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Fast Screening of Authentic Ginseng Products by Surface Desorption Atmospheric Pressure Chemical Ionization Mass Spectrometry

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Key words
- *Panax* species
- Araliaceae
- ginseng
- ginsenoside
- chemical marker
- surface desorption atmospheric pressure chemical ionization
- mass spectrometry

Abstract

Surface desorption atmospheric pressure chemical ionization mass spectrometry was developed as a rapid online detection technology for the chemical fingerprints of ginseng products without any sample pretreatment. More than 20 ginsenosides were detected in the ginseng tissue and identified by their tandem mass spectrometry. Data were well matched with their reference compounds. Herein, surface desorption atmospheric pressure chemical ionization mass spectrometry was first applied to study the nonvolatile compounds in ginseng. White and red ginseng have been successfully differentiated from their counterfeits using some ginsenosides as chemical markers. Ginsenoside can be used to differentiate between white ginseng, red ginseng, unboiled ginseng, and their counterfeits. Ginsenosides Ra_{1-3}, Rb_{2-3}, and Rc might be used to differentiate between white ginseng and boiled ginseng. Our result showed that surface desorption atmospheric pressure chemical ionization mass spectrometry not only could be used for fast screening authentic ginseng products but also might become a useful promising technique for the characterization of nonvolatile compounds in medicinal herbs to save researchers the laborious effort of sample pretreatment.

Introduction

Ginseng is a famous medicinal herb and its root has been traditionally used as a precious medicine and nutrient, often in a dried form. Ginseng is believed to strengthen our normal body functions, reduce stress, stimulate the central nervous system (CNS), and combat diabetes and cancer [1–4]. Ginsenosides, *O*-glycosides of the triterpen dammarane saponins, have been known as the exclusive bioactive components of ginseng and have demonstrated useful pharmacological effects on the central nervous, cardiovascular, and endocrine systems. Ginsenosides could be classified into three types based on their structures: protopanaxadiol type (Ra1, Ra2, Ra3, Rb1, Rb2, Rb3, Rc, Rd, Rg3, Rh2, Rh3, mRb1, mRb2, and mRd), protopanaxatriol type (Re, Rf, Rg1, Rg2, Rh1, and Rk3), and oleanolic acid type (Ro). Ginsenoside content can vary widely depending on species, location of growth, cultivation method, plant part, age, and commercial manufacturers. So far, more than 70 ginsenosides have been isolated from ginseng plants. The ginseng roots are normally available in white or red. White ginseng is fresh ginseng which has been air-dried in the sun and may contain less therapeutic constituents. Red ginseng is usually fresh ginseng which has been steamed at 100 °C for 3 h and then dried. There are more ginsenoside types in red ginseng than in white ginseng because of the steaming process [5–8]. Less polar ginsenosides, such as Rg3, Rh1, Rh2, and Rh3, are known to be major constituents of red ginseng. Rg3 is used as a major active component in antitumor and anticancer drugs in China. The cytotoxicity of ginsenoside Rg3 against tumor cells increases when Rg3 is metabolized into Rh2 or protopanaxadiol [9, 10].

In recent years, ginseng products have become popular around the world. However, some cheap herbs, such as balloonflower root, pokeweed, Radix Adenophorea, and *Salvia*, are often disguised as ginseng. This kind of counterfeit ginseng might delay the treatment of disease and even lead to the deterioration of the disease. It becomes important for us to discriminate ginseng from such imposters in order to ensure the au-

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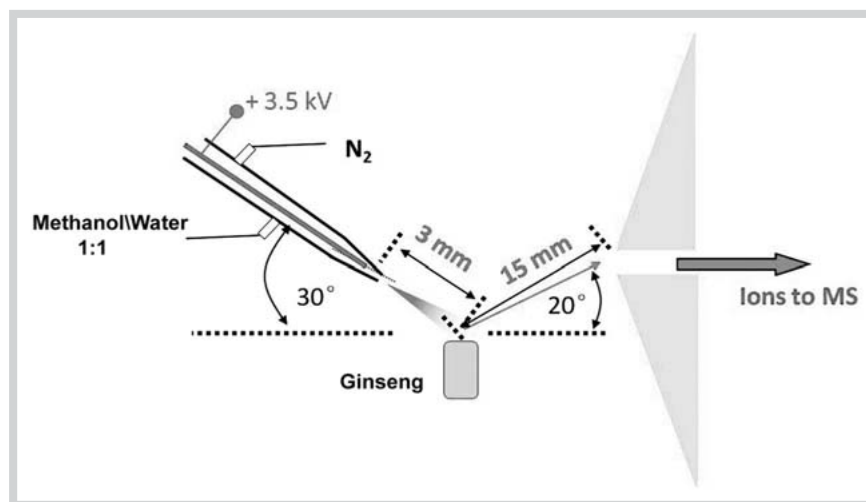

