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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 Araliaceae 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 ocotillol- (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 Araliaceae 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

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 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 Rb_1, Rb_2, Rb_3, Rc, Rd, Rg_3, and Rh_2, and protopanaxatriol-(PPT-) type saponins, for which the aglycone is 20(s)-PPT, including ginsenoside Re, Rf, Rg_1, and Rh_1. 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 ocotillol-(OCO-) type saponins, such as pseudoginsenoside F_{11} and pseudoginsenoside RT_4 [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.

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 Watsons 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 separation was carried out by gradient elution, where the 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

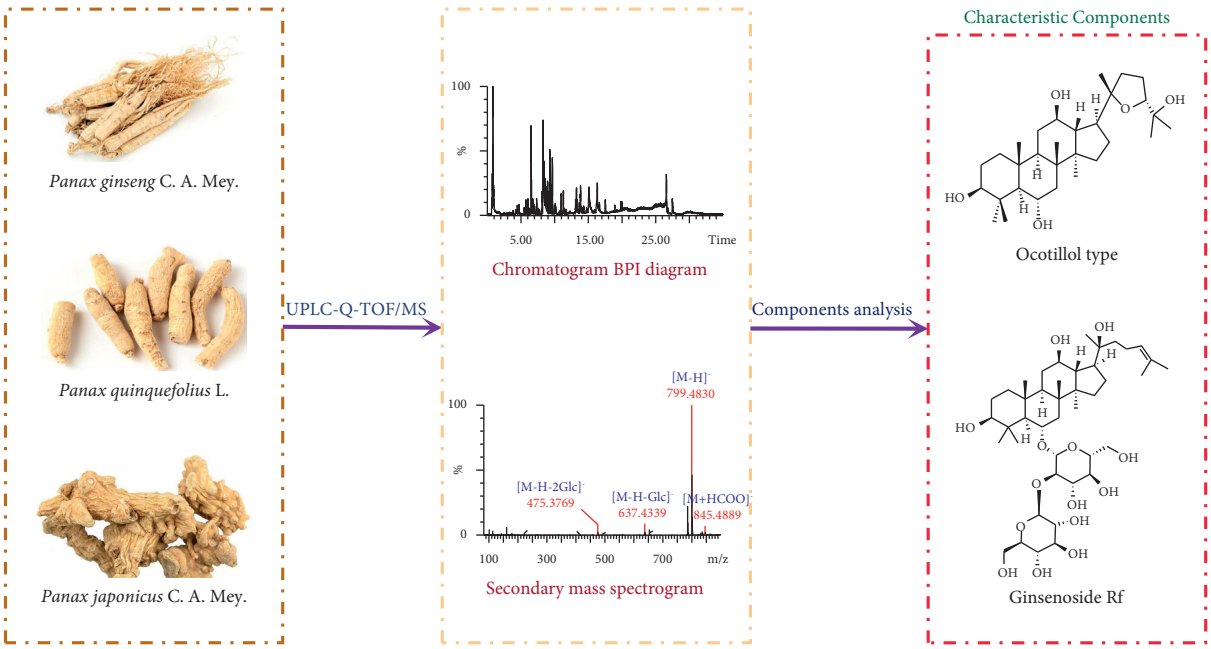


Figure 1: The rapid identification strategy of three traditional Chinese medicines in the genus *Panax*.

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.

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. These lost free-radicals or molecules are known as NLs, which aid the screening and identification of substances [17–22]. Therefore, 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, Rb_2, Rc, and Rg_3, 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 $[C_{36}H_{61}O_8]^-$ and *m/z* 459 $[C_{30}H_{51}O_3]^-$. At the same time, the product ions observed in the MS^2 profiles

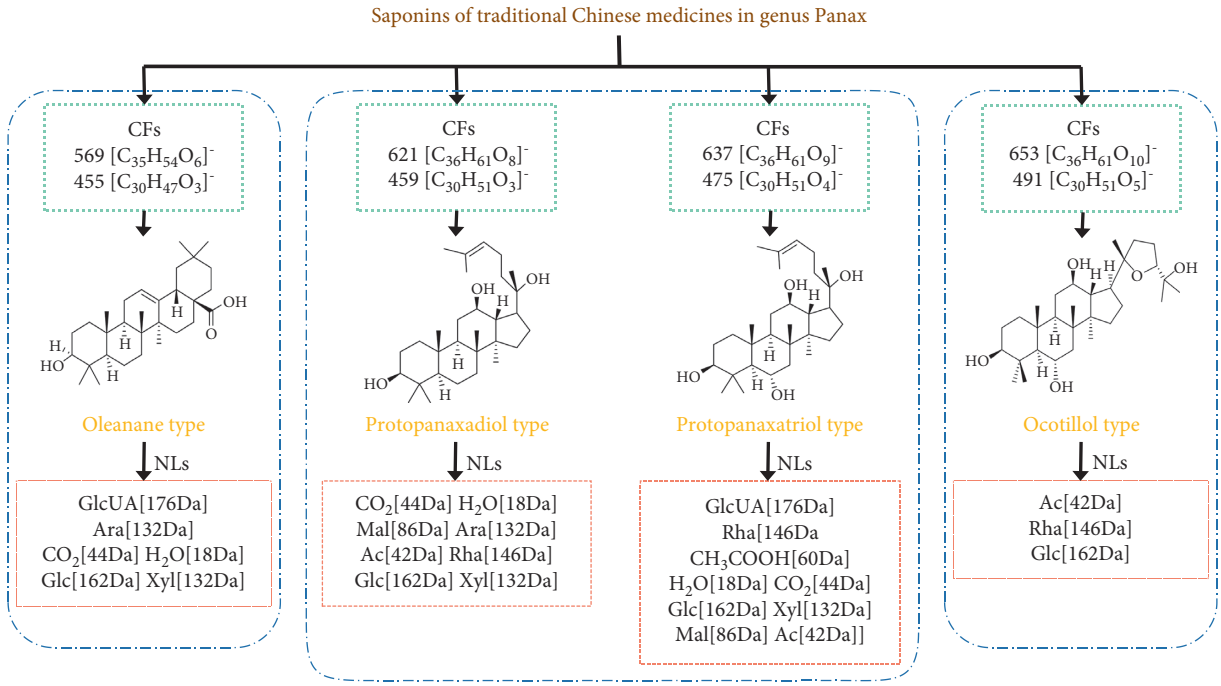
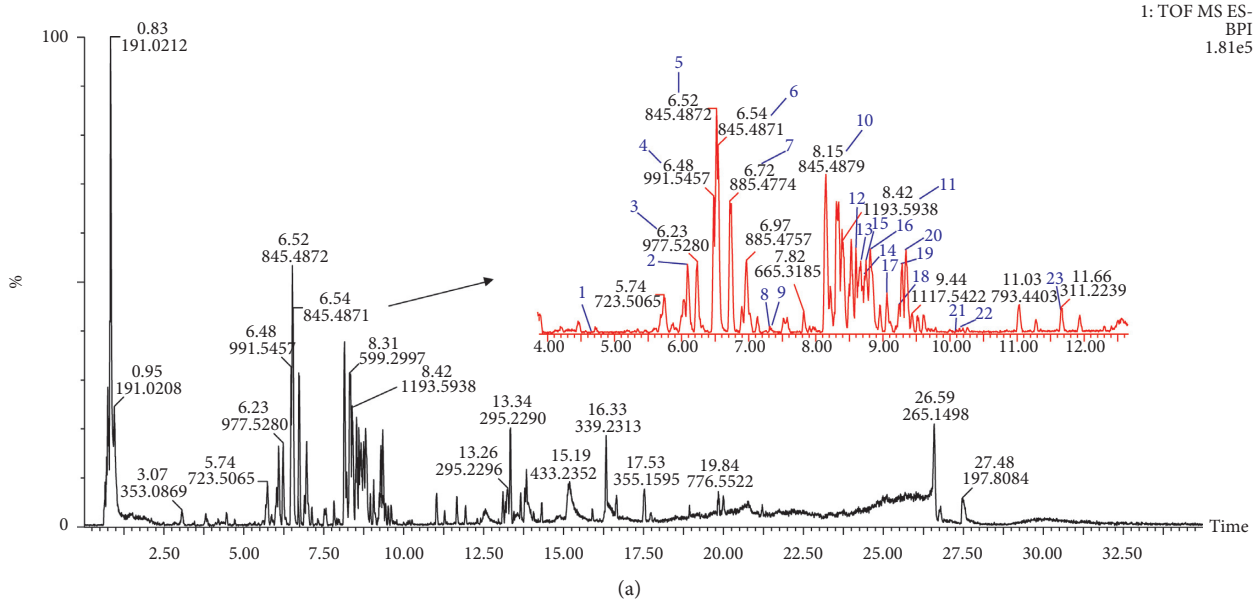


