Structural Characterization of Chemical Compounds Based on Their Fragmentation Rules in *Sophorae Fructus* by UPLC-QTOF-MS/MS

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Abstract

This study aims to identify the chemical components in *Sophorae Fructus*, and explore the mass spectrometric cleavage rules using the UPLC-Q-TOF-MS/MS method. The main characteristic fragments of the compounds were analyzed by electrospray ionization (ESI) ion source under positive and negative ion modes. The compounds were identified by molecular formula, multistage mass spectrometry, ultraviolet spectrum, and the fragmentation patterns of standards. A total of 142 compounds were identified, including 67 flavonoids, 39 saponins, 18 organic acids, 10 amino acids and sugars, 2 phenytoinanes, 3 fatty acids and 3 other types. 43 components were first reported from the genus *Sophora*.

Keywords

► *Sophorae Fructus*
► flavonoid glycosides
► saponins
► UPLC-Q-TOF-MS/MS
► fragmentation

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Introduction

Sophorae Fructus is the dry and mature fruit of Sophora japonica (L.), a leguminous plant. It has the functions of clearing away heat and toxic material, cooling blood and stopping bleeding, and is usually used for treating intestinal heat, hematochezia, nevus swelling and bleeding, dizziness, as well as red eyes. It also has anticancer and estrogen-like effects, and plays a roles in prevention and treatment of cardiovascular disease, osteoporosis, and female menopause syndrome. The study of the chemical components of S. japonica is of great significance for its quality control and clinical application. The main components of Sophorae Fructus are flavonoids, isoflavones, alkaloids, triterpenoid saponins, amino acids, stearic acids etc., among which isoflavones and their glycosides are the highest. However, up to now, there are few reports on the analysis of the total components of Sophorae Fructus. Sun et al. identified and inferred 24 common compounds and 21 variance compounds in Sophorae Fructus from different producing areas by ultra-performance liquid chromatography-quadrupole time-of-flight mass spectrometry (UPLC-Q-TOF/MS). Zhang identified 131 compounds from the total extract of Sophorae Fructus in positive and negative ion modes by UPLC-Q-TOF/MS. The structural types include 81 flavonoids, 18 triterpenoid saponins, 5 steroids, 2 anthraquinones, 3 phenols, and 22 others. Triterpenoid saponins were less identified, and flavonoids were mainly reported.

Traditional methods for phytochemical isolation and identification are time-consuming and labor-intensive. In recent years, techniques combining the efficient separation ability of liquid chromatography and strong identification ability of MS have been widely used in the separation and qualitative and quantitative analysis of complex Chinese medicines. In this study, UPLC-Q-TOF/MS was used to rapidly identify the chemical composition of Sophorae Fructus. We established a UPLC-Q-TOF/MS qualitative analysis method to analyze the constituents of Sophorae Fructus, which lay a foundation for the study of its pharmacodynamic substance basis and quality control.

At present, the studies on MS pyrolysis are relatively scattered. The electrospray ionization MS of saponin and flavonoid components has been reported. Flavonoid species can be identified according to the ultraviolet (UV) absorption characteristics of compounds and the characteristic ion fragments of the parent nuclei. But there are few literature reports on determining the connection mode between glycosyl groups in flavonoid glycosides by using the cleavage rule of MS. In this study, through the comparison of the MS data of 21 reference substances, including flavonoid oxyglycosides, flavonoid carbon glycosides, dihydro-flavanoid glycosides, isoflavone glycosides and saponins, and a large number of literature reports, we systematically deduced the cleavage characteristics of these compounds, so as to provide reference for the MS structure identification of such components.

Materials and Methods

Materials and Reagents

The prepared slices of Sophorae Fructus is obtained from Tianjin Darentang TCM Chinese Herbal Medicine Co., Ltd (Bozhou, China). Reference standards citric acid (97.0%), gallic acid (90.8%), protocatechuic acid (97.7%), protocatechuic aldehyde (99.6%), baicalin (97.9%), apigenin (99.4%), rutin (91.6%), kaempferol (93.2%), isoquercitrin (97.2%), genistein (98.8%), kaempferol-3-O-rutinoside (94.0%), kaempferol-3-O-gentiobiose (93.1%), isorhamnetin-3-O-neohesperidin (93.0%), naringin (93.5%), hesperidin (95.3%), neohesperidin (99.4%), genistin (99.9%), sophoricoside (99.6%), puerarin (95.4%), vitexin (99.1%), asperosaponin VI (94.3%), mogroside V (96.1%), ginsenoside Re (96.0%), jujuboside A (96.0%), ruscone (98.0%), and oleanolic acid (95.8%) were purchased from National Institute for Food and Drug Control (Beijing, China). Sophorabioside (≥98%) was purchased from Shanghai Standard Biotech Co., Ltd (Shanghai, China). Kaempferol-3-O-sophoroside (≥98%) was purchased from Chengdu Purifa Technology Development Co., Ltd. Kaempferol-3,7-di-O-glucoside (≥98%) and kaempferol-3-O-(2″-O-β-D-glucosyl)-β-D-rutinoside (≥98%) was purchased from Chengdu Push Biotechnology Co., Ltd (Chengdu, China). Isorhamnetin-3-O-β-D-rutinoside (≥98%) and kaempferol-3-O-β-D-sophorae-7-O-α-L-rhamnoside (≥98%) were self-made in the laboratory. Liquid chromatography-MS (LC-MS)-grade acetonitrile (ThermoFisher, United States), methanol (ThermoFisher, United States), formic acid (ThermoFisher, United States), and deionized water prepared by a Millipore Alpha-Q water purification system (Millipore, United States) were used as the mobile phase for the chromatographic separation. Other reagents were of analytical grade.

Preparation of Standards and Samples

All reference materials were dissolved in methanol and each was prepared into a solution of 0.1 mg/mL. In brief, 1.0 g of Sophorae Fructus powder (through No. 3 sieve) was accurately weighed and ultrasonicated with 30 mL 70% methanol.
(v/v) (250 W, 40 kHz) for 60 minutes. The sample solution and standard solution were filtered through 0.22 μm micro-
porous filter membrane.

**Instrumentation and Conditions**

The UPLC-QTOF MS/MS analysis was performed using a Waters Acquity UPLC system coupled with a Xevo G2-XS QTOF mass spectrometer (Waters, United States) with an electrospRAY ionization ion source in MSE mode.