Fig. 1 Schematic diagram of the DAPCI source for ginseng sample detection.

thenticity, quality, safety, and efficacy of ginseng products. So far, high-performance liquid chromatography (HPLC)-MS, ultra-performance liquid chromatography (UPLC)-MS, electrospray ionization (ESI)-MS, and APCI-MS have been applied to analyze ginseng with satisfactory sensitivity and good reproducibility [11–18]. However, these methods are time consuming and tedious. Direct profiling technologies are useful for the rapid evaluation of composition or authentication of ginseng, quality control, and metabolomics. Traditional technologies are nuclear magnetic resonance (NMR), infrared (IR), and Raman spectroscopy. Newly developed ambient ionization (API) techniques, such as desorption electrospray ionization (DESI), surface desorption atmospheric pressure chemical ionization (DAPCI), direct analysis in real time (DART), dielectric barrier discharge ionization (DBDI), ionization by a low-temperature plasma (LTP), later renamed easy ambient sonic spray ionization (EASI), and laser ablation electrospray ionization (LAESI), have been widely utilized for the fast detection of analytes on solid surfaces, normally without any sample pretreatment [19–28]. Surface desorption atmospheric pressure chemical ionization mass spectrometry (DAPCI-MS), as one of the ambient mass spectrometries, has been used for direct analysis of powdered samples, sticky liquids, and biological tissues without a notable loss of sensitivity [20, 21, 29, 30].
In this study, DAPCI-MS has been used for the direct analysis of various ginseng samples for the first time without sample pretreatment. As demonstrated in our report, the DAPCI technique is able to study nonvolatile compounds in plant tissue, and provide a fast screening technology to differentiate authentic ginseng and its counterfeits, and shows a promising application to nonvolatile compounds in medicinal herbs.

Materials and Methods

Materials

Methanol was HPLC grade and other reagents were analytical grade. Deionized water was prepared using a Millipore water purification system. The ginseng samples (white ginseng WG-01 to 12 and red ginseng RG-01 to 12) and their counterfeits (BG-01 to 05), balloonflower root (20080630–01 to 05), pokeweed (20080224–01 to 05), Radix Adenophorea (20080508–01 to 05), and *Salvia* (20080926–01 to 05), were kindly provided by Jilin Zixin Pharmaceutical Industrial Co., LTD. According to the Chinese Pharmacopoeia 2005 and National Standard GB/T 19056–2009, the quality of genuine white and red ginseng samples used here were tested by using a standard protocol for ginseng identification. The thickness of ginseng slices is only 2 mm and can be cut by a clean steel saw (Bosi, BS-E306, 12″/300 mm). Ginsenoside standards Ra_1 (20090822-Ra_1), Ra_2 (20090822-Ra_2), Ra_3 (20090822-Ra_3), Rb_1 (20090822-Rb_1), Rb_2 (20090822-Rb_2), Rc (20090822-Rc), Rd (20090822-Rd), Re (20090822-Re), Rf (20090822-Rf), Rg_1 (20090822-Rg_1), Rg_2 (20090822-Rg_2), Rg_3 (20090822- Rg_3), Rh_1 (20090822-Rh_1), Rh_2 (20090822-Rh_2), Rh_3 (20090822-Rh_3), Rk_3 (20090822-Rk_3), Ro (20090822-Ro), mRb_1 (20090822-mRb_1), mRb_2 (20090822-mRb_2), and mRd (20090822-mRd) were purchased from Nanjing Zelang Co. The purities of these authentic compounds were more than 98%.