Figure 2: Characteristic fragments and neutral losses of different types of saponins in genus *Panax*. Ac: acetyl; Mal: malonyl; Glc: glucose residue; Ara: arabinose residue; Rha: rhamnose residue; Xyl: xylose residue; GlcUA: glucuronic acid.



(a)

Figure 3: Continued.

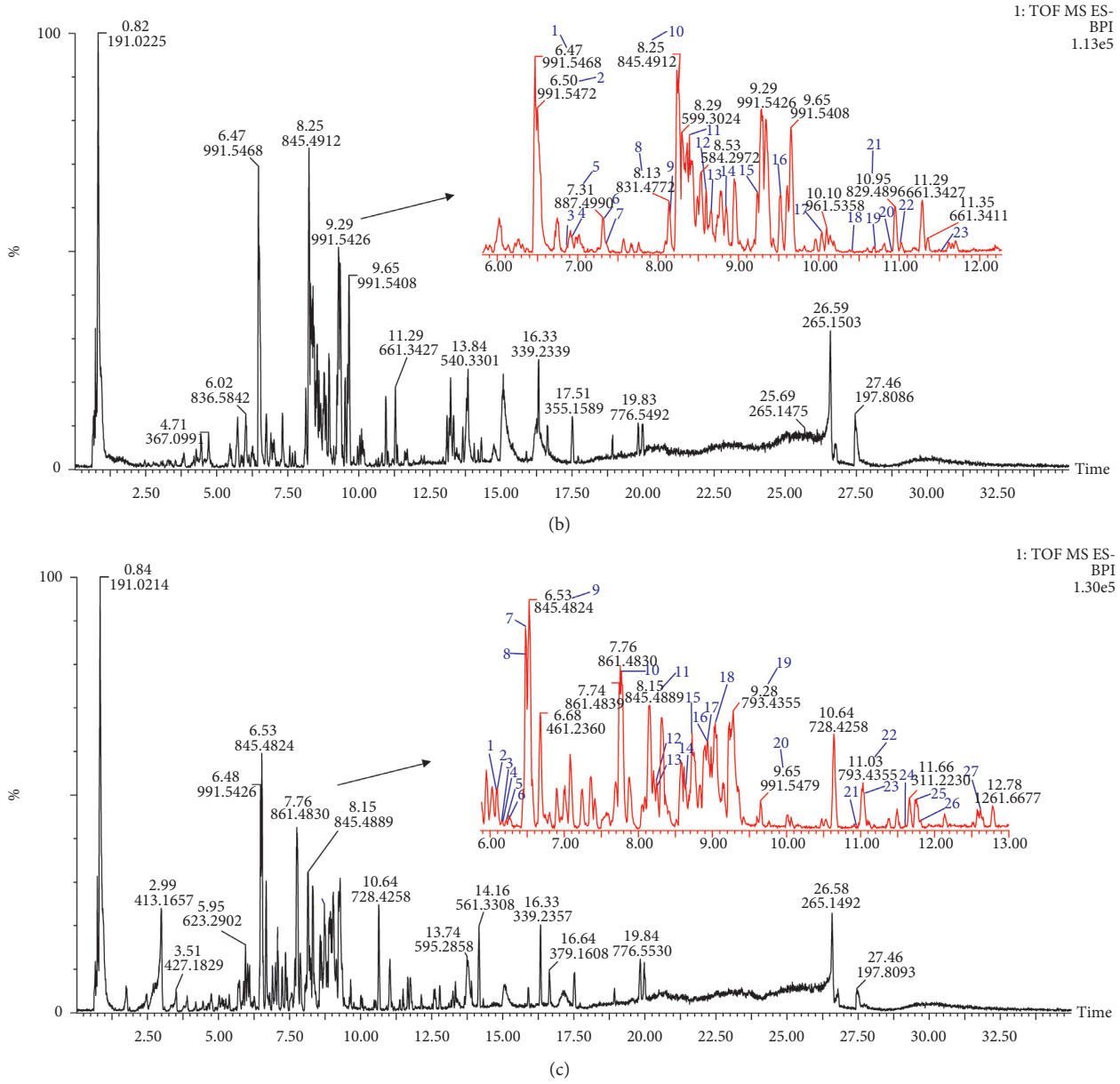


Figure 3: Chromatogram BPI diagram of PG, PJ, and PQ under negative ions (a) PG, (b) PQ, and (c) PJ.

of the PPD-type saponins generally resulted in the following NLs: CO_2 (44 Da), H_2O (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 $C_{57}H_{94}O_{26}$. In the negative ion mode, compound 11 produced a precursor ion at *m/z* 1193.5938 $[M\text{-}H]^-$ 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 CO_2 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, product ions with *m/z* 783.4828 $[M\text{-}H\text{-}Mal\text{-}2Glc]^-$, *m/z* 621.4205 $[M\text{-}H\text{-}Mal\text{-}3Glc]^-$, and *m/z* 459.3793$[M\text{-}H\text{-}Mal\text{-}4Glc]^-$ were formed. When the product ion with a peak at *m/z* 783.4828 lost one H_2O molecule (18 Da), the product ion at *m/z* 765.4836 $[M\text{-}H\text{-}Mal\text{-}2Glc\text{-}H_2O]^-$ was formed. Therefore, compound 11 (Table 2) was identified as malonyl-ginsenoside Rb_1 from its molecular ion and secondary mass spectral fracture pattern [24, 30]. The cleavage pathway of malonyl-ginsenoside Rb_1 in negative ion mode is shown in Figures 4 and 5.

Table 2: Cracking information of chemical components in PG under negative ion mode.