The chromatographic separation process of flavonoids was performed on an ACQUITY CSH C18 (150 mm × 2.1 mm, 1.7 μm; Waters, United States) at 35°C, with a mobile phase consisting of methanol (B) and 0.05% formic acid aqueous solution (A). The gradient elution was as follows: 0–9 minutes, 10–20% eluent B; 9–27 minutes, 20–40% eluent B; 27–30 minutes, 40% eluent B; 30–39 minutes, 40–60% eluent B; 39–42 minutes, 60% eluent B; 42–48 minutes, 60–80% eluent B; 48–50 minutes, 80% eluent B; 50–50.1 minutes, 80–10% eluent B; 50.1–65 minutes, 10% eluent B. The flow rate was 0.2 mL/min.

Saponins were separated by Hypersil Gold (100 mm × 2.1 mm, 1.9 μm; ThermoScientific, United States) at 35°C. The flow rate was 0.3 mL/min. The mobile phase was acetonitrile (B) and 0.1% formic acid (A) in water. The gradient elution was as follows: 0–1 minute, 99% eluent A; 1–5 minutes, 99–91% eluent A; 5–9 minutes, 91–84% eluent A; 9–12 minutes, 84% eluent A; 12–18 minutes, 84–67% eluent A; 18–23 minutes, 67–63% eluent A; 23–29 minutes, 63–49% eluent A; 29–34 minutes, 49–0% eluent A; 34–36 minutes, 0–99% eluent A; 36–37 minutes, 99% eluent A. The injection volume for all was 1 μL.

MS conditions were operated in both positive and negative ion modes and applied as the following: solvent gas temperature (nitrogen), 450°C; capillary voltage, 3.0/2.5 kV; an ion source temperature, 120°C; desolvation gas flow, 500 L/h; cone gas flow, 100 L/h; the high collision energy, 6 V; the high collision energy, 25 to 60 V.

**Data Processing and Compound Identification**

Masslynx 4.1 software (Waters, United States) was used to analyze the mass spectra peaks of *Sophora Fructus* in positive and negative ion modes. According to the comparison of reference standards or references, the compounds were identified by UV spectrum, retention time, excimer ion peak, molecular formula, fragment ions, and other information combined with SciFinder database.

**Results and Discussion**

To systematically and qualitatively analyze the chemical components in *Sophora Fructus*, the MS behavior of the existing reference standards was studied to summarize their chromatographic retention behavior, UV absorption, cracking rule, and characteristic fragment ions.

**The Cracking Rules of the Deglycosylation Group of Flavone-O-diglycoside**

Kaempferol-3-O-sophoroside (tR = 26.28 minutes) and kaempferol-3-O-gentiobioside (tR = 28.33 minutes) are iso-

mers, their mass spectra in negative and positive ion modes are shown in **Fig. 1**. In the negative ion mode (**Fig. 1A**), kaempferol-3-O-sophoroside can obtain fragment ions of m/z 429.0819 [M–H–162–H2O]+. In the positive ion mode (**Fig. 1C**), it could generate fragment ions of m/z 449.1071 [M+H–162–H2O]-, and the relative abundance (10%) was higher than that of kaempferol-3-O-gentiobioside (<10%, **Fig. 1D**).

Similarly,isorhamnetin-3-O-β-D-neohesperidoside produces fragment ions of m/z 459.0932 [M–H–146–H2O]- in the negative ion mode. The relative abundance of m/z 479.1197 [M+H–146]+ fragment ion (>50%) was higher than that of isorhamnetin-3-O-β-D-rutinoside (<50%) in the positive ion mode. The retention time and ion fragments of the four reference substances showed the following regularities: (1) the polarity of flavone-O-diglycoside linked to monosaccharides in 1→2 mode was greater than that of flavone-O-diglycoside linked to monosaccharides in 1→6 mode; (2) in the negative ion mode, when the flavone-O-
diglycoside is linked in 1→2 mode, it can produce [M–H – monosaccharide–H2O]– characteristic fragment ion, but when it is linked in 1→6 mode, it can only produce [M–H–monosaccharide]– fragment ion, which is the same as reported in the literature, (3) the relative abundance of [M+H–monosaccharide]– fragment ions produced by 1→2 linkage between glyco-groups is higher than that of the same fragment ions produced by 1→6 linkage between glyco-

groups. It is consistent with the cleavage law of *Fructus aurantii* flavone diglycosides in the positive ion mode reported in the literature. The rules can provide a basis for identifying the most common two disaccharide connection modes (1→6, 1→2) in flavonoid oxyglycosides.

**The Cracking Rules of the Deglycosylation Group of Flavone-O-triglycoside**

Kaempferol-3-O-β-D-sophoroside-7-O-α-L-rhamnoside (tR = 19.66 minutes) and kaempferol-3-O-(2"-O-β-D-glucopy-
ranosyl)-β-D-rutinoside (tR = 25.33 minutes) are isomers. Their mass spectrometric cleavage pathways in positive and negative ion modes are shown in **Fig. 2**. In the negative ion mode, kaempferol-3-O-β-D-sophoroside-7-O-α-L-rhamnoside can obtain fragment ions of m/z 755.1894, 609.1498, 449.1126, and 284.0459, indicating that rhamnose on the C7 position was lost first and then glucose groups on the C3 position were lost successively. However, in the positive ion mode, the glyco-group at the end of C3 site was lost first, and the fragment ion of m/z 595.1671 was detected. Then, after the loss of all glyco-groups at the C3 site, the rhamnose group at the C7 site was lost, and the fragment ion with m/z of 433.1140 and 287.0568 appeared (**Fig. 2A**). Kaempferol-3-O-(2"-O-β-D-glucopyranosyl)-β-D-rutinoside in the negative ion mode could generate fragment ions of m/z 755.1838, 593.1495, 575.1411, and 284.0424. In the positive ion mode, it could generate fragment ions of m/z 779.1974, 595.1671, 493.1533, 449.1071, and 287.0568. This shows that whether in the positive or the negative ion mode, the glucose connected with 1→2 at the end was lost first, then the rhamnose connected with 1→6 was lost, and finally the glucose connected with aglycone was lost (**Fig. 2B**).
Therefore, we come to the conclusion that: (1) the polarity of flavonol glycoside substitution at the C3 and C7 sites is greater than that of glycoside substitution at the C3 site only. (2) Flavonol glycosides replaced by glycogroups at the C3 and C7 sites lose the glycogroups on the C7 position first and then the glycogroups on the C3 position is lost in turn in the anion mode. In the positive ion mode, the glycogroups at the end of position C3 were lost successively, and then the glycogroups at the C7 site were lost, which was consistent with the pyrolysis rule of flavonoids in Herba Epimedii in the positive ion mode described in the literature.13 (3) The three monosaccharides in flavone-O-triglycoside are connected to each other. Whether in the positive or negative electrode, the glycosyl connected at the end with 1→2 is lost first, then the glycosyl connected with 1→6 is lost, and finally the loss of the glycosyl connected with aglycone.