Instruments

An LTQ-XL linear ion trap mass spectrometer (Finnigan) coupled with a novel DAPCI source was used for the experiments (**Fig. 1**). The DAPCI source assembly was coaxially coupled to the LTQ mass spectrometer, allowing a 15-mm distance between the sample surface and the ion entrance capillary. The ginseng samples were directly supplied to the DAPCI source placed at 2–3 mm from the discharge tip. The angle formed between the discharge needle and the sample holder was about 30°, and the angle formed by the ion entrance capillary with respect to the sample holder was about 20°. The spot size that was used for analysis was less than 3 mm^2 and the APCI beam focus diameter was 0.2 mm. A 3.5-kV high voltage was applied to the sharp needle of the DAPCI source and the samples were directly ionized in the open environment. The temperature of the heated capillary of the LTQ was maintained at 150 °C. The collision gas was helium and collision-induced dissociation (CID) was performed with 20–35% collision energy (CE) to the precursor ions of interest, which were isolated with a mass window width of 2 *m/z* units. A 50% methanol solution was used as a reagent to improve chemical ionization efficiency. A low rate of nitrogen was used to blow the surface of ginseng for ginsenoside dispersion. The positive mode was adopted and capable of analyzing ions up to *m/z* 2000.

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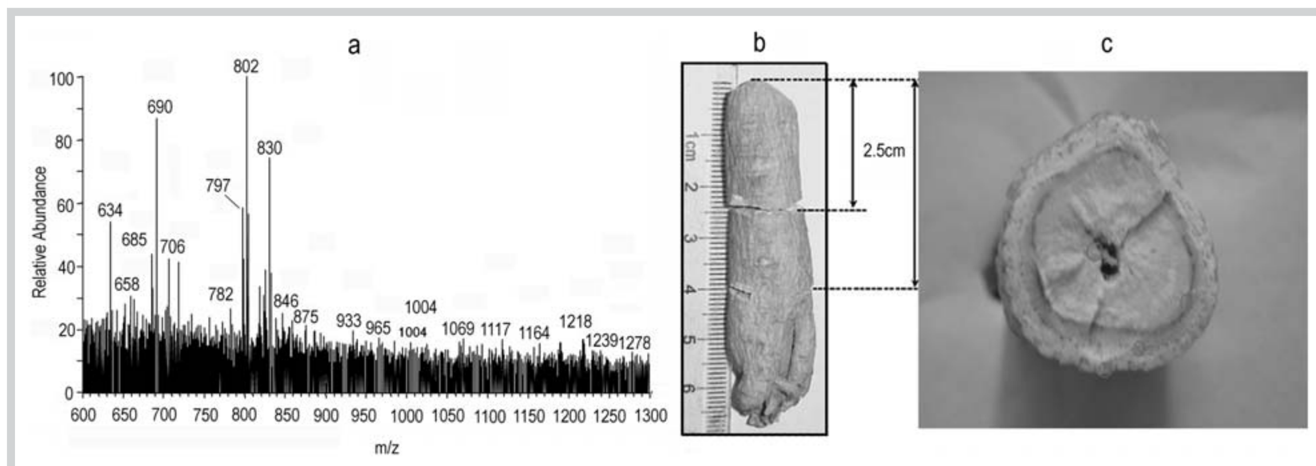

Fig. 2 Full scan spectrum of white ginseng (**a**), the cutting area of the ginseng sample (**b**), and 4 spots on the ginseng slice were measured using DAPCI-MS (**c**).

Results and Discussion

The relative intensity of $[M + Na]^+$ corresponding to ginsenoside was more abundant than that of $[M + H]^+$ because ESI-MS is more favorable to the generation of the $[M + Na]^+$ ions than the $[M + H]^+$ ions compared with DAPCI [14]. In our experiment, 10 mM NaCl were added to the surface of ginseng in order to produce a stronger $[M + Na]^+$ ion signal. The NaCl solution was sprayed onto the sample surface before the MS experiment. To ensure sufficient reagent and obtain reproducible results, a 50% methanol solution was used to enhance the abundance of $[M + Na]^+$ ions relative to $[M + H]^+$ ions, because under the condition of APCI [13], the $[M + H]^+$ ions are more easily fragmented by the APCI voltage and temperature than the $[M + Na]^+$ ions.

In the full scan spectrum of white ginseng (**Fig. 2 a**), few ginsenosides were observed. The reason could be that some ion peaks of background compounds interfered with the analysis of ginsenosides when the ginsenosides were at such a lower level on the surface of ginseng. For ginseng root, the organ most often used, the contents of ginsenosides were more abundant in the cortex than those in the periderm and xylem [31]. This conclusion was confirmed by the abundance of the ginsenoside mass peak in the selected spots (**Fig. 2 c**). Furthermore, the ginsenoside composition in the adventitious root and lateral root was higher than that in the main root and rhizome. The quality of the ginseng main root was the steadiest among ginseng products. The ginseng slice sample was cut according to the positions indicated in **Fig. 2 b**, and four spots on the ginseng slice were chosen for DAPCI-MS (**Fig. 2 c**). The four selected scan spots correspond to four different parts of the ginseng's cross-section, which are supposed to stand for the whole ginseng because of the homogenous distribution of ginseng.

