H-Glc]^−, while the molecular ion at m/z 945.5381 [M-H]^− lost one rhamnose residue (146 Da) at C-6 to generate the product ion at m/z 799.4808 [M-H-Rha]^−. When the molecular ions simultaneously lost a glucose and rhamnose residue (162 Da + 146 Da), a product ion peak was produced at m/z 637.4294 [M-H-Glc-Rha]^−. The fragment ion at m/z 475.3801 [M-H-2Glc-Rha]^− was produced when the product ion at m/z 783.4891 lost a glucose and rhamnose residue (162 Da + 146 Da) simultaneously. The fragmentation pathway of ginsenoside Re in negative-ion mode is shown in Figures 6 and 7.

Compound 11 (Table 4) had a retention time of 8.15 min and molecular formula of C_{48}H_{72}O_{14}. In negative ion mode, compound 11 produced a precursor ion at m/z 845.4889 [M+HCOO]^− and three fragment ion peaks at m/z 799.4830, 637.4339, and 475.3769. Based on the product ion peaks at m/z 637.4339 and 475.3769, compound 11 was preliminarily considered to be a PPT-type saponin. When this observation was further combined with the retention time, along with the molecular ion and fragment information, compound 11 (Table 4) was identified as ginsenoside Rf [31, 32]. The cleavage pathway of ginsenoside Rf was as follows: the product ion peak at m/z 637.4339 was generated by the loss of one glucose residue (162 Da) from the molecular ion at m/z 799.4830. The fragment ion peak at m/z 475.3769 was generated when the product ion at m/z 637.4339 lost one glucose residue (162 Da). The fragmentation information and process for ginsenoside Rf are shown in Figures 8 and 9.

3.2. Analysis of OLE-Type Saponins by MS. Pentacyclic triterpenoid saponins of the OLE-type are characteristic components of ginseng. There are differences in the species and availability of different ginseng plants [36]. The CFs of the OLE-type saponins occurred at m/z 569 [C_{35}H_{54}O_{6}] and 455 [C_{30}H_{47}O_{3}], and the common neutral losses corresponded to GlcUA (176 Da), Ara (132 Da), CO_{2} (44 Da), H_{2}O (18 Da), Glc (162 Da), and Xyl (132 Da). Therefore, the OLE-type saponins could be quickly identified and described using the CF information and the retention times of the fractured C-3 and C-28 ester bases.

Compound 13 (Table 2) had a retention time of 8.64 min and a molecular formula of C_{48}H_{76}O_{19}. In negative ion mode, compound 13 was detected by the molecular ion peak at m/z 955.4875 [M-H]^− and product ion peaks at m/z 793.4306 [M-H-Glc]^−, 569.3799 [M-H-CO_{2}-H_{2}O-2Glc]^−,
Based on the CFs at m/z 569.3799 and 455.3496, the compound was preliminarily determined to be an OLE-type saponin. Combining the mass spectrometry and the remaining fragment ion information (Table 2), compound 13 was identified as ginsenoside Ro [27–29]. ©K_he fragmentation of ginsenoside Ro occurred as follows: when the molecular ion at m/z 955.4875 [M-H]⁻ lost one molecular glucose residue (162 Da), fragment ion peaks were generated at m/z 793.4306, when the molecular ions lost one CO₂ molecule (44 Da), one H₂O (18 Da), and two molecular glucose residues (162 Da + 162 Da), the product ion peak at m/z 569.3799 was produced. When the ions at m/
Ginsenoside Re in Table 2
Rt=6.48 min

Figure 6: Secondary mass spectrogram of ginsenoside Re.

Figure 7: The fragmentation pathway of ginsenoside Re.
3.3. Analysis of OCO-Type Saponins by Mass Spectrometry.

A furan ring was introduced into the C-20 and C-24 positions of the dammarane skeleton through a connection with oxygen, which resulted in the formation of an OCO-type saponin [15]. Studies have shown that ginseng does not contain such saponins, and as a characteristic feature, the types and contents of OCO-type saponins in PQ and PJ are also different. The results showed that the ions at m/z 653 [C₃₆H₆₁O₉]⁻ and m/z 491 [C₂₉H₄₉O₅]⁻ were CFs associated with OCO-type saponins. Ac (42 Da), Rha (146 Da), and Glc (162 Da) were the common NL fragments. From this information, the general cleavage behavior of OCO-type saponins from PQ and PJ could be identified and proposed.

Figure 9: The fragmentation pathway of ginsenoside Rf.