No.	Identity	Formula	Rt	Theoretical value	Actual value	Ppm	Main MS/MS fragments detected	Saponin type	Ref.
1	Ginsenoside Re_5	$C_{42}H_{72}O_{15}$	4.65	861.4848 $[M+HCOO]^-$	861.4824 $[M+HCOO]^-$	−2.79	415.0735 [M-H-GlcUA-Rha-CH_3COOH-H_2O]$^-$	PPT	[23]
2	20-O-glucosylginsenoside Rf	$C_{48}H_{82}O_{19}$	6.09	1007.5427 $[M+HCOO]^-$	1007.5408 $[M+HCOO]^-$	−1.89	961.5369 $[M-H]^-$ 799.4875 [M-H-Glc]$^-$ 637.4326 [M-H-2Glc]$^-$ 475.3742 [M-H-3Glc]$^-$	PPT	[24]
3	Notoginsenoside R_1	$C_{47}H_{80}O_{18}$	6.23	977.5321 $[M+HCOO]^-$	977.5280 $[M+HCOO]^-$	−4.19	931.5211 $[M-H]^-$ 799.4812 [M-H-Xyl]$^-$ 637.4296 [M-H-Xyl-Glc]$^-$ 475.3794 [M-H-Xyl-2Glc]$^-$	PPT	[24]
4	Ginsenoside Re	$C_{48}H_{82}O_{18}$	6.48	991.5478 $[M+HCOO]^-$	991.5457 $[M+HCOO]^-$	−2.12	945.5381 $[M-H]^-$ 799.4808 [M-H-Rha]$^-$ 783.4891 [M-H-Glc]$^-$ 637.4294 [M-H-Glc-Rha]$^-$ 475.3801 [M-H-2Glc-Rha]$^-$	PPT	[24–27]
5	Ginsenoside Rg_1	$C_{42}H_{72}O_{14}$	6.52	845.4899 $[M+HCOO]^-$	845.4871 $[M+HCOO]^-$	−3.31	799.4819 $[M-H]^-$ 637.4293 [M-H-Glc]$^-$ 475.3802 [M-H-2Glc]$^-$	PPT	[27, 28]
6	Ginsenoside Rg_7	$C_{42}H_{72}O_{14}$	6.54	845.4899 $[M+HCOO]^-$	845.4870 $[M+HCOO]^-$	−3.43	799.4816 $[M-H]^-$ 637.4293 [M-H-Glc]$^-$ 475.3775 [M-H-2Glc]$^-$	PPT	[24, 27]
7	Malonyl-ginsenoside Rg_1	$C_{45}H_{74}O_{17}$	6.72	885.4848 $[M-H]^-$	885.4771 $[M-H]^-$	−8.70	841.4857 [M-H-CO_2]$^-$ 799.4765 [M-H-Mal]$^-$ 781.4659 [M-H-Mal-H_2O]$^-$ 637.4263 [M-H-Mal-Glc]$^-$ 619.4142 [M-H-Ma-H_2O-Glc]$^-$ 475.3755[M-H-Mal-2Glc]$^-$	PPT	[27–29]
8	Yesanchinoside D (6'-O-acetyl-ginsenoside Rg_1)	$C_{44}H_{74}O_{15}$	7.31	887.5004 $[M+HCOO]^-$	887.4955 $[M+HCOO]^-$	−5.52	841.4865 $[M-H]^-$ 781.4639 [M-CH_3COOH]$^-$	PPT	[24]
9	Notoginsenoside R_2	$C_{41}H_{70}O_{13}$	7.35	815.4793 $[M+HCOO]^-$	815.4787 $[M+HCOO]^-$	−0.74	769.4833 $[M-H]^-$ 637.4329 [M-H-Xyl]$^-$ 475.3798 [M-H-Xyl-Glc]$^-$	PPT	[27, 30]
10	Ginsenoside Rf	$C_{42}H_{72}O_{14}$	8.15	845.4899 $[M+HCOO]^-$	845.4879 $[M+HCOO]^-$	−2.37	799.4833 $[M-H]^-$ 781.4752 [M-H-H_2O]$^-$ 637.4337 [M-H-Glc]$^-$ 475.3816 [M-H-2Glc]$^-$	PPT	[24]

Table 2: Continued.

No.	Identity	Formula	Rt	Theoretical value	Actual value	Ppm	Main MS/MS fragments detected	Saponin type	Ref.
11	Malonyl-ginsenoside Rb_1	$C_{57}H_{94}O_{26}$	8.42	1193.5955 $[M-H]^-$	1193.5938 $[M-H]^-$	−1.42	1149.6027 $[M-H-CO_2]^-$ 1107.5938 $[M-H-Mal]^-$ 945.5364 $[M-H-Mal-Glc]^-$ 783.4828 $[M-H-Mal-2Glc]^-$ 765.4836 $[M-H-Mal-2Glc-H_2O]^-$ 621.4205 $[M-H-Mal-3Glc]^-$ 459.3793 $[M-H-Mal-4Glc]^-$	PPD	[24, 27, 30]
12	Malonyl-ginsenoside Rc	$C_{56}H_{92}O_{25}$	8.60	1163.5849 $[M-H]^-$	1163.5798 $[M-H]^-$	−4.38	1119.5902 $[M-H-CO_2]-$ 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	$C_{48}H_{76}O_{19}$	8.64	955.4903 $[M-H]^-$	955.4875 $[M-H]^-$	−2.93	955.4875 $[M-H]^-$ 793.4306 $[M-H-Glc]^-$ 569.3799 $[M-H-CO_2-H_2O-2Glc]^-$ 455.3496 $[M-H-2Glc-GlcUA]^-$	OLE	[24, 27]
14	Ginsenoside Rc	$C_{53}H_{90}O_{22}$	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 Rb_2/ginsenoside Rb_3	$C_{53}H_{90}O_{22}$	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 Rb_2	$C_{56}H_{92}O_{25}$	8.81	1163.5849 $[M-H]^-$	1163.5817 $[M-H]^-$	−2.75	1119.5912 $[M-H-CO_2]-$ 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 Rb_3	$C_{56}H_{92}O_{25}$	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 R_1	$C_{42}H_{66}O_{14}$	9.24	793.4374 $[M-H]^-$	793.4355 $[M-H]^-$	−2.39	631.38266 $[M-H-Glc]^-$ 569.3931 $[M-H-Glc-CO_2-H_2O]^-$ 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 $[M-H-CO_2]^-$ 945.5430 $[M-H-Mal]^-$ 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 Rg_3	$C_{42}H_{72}O_{13}$	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]

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

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]$^-$	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]$^-$	PPD	[28]
3	Malonyl-ginsenoside Rc	$C_{56}H_{92}O_{25}$	6.87	1209.5904 $[M+HCOO]^-$	1209.5897 $[M+HCOO]^-$	−0.58	1119.4801 [M-H-CO2]− 1077.7046 [M-H-Mal]− 1077.7046 [M-H-Mal]− 783.4866 [M-H-Mal-Xyl-Glc]−	PPD	[28]
4	Ginsenoside Rg_1	$C_{42}H_{72}O_{14}$	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]$^-$	PPT	[28]
5	Acetyl-ginsenoside Rg_1	$C_{44}H_{74}O_{15}$	7.31	887.5004 $[M+HCOO]^-$	887.4990 $[M+HCOO]^-$	−1.58	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]$^-$	PPT	[28, 31, 32]
6	Vina-ginsenoside R_1	$C_{44}H_{74}O_{15}$	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]$^-$	OCO	[28]
7	Pseudoginsenoside RC_1	$C_{50}H_{84}O_{19}$	7.35	1033.5583 $[M+HCOO]^-$	1033.5575 $[M+HCOO]^-$	−0.77	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]$^-$	PPD	[28]

Table 3: Continued.