To quantify marker compounds, high-quality ginsenoside libraries are required. A lack of reference standards, in spite of improved methods for determining compounds, makes it difficult to evaluate ginseng products. Ginsenoside Rg_1/Rf (MW 800) was used as an important standard for ginseng authenticity according to the Pharmacopoeias of China, Korea, and Japan. Peaks at $[M + H]^+$ 801 and $[M + Na]^+$ 823 corresponded to the ginsenoside Rg_1/Rf protonated molecular ion and Na^+ adduct. It has been reported before that deoxyhexose sugar and hexose sugar were major losses in the ESI-MS/MS spectra of ginsenoside Rg_1/Rf [13]. **Fig. 3 a** shows the DAPCI-MS/MS spectrum of ginsenoside Rg_1/Rf. The precursor ion of *m/z* 823 produced the predominant ion of *m/z* 643, which was ionic residue generated by the loss of glucose from ginsenoside Rg_1/Rf, $[M\text{-glc} + Na]^+$. In addition, the peak at *m/z* 365 corresponded to the ion [M-sapogenin + Na]+. Ginsenoside Rb1 (MW 1108) is the most abundant (0.22–0.62%) among all ginsenosides and can be found both in white and red ginseng. In **Fig. 3 b**, peaks at *m/z* 1131, 789, and 365 corresponded to frag-

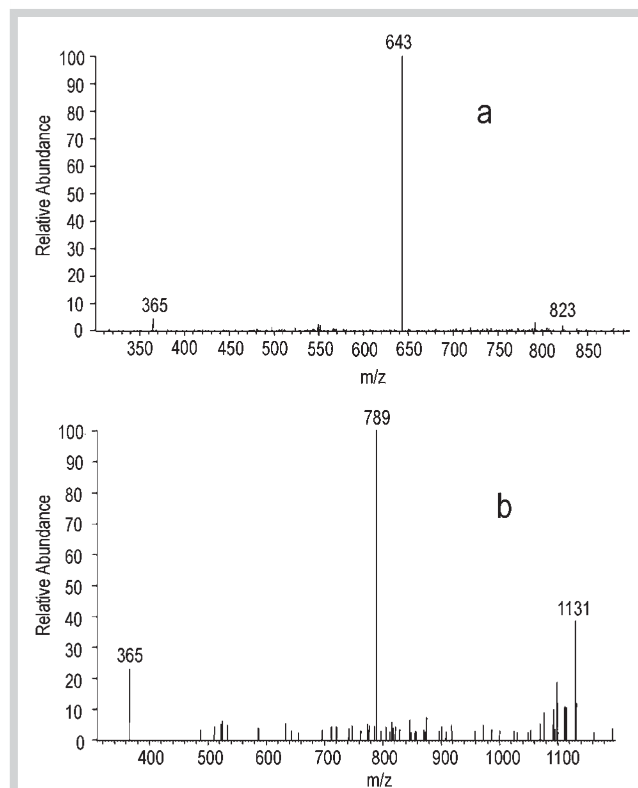

Fig. 3 DAPCI MS/MS spectra of ginsenoside Rg_1/Rf (**a**) and ginsenoside Rb_1 (**b**) in white ginseng.

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Table 1 Comparison of compounds identified in ginseng and its counterfeits by DAPCI-MS/MS.