Compound 10 in Table 3, with a retention time of 8.25 min and a molecular formula of C₄₂H₇₂O₁₄, generated molecular ion peaks at m/z 845.4912 [M + HCOO]⁻ and fragment ion peaks at m/z 799.4830, 653.4296, 491.3707, and 145.0475 in negative ion mode. Based on the CF ion peaks at m/z 653.4296 and m/z 491.3707, the compound was identified as an OCO-type saponin. When this observation was combined with the literature data and molecular weight, the compound was identified as pseudoginsenoside F₁₁ [33, 34]. The cleavage pathway is as follows: when the molecular ion at m/z 799.4830 [M - H]⁻ lost one molecular rhamnose residue (146 Da), the product ion at m/z 653.4296 [M - H - Rha]⁻ was produced. Subsequently, the fragment ion peak at m/z 491.3707 [M - H - Rha - Glc]⁻ was produced by the loss of one molecular rhamnose residue and one molecular glucose residue (146 Da + 162 Da). In negative ion mode, the product ion peak at m/z 145.0475 [Rha - H]⁻ was examined for free rhamnose residues. The cleavage pathway of pseudoginsenoside F₁₁ is shown in Figures 12 and 13.
3.4. Analysis of Differences in Saponins. From identification of the chemical components, the characteristic absence of ginsenoside Rf in PQ was noted; on this premise, PQ can be differentiated. OCO saponins were not found in PG, which could be useful in identifying PG and PJ. Based on the information in Tables 2–4, the distribution of saponins among PG, PQ, and PJ are shown in the Venn diagram in Figure 14(a). The results show that ginsenoside Rg1, zingiberisde R1, ginsenoside Re, ginsenoside Ro, and ginsenoside Rd were the common components of PG, PQ, and PJ. Based on this information, the ginsenoside content in PG, PQ, and PJ was preliminarily analyzed. The main ginsenosides (Rg1, Re, Rb1, Rc, and Rd) generally account for more than 70% of the total content of ginsenosides in PQ [37]. The common components, the characteristic components of the three traditional Chinese medicines, along with ginsenoside Rg1, zingiberisde R1, ginsenoside Re, ginsenoside Rd, ginsenoside Rf, and OCO-type saponins (taking pseudoginsenoside F11 as an example), were selected for comparison [38, 39]. The contents of these six components in the nine batches of medicinal materials were analyzed (Figure 14(b)). These results show that the common chemical components in PG, PQ, and PJ were present in significantly different contents and that characteristic components only existed in specific medicinal materials. Considering that the differences in the saponins in PG, PQ, and PJ were preliminarily analyzed,
Figure 12: Secondary mass spectrogram of pseudoginsenoside F11.

Figure 13: The fragmentation pathway of pseudoginsenoside F11.

Figure 14: (a) Venn diagram of the distribution of saponins among PG, PQ, and PJ. (b) Contents of six components in PG, PQ, and PJ.
future studies on the three kinds of medicinal materials from the genus *Panax* are needed. Nonetheless, the results have provided a foundation for the quantitative study of PG, PQ, and PJ and for screening the pharmacological components.

4. Conclusions
In this study, fragment ions associated with the chemical constituents in PG, PQ, and PJ were studied. Additionally, mass spectra fragmentation rules for the DAM-type (including PPD- and PPT-type), OLE-type, and OCO-type saponins were presented. The chemical constituents and different saponins from PG, PQ, and PJ were analyzed using UPLC-Q-TOF/MS. With the aid of the fragmentation rules for various components, 23 chemical components were identified in PG, 27 chemical components were identified in PQ, and 27 chemical components were identified in PJ. Among them, PG did not contain OCO-type saponins; thus, it was distinguishable from PQ and PJ. Additionally, ginsenoside Rf, a characteristic component, was not found in PQ, which provides a basis for differentiating between PQ and PJ. Through rapid classification and identification of the components, we differentiated among three types of traditional Chinese medicinal herbs from the genus *Panax*. This study provides a foundation for pharmacodynamic research and the development of MS in the identification of traditional Chinese medicine. Thus, this study presents a guaranteed approach for the determination of chemical components, along with the development and application of ginseng in traditional Chinese medicine.

Data Availability
No data were used to support this study.

Conflicts of Interest
The authors declare that there are no conflicts of interest with respect to the research, authorship, and/or publication of this article.

Authors’ Contributions
Liu Jinbiao, Zhang Xinyue, and Yang Shenshen contributed equally to this work.

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