No.	Identity	Formula	Rt	Theoretical value	Actual value	Ppm	Main MS/MS fragments detected	Saponin type	Ref.
8	Pseudoginsenoside RT_2	$C_{41}H_{70}O_{14}$	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 R_2	$C_{41}H_{70}O_{14}$	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 F_{11}	$C_{42}H_{72}O_{14}$	8.25	845.4899 $[M+HCOO]^-$	845.4912 $[M+HCOO]^-$	1.54	799.4871 $[M-H]^-$ 653.4296 [M-H-Rha]$^-$ 491.3707 [M-H-Rha-Glc]$^-$ 145.0475 [Rha-H]$^-$	OCO	[28, 33, 34]
11	Malonyl-ginsenoside Rb_1	$C_{57}H_{94}O_{26}$	8.39	1193.5955 $[M-H]^-$	1193.5978 $[M-H]^-$	1.93	1149.6088 [M-H-CO_2]$^-$ 1107.5940 [M-H-Mal]$^-$ 945.5502 [M-H-Mal-Glc]$^-$ 783.4980 [M-H-Mal-2Glc]$^-$ 621.4172 [M-H-Mal-3Glc]$^-$ 459.3224 [M-H-Mal-4Glc]$^-$	PPD	[28]
12	Malonyl-ginsenoside Rb_2	$C_{56}H_{92}O_{25}$	8.60	1163.5849 $[M-H]^-$	1163.5861 $[M-H]^-$	1.03	1119.4962 [M-H-CO_2]– 1077.5817 [M-H-Mal]– 945.5414 [M-H-Mal-Xyl]– 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	$C_{48}H_{76}O_{19}$	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-CO_2-H_2O-2Glc]$^-$ 455.3648 [M-H-2Glc-GlcUA]$^-$	OLE	[28]

Table 3: Continued.

No.	Identity	Formula	Rt	Theoretical value	Actual value	Ppm	Main MS/MS fragments detected	Saponin type	Ref.
14	Malonyl-ginsenoside Rb_3	$C_{56}H_{92}O_{25}$	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 R_1	$C_{42}H_{66}O_{14}$	9.25	793.4374 $[M-H]^-$	793.4337 $[M-H]^-$	−4.66	793.4332 $[M-H]^-$ 631.3823 $[M-H-Glc]^-$ 569.3790 $[M-H-Glc-CO_2-H_2O]^-$ 455.3538 $[M-H-Glc-GlcUA]^-$	OLE	[28]
16	Ginsenoside Rd	$C_{48}H_{82}O_{18}$	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	$C_{50}H_{84}O_{19}$	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	$C_{50}H_{84}O_{19}$	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	$C_{52}H_{86}O_{19}$	10.70	1059.5740 $[M+HCOO]^-$	1059.5701 $[M+HCOO]^-$	−3.68	945.5345 $[M-H-C_4H_4O]^-$ 783.4911 $[M-H-C_4H_4O-Glc]^-$ 621.4280 $[M-H-C_4H_4O-2Glc]^-$ 161.0440 $[Glc-H]^-$	PPD	[28, 29]

Table 3: Continued.

No.	Identity	Formula	Rt	Theoretical value	Actual value	Ppm	Main MS/MS fragments detected	Saponin type	Ref.
20	Ginsenoside Rg_5/ginsenoside Rg_6/ginsenoside Rk_1/ ginsenoside Rg_4	$C_{42}H_{70}O_{12}$	10.91	811.4844 $[M+HCOO]^-$	811.4832 $[M+HCOO]^-$	−1.48	765.4765 $[M-H]^-$ 619.4148 [M-H-Rha]$^-$ 603.2623 [M-H-Glc]$^-$ 457.2162 [M-H-Rha-Glc]$^-$ 161.0476 [Glc-H]$^-$	PPD	[28]
21	Ginsenoside Rg_2	$C_{42}H_{72}O_{13}$	10.95	829.4949 $[M+HCOO]^-$	829.4896 $[M+HCOO]^-$	−6.39	783.4891 $[M-H]^-$ 621.4318 [M-H-Glc]$^-$ 459.3699 [M-H-2Glc]$^-$	PPT	[28]
22	Chikusetsusaponin IVa	$C_{42}H_{66}O_{14}$	11.02	793.4374 $[M-H]^-$	793.4336 $[M-H]^-$	−4.79	793.4336 [M-H]− 631.3883 [M-H-Glc]− 569.3820 [M-H-Glc-CO_2-H_2O]− 455.3252 [M-H-Glc-GlcUA]−	OLE	[28]
23	Ginsenoside Rg_3/ginsenoside F_2	$C_{42}H_{72}O_{13}$	11.62	829.4949 $[M+HCOO]^-$	829.4918 $[M+HCOO]^-$	−3.74	783.4839 $[M-H]^-$ 637.6862 [M-H-Rha]$^-$	PPD	[28]

Table 4: Cracking information of chemical components in PJ under negative ion mode.

No.	Identity	Formula	Rt	Theoretical value	Actual value	Ppm	Main MS/MS fragments detected	Saponin type	Ref.
1	Notoginsenoside N/M/R_6/R_3/20-glc-ginsenoside-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 Re_1/Re_2/Re_3	$C_{48}H_{82}O_{19}$	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 R_7	$C_{53}H_{90}O_{22}$	6.13	1123.5900 $[M+HCOO]^-$	1123.5768 $[M+HCOO]^-$	−1.75	1077.5750 $[M-H]^-$ 945.5393 $[M-H-Xyl]^-$ 621.2886 $[M-H-Xyl-2Glc]^-$	PPD	[31, 32]
4	Ginsenoside Rb_3/ginsenoside Rc	$C_{53}H_{90}O_{22}$	6.14	1123.5900 $[M+HCOO]^-$	1123.5845 $[M+HCOO]^-$	−4.90	945.5501 $[M-H-Xyl/Ara]^-$ 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 R_1/ginsenoside Re_4/quinquenoside L_{17}	$C_{47}H_{80}O_{18}$	6.23	977.5321 $[M+HCOO]^-$	977.5490 $[M+HCOO]^-$	17.29	931.5217 $[M-H]^-$ 799.4762 $[M-H-Xyl]^-$ 637.4242 $[M-H-Xyl-Glc]^-$ 475.3714 $[M-H-Xyl-2Glc]^-$	PPT	[31]
6	Yesanchinoside B	$C_{48}H_{82}O_{20}$	6.23	977.5321 $[M-H]^-$	977.5203 $[M-H]^-$	−12.07	977.5415 $[M-H]^-$ 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	945.5347 $[M-H]^-$ 799.4775 $[M-H-Rha]^-$ 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	945.5326 $[M-H]^-$ 783.4836 $[M-H-Glc]^-$	PPD	[31, 32]
9	Ginsenoside Rg_1	$C_{42}H_{72}O_{14}$	6.53	845.4899 $[M+HCOO]^-$	845.4824 $[M+HCOO]^-$	−8.87	799.4767 $[M-H]^-$ 637.4272 $[M-H-Glc]^-$ 475.3758 $[M-H-2Glc]^-$	PPT	[31, 32]
10	Majonoside R_1	$C_{42}H_{72}O_{14}$	7.77	861.4848 $[M+HCOO]^-$	861.4969 $[M+HCOO]^-$	14.05	815.4773 $[M-H]^-$ 653.4257 $[M-H-Glc]^-$ 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 $[M-H-Glc]^-$ 475.3769 $[M-H-2Glc]^-$	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 F_{11}	$C_{42}H_{72}O_{14}$	8.24	845.4899 $[M+HCOO]^-$	845.4893 $[M+HCOO]^-$	−0.71	799.4825 $[M-H]^-$ 653.4245 $[M-H-Rha]^-$	OCO	[32]

Table 4: Continued.