Cleavage Rules of Flavonoid Carboglycosides
The mass spectrum of puerarin in positive and negative ion modes showed fragment ions of m/z 325.0699 [M – H - 90]−, 295.0578 [M – H - 120]−, 297.0750 [M + H - 120]+, and a series of dehydration peaks m/z 399.1077/381.0974/363.0857 were generated by the ionization peaks of [M + H]+ m/z 417.1158, and [M – H - 120]− and [M + H - 120]+ are the main characteristic fragments with high abundance (► Fig. 3). Vitexin showed the same cleavage pattern, indicating that if the fragment peak of the disaccharide group does not appear first, but there are [M – H - 90]− and [M – H - 120]− ion fragments and [M – H - 120]− or [M + H - 120]+ are the main characteristics, the fragments can basically be determined as hexacarbon flavonoid carboglycoside compounds. This is consistent with the research of Liu et al.14 Meanwhile, according to relevant literature,14–17 in the positive ion scanning mode, the continuous dehydration of glycosyl mainly occurred, and the negative ion scanning mode has more obvious mass spectrum characteristics than the positive ion scanning mode.

Cleavage of Dihydroflavonoid Glycosides and Isoflavone Glycosides
Through the secondary mass spectra of naringin (tR = 29.63 minutes), hesperidin (tR = 30.23 minutes), and neohesperidin (tR = 31.42 minutes) (► Table 1), we found that: (1) the polarity of dihydroflavonoid glycosides connected in the way of 1→2 between the monosaccharides substituted on the C7 position of dihydroflavonoid glycosides is less than that connected in the way of 1→6. (2) In the negative ion mode, in the secondary mass spectra of naringin and neohesperidin, in addition to the conventional ions [M – H - Rha]+, [M – H - Rha - Glu]−, there was also special ion [M – H

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**Fig. 1** Mass spectra and cleavage of (A) kaempferol-3-O-sophoroside and (B) kaempferol-3-O-gentiobioside in negative ion mode, and mass spectra of (C) kaempferol-3-O-sophoroside and (D) kaempferol-3-O-gentiobioside in positive ion mode.
-120$]^{-}$ with strong abundance, and the fragment ion [M - H - 162$]^{-}$ could be observed. Hesperidin did not appear as these special ions. It may be due to that the rhamnose linked to the hydroxyl in the C2 position of the glucose at the end of aglycone has rearranged and cleaved and the ion [M - H - 120$]^{-}$ resulted from the loss of a hexose residue in positions 0-3. The conclusion is to be proven by further experiments.  

(3) In the positive ion mode, the relative abundances of ions [M + K - Rha$]^{+}$ and [M + K - O - Rha$]^{+}$ were higher than those of 1-6 connected when the C7-substituted rhamnose and glucose are 1-2 connected. In the negative ion mode, the rhamnose linked to the hydroxyl in the C2 position of the glucose at the end of aglycone is more likely to rearrange, which may be related to the different charge distribution in the positive and negative ion modes. In the positive ion mode, the charge is mainly concentrated on the added sodium ions; and in the negative ion mode, the charge is mainly distributed in the whole sugar chain.  

By comparing genistin ($t_R = 24.04$ minutes), sophoricoside ($t_R = 28.72$ minutes), and sophorabioside ($t_R = 30.28$ minutes), we found that the polarity of isoflavone glycosyl substitution on the C7 position is greater than that at position C4 ($\sim$ Fig. 4). The glycosyl group of genistein substituted at position C7 only lost 120 fragment ions at the negative electrode. Both in the positive and negative electrodes, the glycosyl groups of sophoricoside and sophorabioside substituted at position C4 detected the loss of 120 fragment signal, and the positive signal intensity is higher. However, whether the lost fragment signal (120 U) can be used as the diagnostic fragment of isoflavone glycosides needs further research.  

### Mass Spectrometric Cleavage of Saponins

Full scan and mass spectrometric cleavage analysis were performed for saponin standard under positive and negative ion modes. The analysis results of characteristic fragments are shown in $\sim$ Table 2, and the mass spectrometric cleavage pathway of asperosaponin VI is shown in $\sim$ Fig. 5. The summary rules are as follows: (1) In the negative ion mode, the saponin parent nucleus fragments are not obvious, mainly the deglycosylated fragments and [M + Cl$]^{-}$, [M - H$]^{-}$ excimer ion peaks; in the positive ion mode, a series of dehydrated fragments and [M + Na$]^{+}$ excimer ion peaks in the mother nucleus were mainly detected, while the response of deglycosylated fragments was weak. (2) The glycosyl group at C3 position in asperosaponin VI, mogroside V, and ginsenoside Re is the last to fall off. Asperosaponin VI first lost the glycosylation at position C28, ginsenoside Re first lost the glycosylation at position C20, and mogroside V first lost the glycosylation at position C23. This may be due to the ester bond and the ether bond on the straight chain is easier to break than the ether bond on the C3 ring. (3) In the positive ion mode, the dehydration reaction of saponin parent nucleus fragments is only related to the number of hydroxyl groups carried on the mother nucleus, not related to the type of saponin, sugar chain...
Fig. 3 Secondary mass spectra of puerarin in (A) negative ion mode, (B) positive ion mode, and (C) its possible cleavage pathways.

Table 1 MS^2 data of naringin, neohesperidin, hesperidin, and the relative abundance (%) of ions