	Ginsenosides	Formula	$[M + Na]^+$	MS/MS	White ginseng	Red ginseng	Ginseng sun-dried after boiling	Counterfeit
1	Ra_1/Ra_2	$C_{58}H_{98}O_{26}$	1233	789	*	ND	ND	ND
2	Ra_3	$C_{59}H_{100}O_{27}$	1263	789	*	ND	ND	ND
3	Rb_1	$C_{54}H_{92}O_{23}$	1131	789, 365	*	W	ND	ND
4	$Rb_2/Rb_3/Rc$	$C_{53}H_{90}O_{22}$	1101	789, 365	*	ND	ND	ND
5	Rd/Re	$C_{48}H_{82}O_{18}$	969	789, 365	*	*	W	ND
6	Rf/Rg_1	$C_{42}H_{72}O_{14}$	823	643, 365	*	*	W	ND
7	Rg_2	$C_{42}H_{72}O_{13}$	807	643	*	*	W	ND
8	Rg_3	$C_{42}H_{72}O_{13}$	807	627	*	*	W	ND
9	Rh_1	$C_{36}H_{62}O_9$	661	481	ND	*	*	ND
10	Rh_2	$C_{36}H_{62}O_8$	645	465	ND	*	*	ND
11	Rh_3	$C_{36}H_{60}O_7$	627	447	ND	*	*	ND
12	Rk_3	$C_{36}H_{60}O_8$	643	481, 365	ND	*	*	ND
13	Ro	$C_{46}H_{76}O_{19}$	979	817	*	*	W	ND
14	mRb_1	$C_{57}H_{94}O_{26}$	1217	1173, 875	ND	*	ND	ND
15	mRb_2	$C_{56}H_{92}O_{25}$	1187	1155, 875	ND	*	ND	ND
16	mRd	$C_{51}H_{84}O_{21}$	1055	875	ND	*	ND	ND

ND not detected; W weak; * chemical marker for identification

mentation ions of $[M + Na]^+$, $[M\text{-glc-ara} + Na]^+$, and $[M\text{-sapogenin} + Na]^+$, respectively.

Based on the above-mentioned methods, more than 20 ginsenosides were found in white ginseng (**Table 1**) and identified according to their tandem MS data matched with their reference compounds. Ginsenosides Rf/Rg_1 and Rg_2 can be used to differentiate between white ginseng, red ginseng, unboiled ginseng, and their counterfeits. The differences of ginsenosides Rf and Rg1 were more obvious than those of ginsenosides Rb1 and Re according to the intensities of their MS spectra.

The herbs of balloonflower root, pokeweed, Radix Adenophorea, and *Salvia* are usually used as counterfeit ginseng by some unscrupulous traders. The slices of several of the above-mentioned herbs were analyzed by DAPCI-MS. Their full mass spectra and tandem mass spectra were obtained, and the analytical time for each run was less than 2 minutes. But the fragmentation ion *m/z* 789 $[M\text{-glc} + Na]^+$ resulting from the ion *m/z* 969 of Rd/Re could be detected in the MS/MS spectra of white ginseng, red ginseng, and sun-dried ginseng after boiling (**Fig. 4a–c**). For ginsenoside Rd/Re, the loss of a sugar molecule from the daughter ion wasn't found in the MS/MS spectra of the counterfeit ginseng (**Fig. 4d–g**), i.e., ginsenoside Rd/Re in the above-mentioned fake herbs was not detected, and these spectra looked noisy because no major compounds were detected.

Normally, ginseng sun-dried after boiling means that the ginseng is dried in the sun after ginsenosides are partly extracted from the ginseng during the boiling procedure. Ginseng sun-dried after boiling is still sold at the same price as that of genuine ginseng by those unscrupulous traders, although the concentration of ginsenosides is lower than that in genuine ginseng. Ginsenosides, such as Rh2 and Rg3, could be found in ginseng without boiling as well as after boiling, because Ra1-3, Rb1-3, and Rc hydrolyzed to Rh2 and Rg3 while heated by water. Therefore, the detection of Rh2 and Rg3 could not be used as chemical markers to differentiate between ginseng and ginseng after boiling. On the other hand, ginsenoside Rb1 was also detected in red ginseng (**Fig. 4b**), which has been found and identified in more than 20 samples of red ginseng produced by different manufactures, and can be used as a chemical marker to discriminate white and red ginseng from their counterfeit products. Similarly, ginsenosides Ra and Rb/Rc could only be found in white ginseng that had not been boiled. It is possible that DAPCI-MS might not provide enough sensitivity to detect low, abundant ginsenosides Ra and Rb/Rc in red ginseng and ginseng after boiling. However, our MS results at least showed that Ra and Rb/Rc could be used as chemical markers to differentiate between white ginseng and boiled ginseng. Especially ginsenosides with longer glycosylation chains may be used as a chemical marker to differentiate between boiled and unboiled ginseng. This is because long glycosylation chains in ginsenosides might break up during the boiling process which could lead to the result that ginsenosides have a much shorter glycosylation chain in boiled ginseng than in unboiled ginseng. However, we need to find out what the normal glycosylation length is in ginsenosides for unboiled white ginseng and boiled ginseng. Ginsenosides with a certain length of glycosalation chain, including ginsenosides Ra1-3 and Rb1-3, might be used as chemical markers for ginseng authenticity when ginseng is boiled.