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 $[M-H-H_2O-2Glc]^-$ 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_1/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	763.4263 $[M-H-Glc]^-$ 613.3727 $[M-H-Glc-Xyl-H_2O]^-$ 569.3864 $[M-H-Glc-Xyl-H_2O-CO_2]^-$	OLE	[31, 32]
18	Chikusetsusaponin IV	$C_{47}H_{74}O_{18}$	9.04	925.4797 $[M-H]^-$	925.4793 $[M-H]^-$	−0.43	613.3701 $[M-H-Glc-Ara-H_2O]^-$ 569.3853 $[M-H-Glc-Ara-H_2O-CO_2]^-$	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	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]
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 $[Glc-H]^-$	PPD	[31, 32]
21	Ginsenoside Rg_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	793.4328 $[M-H]^-$ 631.3818 $[M-H-Glc]^-$ 569.3826 $[M-H-Glc-CO_2-H_2O]^-$	OLE	[31, 32]

Table 4: Continued.

No.	Identity	Formula	Rt	Theoretical value	Actual value	Ppm	Main MS/MS fragments detected	Saponin type	Ref.
24	Ginsenoside Rg_5	$C_{42}H_{70}O_{12}$	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 Rp_1	$C_{41}H_{64}O_{13}$	11.77	763.4269 $[M-H]^-$	763.4222 $[M-H]^-$	−6.16	613.3658 $[M-H-Xyl-H_2O]-$ 569.3800 $[M-H-Xyl-H_2O-CO_2]-$	OLE	[31, 32]
26	Ginsenoside Rk_1	$C_{42}H_{70}O_{12}$	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; GlcUA: glucuronic acid; PPD: protopanaxadiol type; PPT: protopanaxatriol type; OLE: oleanane type; OCO: ocotillol type.

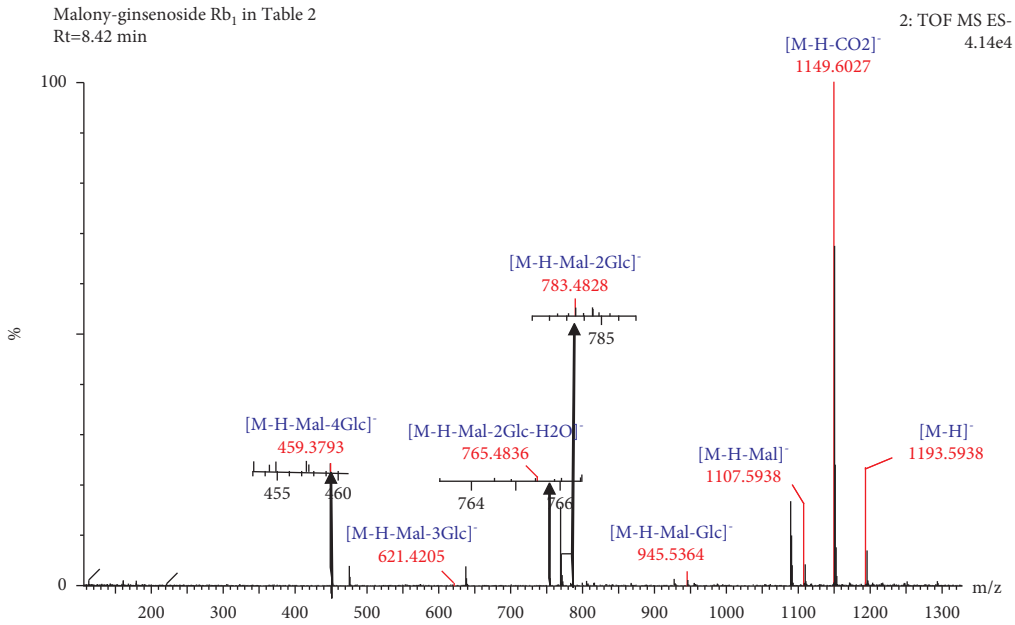


Figure 4: Secondary mass spectrogram of malonyl-ginsenoside Rb_1.

3.1.2. PPT-Type Saponins. Thus far, PPT-type saponins, such as ginsenoside Re and ginsenoside Rg_1, have been found in ginseng plants. Notably, PQ did not contain ginsenoside Rf. The CFs of these saponins occurred at *m/z* 637 $[C_{36}H_{61}O_9]^-$ and *m/z* 475 $[C_{30}H_{51}O_4]^-$ and include GlcUA (176 Da), Rha (146 Da), CH_3COOH (60 Da), H_2O (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 $C_{48}H_{82}O_{18}$. 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 $[M\text{-}H]^-$, 799.4808 $[M\text{-}H\text{-}Rha]^-$, 783.4891 $[M\text{-}H\text{-}Glc]^-$, 637.4294 $[M\text{-}H\text{-}Glc\text{-}Rha]^-$, and 475.3801 $[M\text{-}H\text{-}2Glc\text{-}Rha]^-$. 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 $[M\text{-}H]^-$ lost one glucose residue (162 Da) at C-20 to generate the product ion peak at *m/z* 783.4891 $[M\text{-}H\text{-}Glc]^-$, while the molecular ion at *m/z* 945.5381 $[M\text{-}H]^-$ lost one rhamnose residue (146 Da) at C-6 to generate the product ion at *m/z* 799.4808 $[M\text{-}H\text{-}Rha]^-$. 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 $[M\text{-}H\text{-}Glc\text{-}Rha]^-$. The fragment ion at *m/z* 475.3801 $[M\text{-}H\text{-}2Glc\text{-}Rha]^-$ 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 $C_{42}H_{72}O_{14}$. 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_2O (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 $[M\text{-}H]^-$ and product ion peaks at *m/z* 793.4306 $[M\text{-}H\text{-}Glc]^-$, 569.3799 $[M\text{-}H\text{-}CO_2\text{-}H_2O\text{-}2Glc]^-$,