| Compound      | MS^2 (ESI^-)                                                                 | MS^2 (ESI^+)                                                                 |
|---------------|------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Naringin      | 579.1885 [M-H]^−                                                             | 619.1328 [M+K]^+ (23.2)                                                    |
|               | 459.1290 [M-H - 120]^− (100)                                                 | 603.1697 [M+Na]^+ (100)                                                    |
|               | 433.1394 [M-H - Rha]^− (17.9)                                                | 473.0746 [M+K - Rha]^+ (4.1)                                               |
|               | 415.1147 [M-H - 164]^− (24.6)                                                | 457.1020 [M+K - O - Rha]^+ (3.3)                                           |
|               | 271.0694 [M-H - Rha - Glu]^−                                                 | 273.0744 [M+H - Rha - Glu]^+ (39.8)                                        |
| Neohesperidin | 609.1806 [M-H]^−                                                             | 649.1487 [M+K]^+ (18.7)                                                    |
|               | 489.1284 [M-H - 120]^− (100)                                                 | 633.1815 [M+Na]^+ (100)                                                    |
|               | 463.1176 [M-H - Rha]^− (6.6)                                                 | 503.0856 [M+K - Rha]^+ (6.6)                                               |
|               | 449.0977 [M-H - 160]^− (89.3)                                                | 487.1154 [M+K - O - Rha]^+ (2.0)                                           |
|               | 447.0865 [M-H - 162]^− (9.4)                                                 | 303.0862 [M+H - Rha - Glu]^+ (34.7)                                        |
|               | 301.0676 [M-H - Rha - Glu]^−                                                 |                                                               |
| Hesperidin    | 609.1806 [M-H]^−                                                             | 649.1539 [M+K]^+ (21.6)                                                    |
|               | 463.1176 [M-H - Rha]^−                                                       | 633.1815 [M+Na]^+ (100)                                                    |
|               | 301.0711 [M-H - Rha - Glu]^−                                                 | 503.0810 [M+K - Rha]^+ (2.6)                                               |
|               |                                                                              | 487.1064 [M+K - O - Rha]^+ (1.4)                                           |
|               |                                                                              | 303.0862 [M+H - Rha - Glu]^+ (22.1)                                        |
and substitution position, and the number of dehydrated fragments is consistent with the number of hydroxyl groups on the mother nucleus, which is consistent with the literature report.\(^{(19)}\) (4) Saponin aglycone: triterpenoid saponin oleanolic acid has a \([M - H]^-\) eximer ion peak in the negative ion mode, while steroidal saponin ruscogenin has a \([M + H]^+\) excimer ion peak in the positive ion mode.

**Identification of Chemical Constituents of Sophorae Fructus**

**Identification of Flavonoids**

When analyzed the test sample according to chromatographic conditions (1), under the negative (\(-\text{Fig. 6A}\)) and positive (\(-\text{Fig. 6B}\)) ion scanning modes, the separation degree and ionization degree of each component of *Sophorae Fructus* meet the requirements. Identification of flavonoids: first, the types of flavonoids were speculated according to the characteristics of UV spectrum. Combined with the above MS rules and literature references, 84 compounds were finally identified in positive and negative ion modes, including 51 flavonoids, 12 isoflavones, 3 dihydroflavonoids, 8 organic acids and 10 amino acids, and sugars, as shown in \(-\text{Table 3}\).

Among the flavonoids, flavonol is the most abundant. Take compound 35 in \(-\text{Table 3}\) as an example to illustrate the identification process. According to the UV maxima at 260 and 353 nm, the structural type was flavonol with substitution at the C3 position. In the negative ion mode, the MS\(^2\) of the aglycon-related ions were \(m/z\) 315.0502, 300.0277, 284.0320, 269.0450, 255.0295, 243.0678, 215.0729, 125.0258, which is identified as isorhamnetin by comparison with the literature.\(^{(20)}\) Compound 35 displayed a \([M - H]^+\) ion at \(m/z\) 785.2151 and ions at \(m/z\) 639.1575 \([M - H - Rha]^-\), \(m/z\) 459.1283 \([M - H - Rha - Glu - H_2O]^-\), as well as \(m/z\) 315.0502 \([M - H - Rha - 2Glu]^-\). It was noted the presence of the \(m/z\) 459.1283 ion, which results from the loss of a hexose (180 u). This H\(_2\)O loss shows that the dihexosyl should have a 1–2 interglycosidic linkage because, as referred to above when the 1–2 bond versus the 1–6 bond was compared, the 1–6 bond is difficult to break. In the positive ion mode, compound 35 produced \([M + H]^+\) ion at \(m/z\) 787.2308 and in its MS\(^2\) fragmentation of these ions \((m/z\) 625.1698 \([M + H - Glu]^- - m/z\) 463.1243 \([M + H - 2Glu]^- - m/z\) 317.0664 \([M + H - 2Glu - Rha]^-\)) can be observed. Combined with the above flavone cleavage rules, rhamnose was bound to a phenolic hydroxyl at position C7, dihexosides with interglycosidic linkage 1–2 was substituted at position C3. Therefore, compound 35 was proposed to be isorhamnetin-3-O-sophoroside-7-O-rhamnoside by comparison with the literature.\(^{(11)}\)

**Identification of Saponins**

After analyzing the test sample according to chromatographic conditions (2), the total ion flow diagram is shown in \(-\text{Fig. 6C}\) (negative ion scanning mode) and \(-\text{Fig. 6D}\) (positive ion scanning mode). A total of 58 compounds were identified by using the above saponin cleavage rules in combination with relevant literature and reference standards, including 39 saponins, 10 phenolic acids, 3 fatty acids, 2 phenylpropa- noids, 1 flavonol, and 3 others (\(-\text{Table 4}\)).

Triterpenoid saponins are mainly contained in *Sophorae Fructus*, and the structure is mostly oleanene type. The sugar chain structure in saponins is easy to be removed during cracking. If it is a branched glycosyl group and the two terminal glycosyl groups are different, the fragment peaks that lose the two terminal glycosyl groups will appear, so it is easy to distinguish between branched glycosyl groups and straight chain glycosyl groups.\(^{(21)}\) Compound 104 in \(-\text{Table 4}\) is taken as an example to derive the cracking rule of these compounds. Compound 104 was detected at \(m/z\) 941.5151 \([M - H]^+\) in the negative ion mode. The fragment ion at \(m/z\) 795.4539 indicated the loss of a deoxyhexose residue (146 u); peaks at \(m/z\) 615.3890 \([\text{aglycone} + \text{GluA} - \text{H}_2\text{O} - \text{H}]^+\), \(m/z\) 457.3663 \([\text{aglycone} - \text{H}]^+\), and \(m/z\) 483.1363 \([\text{Rha} + \text{Glu} + \text{GluA} - \text{H}]^+\) were presented in spectra. In the positive ion mode, the characteristic fragment ions at \(m/z\) 965.5106,
Table 2 ESI-MS cleavage characteristics of six saponins