In this study, DAPCI-MS could provide a rapid technique for the detection of ginsenosides in ginseng without any sample pretreatment. This technology can utilize some ginsenosides as chemical markers to discriminate genuine ginseng from counterfeit products. Ginsenoside can be used to differentiate between white ginseng, red ginseng, boiled ginseng, and their counterfeits. Although, under DAPCI-MS conditions, further quantification of these ginsenoside markers and optimum instrumental conditions still needs to be performed, and a new MS method for fast screening ginseng products could be established.

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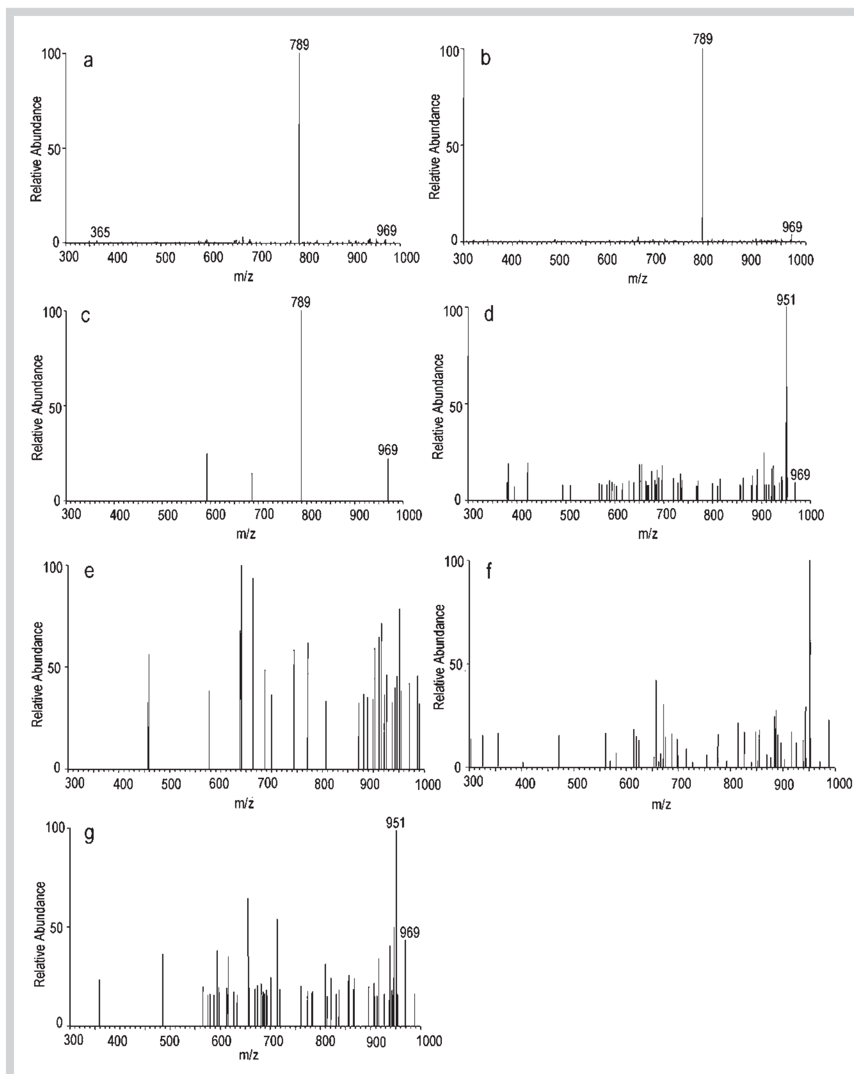

Fig. 4 DAPCI-MS/MS spectra of ginsenosides at *m/z* 969 in white ginseng (**a**), red ginseng (**b**), boiled sun-dried ginseng (**c**), balloonflower root (**d**), pokeweed (**e**), Radix Adenophorea (**f**), and *Salvia* (**g**).

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Conflict of Interest

On the behalf of Hao Yue, Li Ma, Zifeng Pi, Huanwen Chen, Yang Wang, Bin Hu, we declare that we have no financial and personal relationships with the people or organizations that can inappropriately influence our work. There is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in Planta Medica, the manuscript entitled "Fast screening of authentic ginseng products by surface desorption atmospheric pressure chemical ionization mass spectrometry".

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