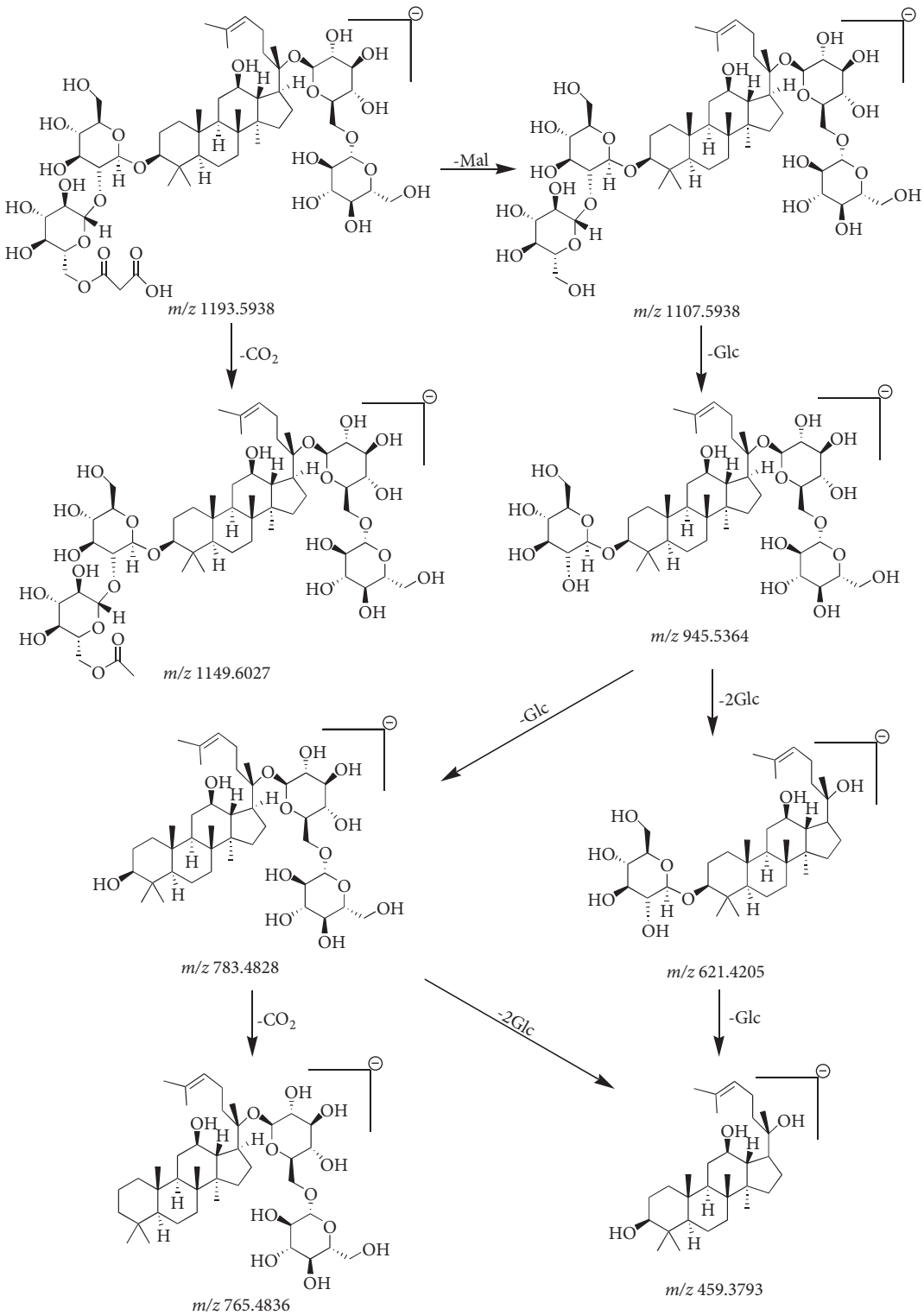


Figure 5: The fragmentation pathway of malonyl-ginsenoside Rb_1.

and 455.3496 [M-H-2Glc-GlcUA]$^-$. 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]. The 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 CO_2 molecule (44 Da), one H_2O (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/*

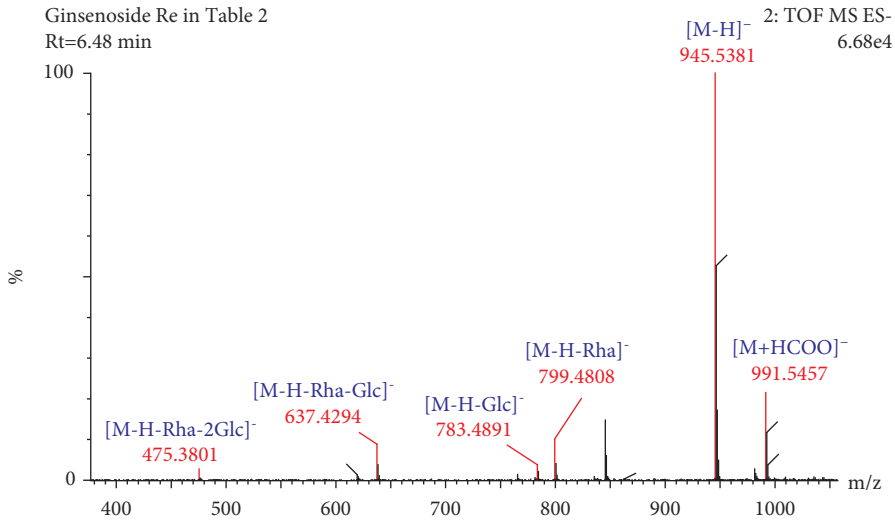


Figure 6: Secondary mass spectrogram of ginsenoside Re.

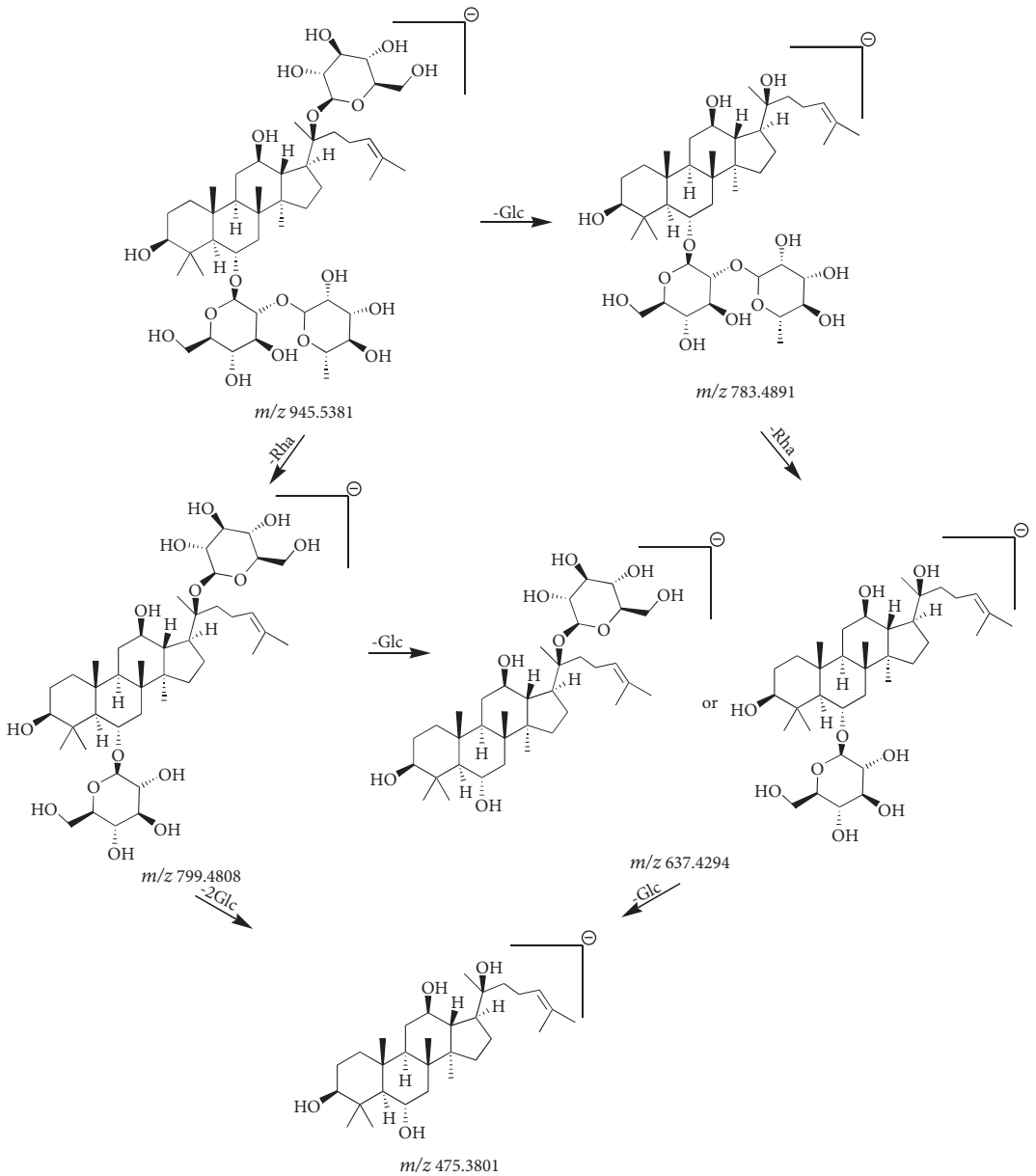


Figure 7: The fragmentation pathway of ginsenoside Re.