| Compounds          | Formula   | RT (min) | Mr       | m/z (ESI⁺)                                      | m/z (ESI⁺)                                      |
|--------------------|-----------|----------|----------|------------------------------------------------|------------------------------------------------|
| Asperosaponin VI   | C₄₇H₇₆O₁₈| 18.64    | 929.1000 | 963.4807 [M + Cl]⁻                                   | 455.3562 [M + H – Glc – Glc – Ara – H₂O]⁺       |
|                    |           |          |          | 927.5045 [M - H]⁻                                   | 437.3417 [M + H – Glc – Ara – 2H₂O]⁺           |
|                    |           |          |          | 603.3326 [M - H – Glc – Glc]⁻                        | 409.3485 [M + H – 2Glc – Ara – 2H₂O – CO]⁺     |
|                    |           |          |          | 471.3488 [M - H – Glc – Glc – Ara]⁻                   | 391.3341 [M + H – 2Glc – Ara – 2H₂O – CO – H₂O]⁺|
| Mogroside V        | C₆₀H₁₀₂O₂₉| 15.78    | 1,287.4300 | 1,331.7566 [M + HCOOH]⁻                               | 1,309.6475 [M + Na]⁺                              |
|                    |           |          |          | 1,321.6241 [M + Cl]⁻                                 | 1,125.6078 [M + H – Glc]⁺                         |
|                    |           |          |          | 1,285.6539 [M – H]⁻                                  | 963.5576 [M + H – 2Glc]⁺                           |
|                    |           |          |          | 1,123.5906 [M – H – Glc]⁻                             | 459.3859 [M + H – 5Glc – H₂O]⁺                  |
|                    |           |          |          | 961.5374 [M – H – 2Glc]⁻                              | 441.3770 [M + H – 5Glc – 2H₂O]⁺               |
|                    |           |          |          | 799.4830 [M – H – 3Glc]⁻                              | 423.3704 [M + H – 5Glc – 3H₂O]⁺               |
|                    |           |          |          | 637.4334 [M – H – 4Glc]⁻                              | 405.3514 [M + H – 5Glc – 4H₂O]⁺               |
|                    |           |          |          | 485.1541 [Glc + Glc + Glc – H]⁻                        |                                                 |
| Ginsenoside Re     | C₄₈H₈₂O₁₈| 15.93    | 947.1500 | 981.5267 [M + Cl]⁻                                   | 969.5428 [M + Na]⁺                              |
|                    |           |          |          | 945.5445 [M – H]⁻                                    | 789.4763 [M + Na – Glc – H₂O]⁺                  |
|                    |           |          |          | 783.4909 [M – H – Glc]⁻                               | 459.3815 [M + H – Glc – Ara – Glc – H₂O]⁺       |
|                    |           |          |          | 765.4784 [M – H – Glc – H₂O]⁻                         | 441.3770 [M + H – Glc – Ara – Glc – 2H₂O]⁺      |
|                    |           |          |          | 637.4334 [M – H – Glc – Rha]⁻                         | 423.3746 [M + H – Glc – Ara – Glc – 3H₂O]⁺     |
|                    |           |          |          | 619.4224 [M – H – Glc – Rha – H₂O]⁻                    | 405.3556 [M + H – Glc – Ara – Glc – 4H₂O]⁺     |
|                    |           |          |          | 475.3793 [M – H – Glc – Rha – Glc]⁻                     |                                                 |
| Jujuboside A       | C₅₈H₉₄O₂₆| 19.29    | 1,207.3500| 1,241.5747 [M + Cl]⁻                                  | 1,229.5935 [M + Na]⁺                              |
|                    |           |          |          | 1,206.6047 [M – H]⁻                                   | 455.3650 [M + H – Ara – 2Glc – Rha – Ara – H₂O]⁺|
|                    |           |          |          | 1,074.5632 [M – H – Ara]⁻                              | 437.3417 [M + H – Ara – 2Glc – Rha – Ara – 2H₂O]⁺|
|                    |           |          |          | 911.5027 [M – H – Ara – Glc]⁻                          |                                                 |
|                    |           |          |          | 749.4507 [M – H – Ara – 2Glc]⁻                        |                                                 |
|                    |           |          |          | 603.3880 [M – H – Ara – 2Glc – Rha]⁻                    |                                                 |
|                    |           |          |          | 471.3444 [M – H – Ara – 2Glc – Rha – Ara]⁻             |                                                 |
| Ruscogenin         | C₂₇H₄₂O₄  | 30.84    | 430.6300 | 311.1677 [M – H – 118]⁻                               | 431.3171 [M + H]⁺                               |
|                    |           |          |          | 311.1677 [M – H – 118]⁻                               | 413.3069 [M + H – H₂O]⁺                           |
|                    |           |          |          | 311.1677 [M – H – 118]⁻                               | 395.3064 [M + H – 2H₂O]⁺                         |
| Oleanolic acid     | C₃₀H₄₈O₃  | 32.65    | 456.3600 | 455.7130 [M – H]⁻                                     | 439.3678 [M + H – H₂O]⁺                           |
|                    |           |          |          | 455.7130 [M – H]⁻                                     | 411.3676 [M + H – H₂O – CO]⁺                    |
|                    |           |          |          | 455.7130 [M – H]⁻                                     | 393.3522 [M + H – H₂O – CO – H₂O]⁺            |
Fig. 5  Mass fragmentation pathways deduced of asperosaponin VI.

Fig. 6  Total ion flow diagram of *Sophorae Fructus* components in (A, C) negative ion mode and (B, D) positive ion mode.
| No. | Component name | Formula | Calculated mass (m/z) | Measured mass (m/z) | Mass error (ppm) | RT (min) | Adducts | Fragment ions (m/z, ESI) |
|-----|----------------|---------|----------------------|---------------------|-----------------|----------|---------|--------------------------|
| 1   | Arginine       | C_{6}H_{14}N_{4}O_{2} | 173.1049 | 173.1036 | –0.62  | 1.02 | [M-H]^- | (173.1036) |
| 2   | Alanine        | C_{3}H_{7}NO_{2} | 134.0464 | 134.0464 | 0.00  | 1.12 | [M+HCOO]^- | (134.0464) |
| 3   | α-Sophora      | C_{12}H_{22}O_{11} | 387.1134 | 387.1134 | 0.00  | 1.30 | [M+HCOO]^- | (387.1134) |
| 4   | Aspartic acid  | C_{6}H_{12}O_{4}N_{2} | 173.1049 | 173.1036 | –0.71  | 1.17 | [M-H]^- | (173.1036) |
| 5   | Arabinose      | C_{5}H_{10}O_{5} | 195.0510 | 195.0514 | 0.23  | 1.37 | [M+HCOO]^- | (195.0514) |
| 6   | Malic acid     | C_{4}H_{6}O_{5} | 133.0142 | 133.0137 | –0.37  | 2.17 | [M-H]^- | (133.0137) |
| 7   | Malic acid     | C_{4}H_{6}O_{5} | 133.0142 | 133.0137 | –0.37  | 2.17 | [M-H]^- | (133.0137) |
| 8   | Citric acid a  | C_{6}H_{8}O_{7} | 191.0191 | 191.0191 | 0.00  | 3.42 | [M-H]^- | (191.0191) |
| 9   | Phenylalanine  | C_{9}H_{11}NO_{2} | 164.0710 | 164.0710 | 0.00  | 4.06 | [M-H]^- | (164.0710) |
| 10  | Gallocatechin   | C_{7}H_{6}O_{5} | 171.0288 | 171.0289 | 0.05  | 4.11 | [M+H]^+ | (171.0289, 125.0219) |
| 11  | γ-Glutamyltyrosine | C_{14}H_{18}N_{2}O_{6} | 309.1088 | 309.1088 | 0.00  | 6.32 | [M-H]^- | (309.1088) |
| 12  | Tryptophan     | C_{11}H_{12}N_{2}O_{2} | 203.0826 | 203.0826 | 0.00  | 7.16 | [M-H]^- | (203.0826) |
| 13  | Gallic acid b  | C_{33}H_{40}O_{21} | 771.1989 | 771.1990 | 0.13  | 8.83 | [M-H]^- | (771.1990, 593.1495, 447.0898, 285.0403) |
| 14  | Protocatechuic acid a | C_{7}H_{6}O_{4} | 153.0193 | 153.0193 | 0.00  | 8.97 | [M-H]^- | (153.0193) |
| 15  | Methyl gallate | C_{8}H_{8}O_{5} | 183.0299 | 183.0296 | –1.64  | 10.13 | [M-H]^- | (183.0296, 169.0179, 125.0219) |
| 16  | 4-(β-D-Glucopyranosyloxy)-3-hydroxyphenyl caffeate b | C_{21}H_{22}O_{11} | 449.1083 | 449.1083 | 0.00  | 10.76 | [M-H]^- | (449.1083, 287.0553) |
| 17  | Protocatechualdehyde a | C_{7}H_{6}O_{3} | 183.0299 | 183.0301 | 1.09  | 10.86 | [M+HCOO]^+ | (183.0301) |
| 18  | 1,6-di-O-galloyl-β-D-glucose | C_{20}H_{20}O_{14} | 483.0791 | 483.0791 | 0.00  | 11.49 | [M-H]^- | (483.0791, 331.0651, 313.0550, 169.0130, 285.0369) |
| 19  | Quercetin-3-O-β-D-gentiobioside-7-O-glucoside b | C_{33}H_{40}O_{21} | 771.1989 | 771.1990 | 0.13  | 12.29 | [M-H]^- | (771.1990, 609.1498, 447.0890, 285.0403) |
| 20  | Quercetin-3-O-(2″-O-β-D-glucopyranosyl)-β-D-rutinoside-7-O-glucoside b | C_{39}H_{50}O_{25} | 917.2574 | 917.2574 | 0.00  | 12.47 | [M-H]^- | (917.2574, 755.2006, 577.1556, 446.0854, 285.0369) |
| 21  | Apigenin-7,4′-di-O-β-D-glucoside | C_{27}H_{30}O_{15} | 595.1657 | 595.1657 | 0.00  | 14.09 | [M+H]^+ | (595.1657, 433.1140, 271.0557) |
| 22  | Apigenin-7′-O-β-D-glucoside | C_{27}H_{30}O_{15} | 595.1657 | 595.1657 | 0.00  | 14.09 | [M+H]^+ | (595.1657, 433.1140, 271.0557) |
| 23  | Apigenin-7,4′-di-O-β-D-glucoside | C_{33}H_{40}O_{21} | 771.1989 | 771.1990 | 0.13  | 14.09 | [M+H]^+ | (771.1990, 609.1498, 447.0890, 285.0403) |
| 24  | Apigenin-7′-O-β-D-glucoside | C_{27}H_{30}O_{15} | 595.1657 | 595.1657 | 0.00  | 14.09 | [M+H]^+ | (595.1657, 433.1140, 271.0557) |