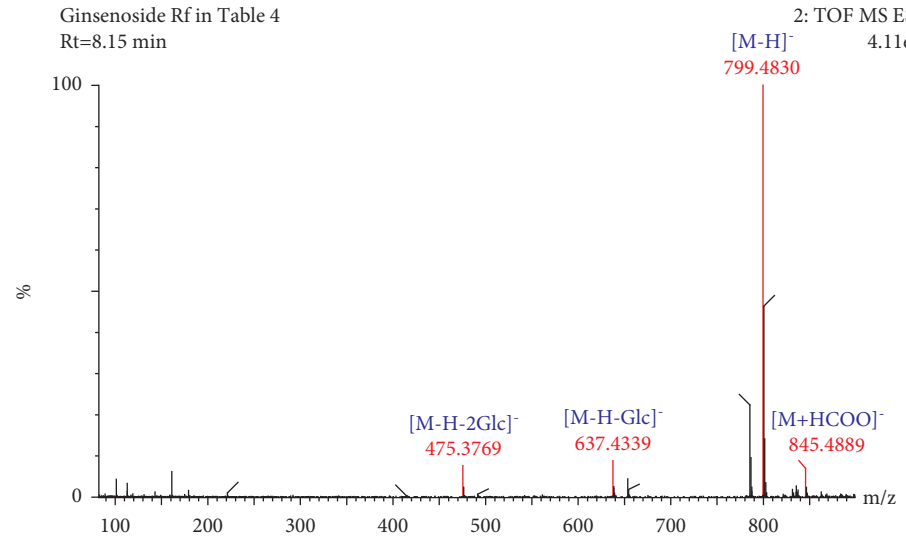


Figure 8: Secondary mass spectrogram of ginsenoside Rf.

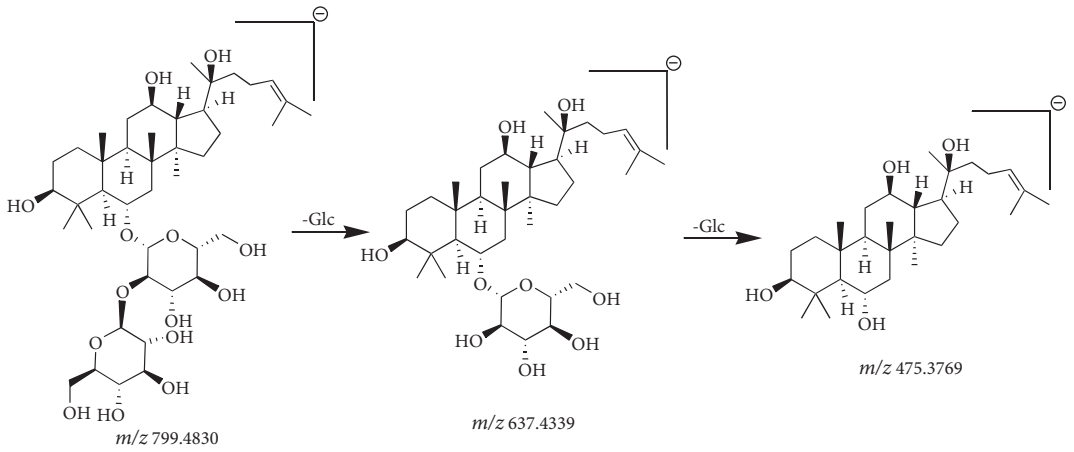


Figure 9: The fragmentation pathway of ginsenoside Rf.

z 955.4875 $[M\text{-}H]^-$ lost two molecular glucose residues (162 Da + 162 Da) and one glucuronic acid molecule (176 Da), a resultant ion peak appeared at *m/z* 455.3496. The fragmentation of ginsenoside Ro is shown in Figures 10 and 11.

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 $[C_{36}H_{61}O_9]^-$ and *m/z* 491 $[C_{30}H_{51}O_5]^-$ 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.

Compound 10 in Table 3, with a retention time of 8.25 min and a molecular formula of $C_{42}H_{72}O_{14}$, generated molecular ion peaks at *m/z* 845.4912 $[M + HCOO]^-$ and fragment ion peaks at *m/z* 799.4871, 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 F_{11} [33, 34]. The cleavage pathway is as follows: when the molecular ion at *m/z* 799.4871 $[M\text{-}H]^-$ lost one molecular rhamnose residue (146 Da), the product ion at *m/z* 653.4296 $[M\text{-}H\text{-}Rha]^-$ was produced. Subsequently, the fragment ion peak at *m/z* 491.3707 $[M\text{-}H\text{-}Rha\text{-}Glc]^-$ 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 $[Rha\text{-}H]^-$ was examined for free rhamnose residues. The cleavage pathway of pseudoginsenoside F_{11} is shown in Figures 12 and 13.

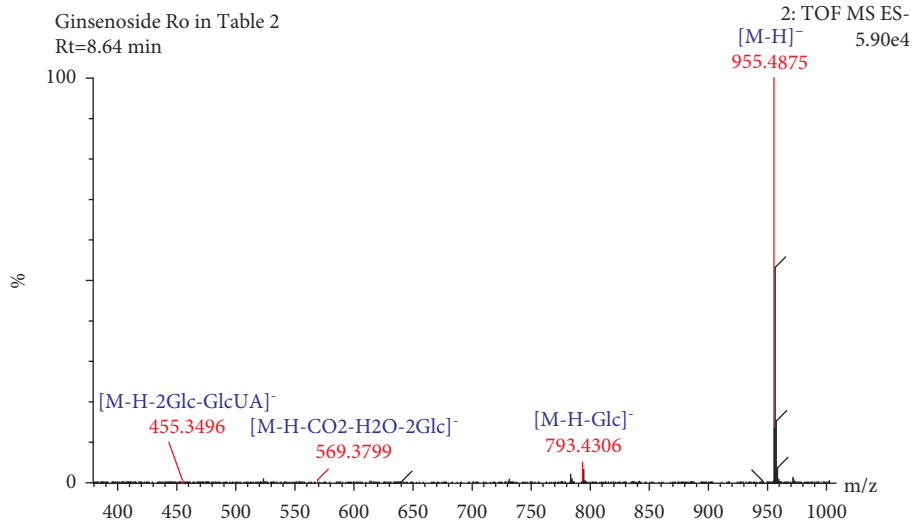


Figure 10: Secondary mass spectrogram of ginsenoside Ro.