(Continued)
| No. | Component name | Formula | Calculated mass (m/z) | Measured mass (m/z) | Mass error (ppm) | RT (min) | Adducts | Fragment ions (m/z, ESI⁻/ESI⁺) |
|-----|----------------|---------|----------------------|---------------------|------------------|----------|---------|--------------------------------|
| 25  | Neoerociarin<sup>b</sup> | C<sub>27</sub>H<sub>12</sub>O<sub>15</sub> | 595.1668 | 595.1653 | -2.52 | 16.08 | [M − H]<sup>−</sup> | 595.1653, 431.0984, 287.0553 |
| 26  | Diosmetin-7-O-sophoroside<sup>b</sup> | C<sub>28</sub>H<sub>32</sub>O<sub>16</sub> | 669.1672 | 669.1663 | -1.35 | 16.33 | [M + HCOO]<sup>−</sup> | 623.1638, 461.1086, 445.0786, 268.0387 |
| 27  | Quercetin-3-O-(2''-O-β-D-glucopyranosyl)-β-D-rutinoside-7-O-rhamnose<sup>b</sup> | C<sub>39</sub>H<sub>50</sub>O<sub>25</sub> | 917.2568 | 917.2533 | -3.82 | 17.30 | [M − H]<sup>−</sup> | 917.2533, 771.1990, 609.1397, 461.1306, 301.0356 |
| 28  | Genistein-7-O-β-D-glucoside-4'-O-neohesperidoside<sup>b</sup> | C<sub>33</sub>H<sub>46</sub>O<sub>19</sub> | 739.2091 | 739.2086 | -0.68 | 17.88 | [M − H]<sup>−</sup> | 739.2086, 577.1654, 431.0984, 415.1070, 268.0454 |
| 29  | Kaempferol-3,7-diglucoside<sup>a</sup> | C<sub>27</sub>H<sub>32</sub>O<sub>16</sub> | 609.1461 | 609.1448 | -2.13 | 18.15 | [M − H]<sup>−</sup> | 609.1448, 447.0977, 285.0403 |
| 30  | Kaempferol-3-O-(4''-O-β-D-glucopyranosyl)-β-D-rutinoside<sup>b</sup> | C<sub>33</sub>H<sub>46</sub>O<sub>20</sub> | 755.2040 | 755.2062 | 2.91 | 18.74 | [M + H]<sup>+</sup> | 755.2062, 593.1545, 446.0854, 285.0403 |
| 31  | Apigenin-7-O-(2''-O-sophorosyl)-β-D-rutinoside<sup>b</sup> | C<sub>39</sub>H<sub>50</sub>O<sub>24</sub> | 903.2765 | 903.2797 | 3.54 | 18.90 | [M + H]<sup>+</sup> | 903.2797, 741.2186, 579.1738, 433.1140, 271.0597 |
| 32  | Ternatmoside VIII<sup>b</sup> | C<sub>39</sub>H<sub>50</sub>O<sub>24</sub> | 901.2619 | 901.2601 | -2.00 | 19.29 | [M − H]<sup>−</sup> | 901.2601, 755.2062, 593.1495, 430.0917, 284.0355 |
| 33  | Kaempferol-3-O-sophoroside-7-O-rhamnose<sup>a</sup> | C<sub>33</sub>H<sub>46</sub>O<sub>20</sub> | 757.2186 | 757.2196 | 1.32 | 19.64 | [M + H]<sup>+</sup> | 757.2196, 595.1671, 433.1140, 287.0568 |
| 34  | Isorhamnetin-3-O-(4''-O-rutinosyl)-β-D-rutinoside<sup>b</sup> | C<sub>40</sub>H<sub>52</sub>O<sub>25</sub> | 933.2870 | 933.2865 | -0.54 | 20.12 | [M + H]<sup>+</sup> | 933.2865, 787.2250, 625.1698, 463.1243, 317.0664 |
| 35  | Isorhamnetin-3-O-sophoroside-7-O- rhamnose<sup>b</sup> | C<sub>34</sub>H<sub>42</sub>O<sub>21</sub> | 785.2146 | 785.2151 | 0.64 | 20.72 | [M − H]<sup>−</sup> | 785.2151, 639.1575, 459.1283, 314.0445 |
| 36  | Kaempferol-3-O-glucoside-7-O-rutinoside<sup>b</sup> | C<sub>33</sub>H<sub>46</sub>O<sub>20</sub> | 755.2040 | 755.2062 | 2.91 | 21.03 | [M − H]<sup>−</sup> | 755.2062, 635.0911, 608.1398, 447.0933, 285.0403 |
| 37  | Dihydrokaempferol 3-O-glucoside | C<sub>21</sub>H<sub>22</sub>O<sub>11</sub> | 449.1089 | 449.1083 | -1.34 | 21.45 | [M − H]<sup>−</sup> | 449.1083, 287.0578 |
| 38  | Genistein-7-O-malonylglucoside-4'-O-glucoside | C<sub>30</sub>H<sub>32</sub>O<sub>18</sub> | 681.1661 | 681.1641 | -2.94 | 21.82 | [M + H]<sup>+</sup> | 681.1641, 433.1140, 271.0597 |
| 39  | Quercetin-3-O-β-D-glucopyranosyl(1→2)-[α-L-rhamnopyranosyl(1→6)]-β-D-glucopyranoside | C<sub>33</sub>H<sub>46</sub>O<sub>21</sub> | 773.2153 | 773.2154 | 2.46 | 22.12 | [M + H]<sup>+</sup> | 773.2154, 611.1609, 465.1011, 303.0498 |
| 40  | Quercetin 3-O-gentiobioside | C<sub>27</sub>H<sub>30</sub>O<sub>17</sub> | 627.1556 | 627.1563 | 1.12 | 23.08 | [M + H]<sup>+</sup> | 627.1563, 465.1033, 303.0494 |
| 41  | Quercetin-3-O-(6''''-O-adipoyl)-β-D-rutinoside<sup>b</sup> | C<sub>33</sub>H<sub>46</sub>O<sub>19</sub> | 739.2080 | 739.2090 | 1.35 | 23.21 | [M + H]<sup>+</sup> | 739.2090, 465.1033, 303.0494 |
| 42  | Quercetin-3-O-(6''-O-(3''''-O-arabinose)-α-L-rhamnosyl)-β-D-neohesperidoside<sup>b</sup> | C<sub>38</sub>H<sub>48</sub>O<sub>24</sub> | 887.2463 | 887.2480 | 1.92 | 23.46 | [M − H]<sup>−</sup> | 887.2480, 741.1857, 609.1448, 301.0356 |
| No. | Component name | Formula | Calculated mass (m/z) | Measured mass (m/z) | Mass error (ppm) | RT (min) | Adducts | Fragment ions (m/z, ESI⁺/ESI⁻) |
|-----|----------------|---------|----------------------|---------------------|------------------|----------|---------|---------------------------------|
| 43  | Compactin b    | C_{27}H_{30}O_{16} | 611.1607 | 611.1609 | 0.33 | 23.67 | [M + H]^+ | 611.1609, 449.1079, 287.0559 |
| 44  | Genistin a     | C_{21}H_{20}O_{10} | 431.0984 | 431.0984 | 0    | 24.03 | [M – H]⁻ | 431.0984, 269.0551 |
| 45  | Apigenin-7-O-(3′′′′′-O-acetyl)-β-D-rutinoside | C_{27}H_{30}O_{15} | 619.1668 | 619.1690 | 3.55 | 24.85 | [M – H]⁻ | 619.1690, 431.0984, 268.0387 |
| 46  | Kaempferol-3-O-(2′′′-O-β-D-glucopyranosyl)-β-D-rutinoside a | C_{33}H_{40}O_{20} | 757.2186 | 757.2182 | -0.53 | 25.04 | [M + H]^+ | 757.2182, 595.1671, 449.1071, 287.0672 |
| 47  | Rhamnocitrin-3-O-β-D-glucopyranosyl(1→2)-D-Apio-α-D-furanoside-4′′-O-glucose | C_{33}H_{40}O_{20} | 757.2186 | 757.2182 | -0.53 | 25.31 | [M + H]^+ | 757.2182, 595.1622, 463.1243, 301.0723 |
| 48  | Isorhamnetin-3-O-sophoroside | C_{28}H_{32}O_{17} | 641.1712 | 641.1703 | -1.40 | 25.94 | [M + H]^+ | 641.1703, 479.1197, 317.0664 |
| 49  | Kaempferol-3-O-sophoroside a | C_{27}H_{30}O_{16} | 609.1461 | 609.1448 | -2.13 | 26.12 | [M – H]⁻ | 609.1448, 429.0819, 285.0507 |
| 50  | Multiflorin B | C_{27}H_{30}O_{15} | 593.1512 | 593.1495 | -2.87 | 26.58 | [M – H]⁻ | 593.1495, 431.0984, 284.0320 |
| 51  | Naringin a | C_{27}H_{30}O_{14} | 579.1719 | 579.1736 | 2.94 | 27.05 | [M – H]⁻ | 579.1736, 433.1239, 271.0601 |
| 52  | Kaempferol-3-O-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranoside | C_{27}H_{30}O_{15} | 593.1512 | 593.1495 | -2.87 | 27.73 | [M – H]⁻ | 593.1495, 447.0933, 429.0776, 285.0403 |
| 53  | 6′-β-D-Xylosegenistin | C_{26}H_{28}O_{14} | 587.1377 | 587.1366 | -1.87 | 28.05 | [M + Na]^+ | 587.1366, 433.1181, 271.0609 |
| 54  | Rutin a | C_{27}H_{30}O_{12} | 633.1432 | 633.1448 | 2.53 | 28.16 | [M + Na]^+ | 633.1448, 465.1033, 303.0565 |
| 55  | Isoquercitrin a | C_{27}H_{30}O_{12} | 463.0882 | 463.0902 | 4.32 | 28.59 | [M – H]⁻ | 463.0902, 300.0323 |
| 56  | Kaempferide-3-O-glucoside | C_{27}H_{30}O_{11} | 463.1235 | 463.1243 | 1.73 | 28.66 | [M + H]^+ | 463.1243, 301.0723 |
| 57  | Sophoricid a | C_{27}H_{30}O_{10} | 433.1129 | 433.1140 | 2.54 | 28.74 | [M + H]^+ | 433.1140, 271.0630 |
| 58  | Helianeanoside A b | C_{33}H_{34}O_{19} | 725.1935 | 725.1947 | 1.66 | 30.06 | [M – H]⁻ | 725.1947, 593.1495, 431.0984, 285.0403 |
| 59  | Sophorobioside b | C_{27}H_{30}O_{14} | 601.1513 | 601.1518 | -2.50 | 30.28 | [M + Na]^+ | 601.1518, 579.1738, 433.1140, 271.0597 |
| 60  | Apigenin-7-O-neohesperidoside | C_{27}H_{30}O_{14} | 577.1563 | 577.1556 | -1.21 | 30.83 | [M – H]⁻ | 577.1564, 431.0984, 413.0867, 269.0450 |
| 61  | Apigenin-7-O-rutinoside | C_{27}H_{30}O_{14} | 577.1563 | 577.1556 | -1.21 | 31.43 | [M – H]⁻ | 577.1556, 431.0984, 269.0450 |
| 62  | Apigenin-4′-O-rutinoside b | C_{27}H_{30}O_{14} | 577.1563 | 577.1556 | -1.21 | 31.81 | [M – H]⁻ | 577.1556, 431.0984, 268.0387 |
| 63  | Kaempferol-3-O-rutinoside a | C_{27}H_{30}O_{15} | 595.1657 | 595.1671 | 2.35 | 32.62 | [M + H]^+ | 595.1721, 449.1071, 287.0603 |
| 64  | Apigenin-7′-O-gentiobioside | C_{27}H_{30}O_{15} | 593.1512 | 593.1495 | -2.87 | 33.02 | [M – H]⁻ | 593.1495, 447.0933, 269.0450 |
| 65  | Isorhamnetin-3-O-β-D-rutinoside a | C_{28}H_{32}O_{16} | 625.1763 | 625.1749 | -2.24 | 33.31 | [M + H]^+ | 625.1749, 479.1197, 317.0664 |
| 66  | Diosmetin-7-O-glucopyranosyl(6→1)-O-arabinopyranoside | C_{27}H_{30}O_{15} | 593.1512 | 593.1495 | -2.87 | 33.80 | [M – H]⁻ | 593.1495, 461.1102, 299.0576 |
| 67  | Apigenin-7-O-[6′′′′′′-O-acetyl-2′′′′′′-O-acetyl-β-D-glucopyranosyl]-β-D-glucoside b | C_{31}H_{34}O_{17} | 677.1723 | 677.1702 | -3.11 | 34.45 | [M – H]⁻ | 677.1702, 473.1059, 268.0372 |