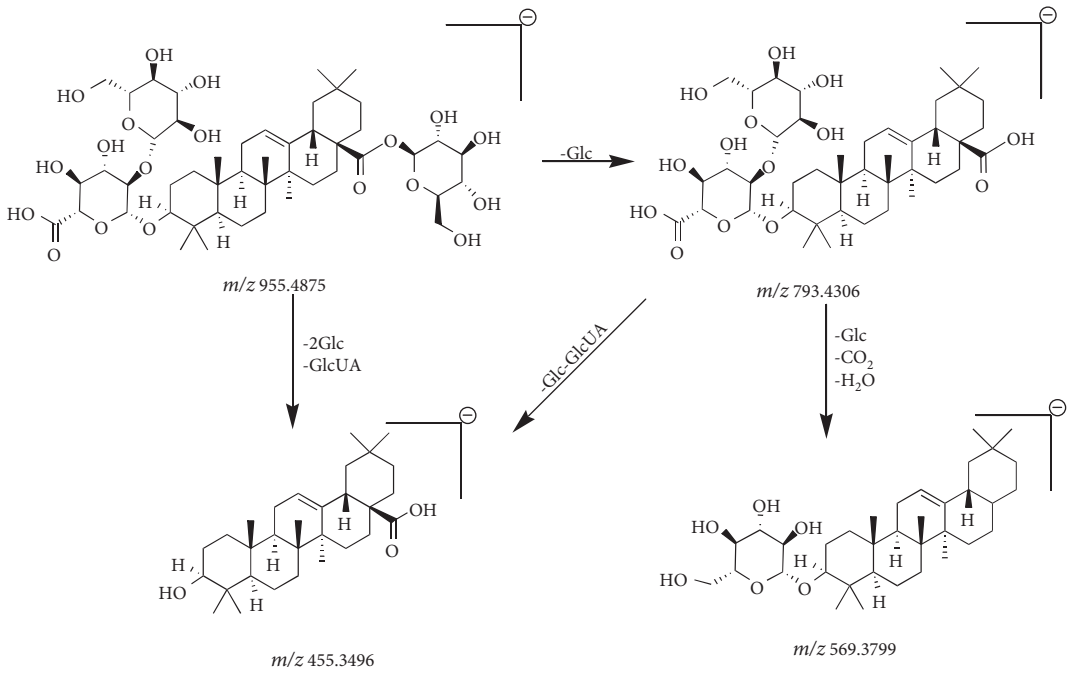


Figure 11: The fragmentation pathway of ginsenoside Ro.

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 Rg_1, zingibroside R_1, 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 (Rg_1, Re, Rb_1, 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 Rg_1, zingibroside R_1, ginsenoside Re, ginsenoside Rd, ginsenoside Rf, and OCO-type saponins (taking pseudoginsenoside F_{11} 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,

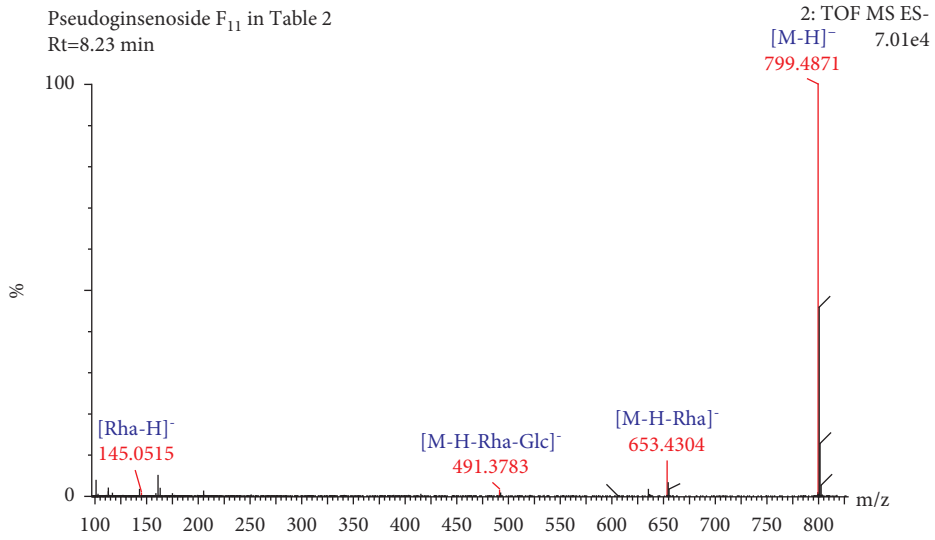


Figure 12: Secondary mass spectrogram of pseudoginsenoside F_{11}.

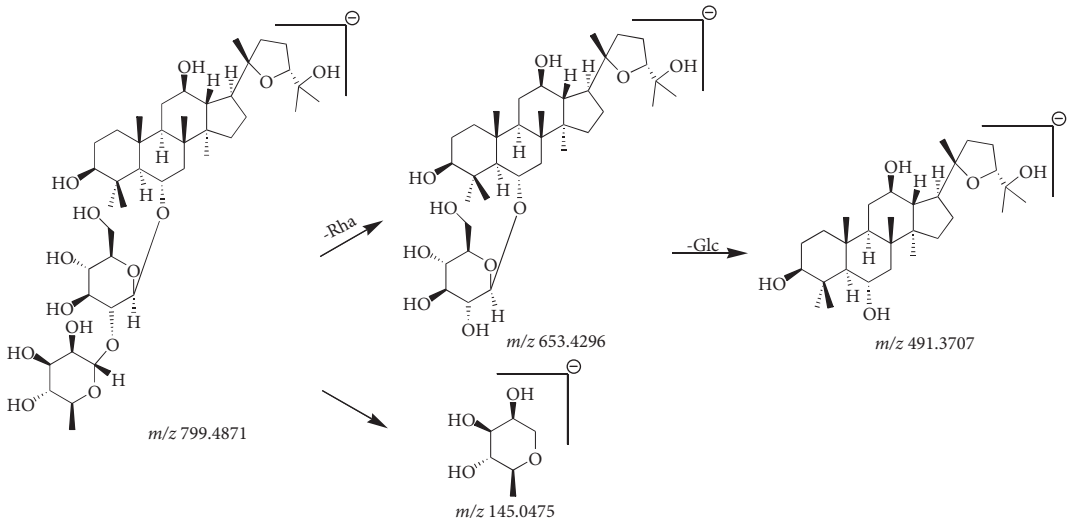


Figure 13: The fragmentation pathway of pseudoginsenoside F_{11}.

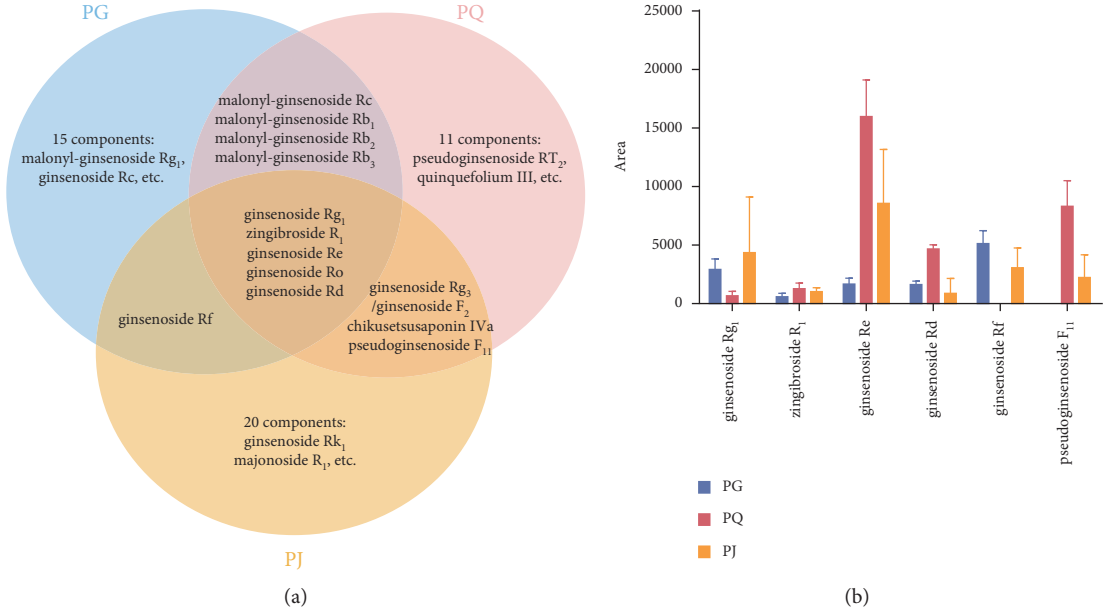


Figure 14: (a) Venn diagram of the distribution of saponins among PG, PQ, and PJ. (b) Contents of six components in PG, PQ, and PJ.

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, 23 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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