(Continued)
| No. | Component name                                                                 | Formula          | Calculated mass (m/z) | Measured mass (m/z) | Mass error (ppm) | RT (min) | Adducts                  | Fragment ions (m/z, ESI⁻/ESI⁺) |
|-----|---------------------------------------------------------------------------------|------------------|-----------------------|---------------------|------------------|----------|--------------------------|-------------------------------|
| 68  | Apigenin-7-O-(4,6-di-O-acetyl)-β-D-glucoside-4’-O-β-D-glucoside<sup>b</sup>      | C<sub>31</sub>H<sub>34</sub>O<sub>17</sub> | 723.1778              | 723.1840            | 8.58             | 34.62    | [M + HCOO]<sup>−</sup>   | 723.1840, 677.1646, 431.0989, 268.0372 |
| 69  | 6’-O-Acetylshrrarinin<sup>b</sup>                                                | C<sub>29</sub>H<sub>34</sub>O<sub>15</sub> | 621.1825              | 621.1818            | -1.13            | 34.72    | [M - H]<sup>−</sup>     | 621.1826, 473.1068, 271.0601 |
| 70  | Genistein-4’-O-malonylglucoside                                                 | C<sub>24</sub>H<sub>22</sub>O<sub>13</sub> | 519.1133              | 519.1116            | -3.28            | 35.04    | [M + H]<sup>+</sup>     | 519.1116, 271.0597 |
| 71  | Kakkanim                                                                       | C<sub>27</sub>H<sub>30</sub>O<sub>14</sub> | 579.1708              | 579.1689            | -3.28            | 35.31    | [M + H]<sup>+</sup>     | 579.1689, 447.1278, 285.0774 |
| 72  | Euryanoside<sup>b</sup>                                                         | C<sub>29</sub>H<sub>32</sub>O<sub>15</sub> | 619.1668              | 619.1639            | -4.68            | 35.48    | [M - H]<sup>−</sup>     | 619.1639, 473.1068, 269.0450 |
| 73  | Acacetin-5-O-α-L-mannopyranosyl(1→2)-α-L-rhamnopyranoside<sup>b</sup>           | C<sub>28</sub>H<sub>32</sub>O<sub>13</sub> | 575.1770              | 575.1411            | -6.24            | 36.11    | [M - H]<sup>−</sup>     | 575.1411, 431.0984, 283.0600 |
| 74  | Apigenin-5-O-acetyl-7-O-neohesperidoside<sup>b</sup>                            | C<sub>29</sub>H<sub>32</sub>O<sub>15</sub> | 619.1668              | 619.1639            | -4.68            | 36.74    | [M - H]<sup>−</sup>     | 619.1639, 473.1068, 311.0552, 269.0450 |
| 75  | Apigenin-7-O-rhamnoside                                                         | C<sub>21</sub>H<sub>20</sub>O<sub>9</sub>  | 415.1035              | 415.1028            | -1.69            | 37.22    | [M + H]<sup>+</sup>     | 415.1028, 268.0387 |
| 76  | Acacetin-7-(6-malonylglucoside)                                                 | C<sub>25</sub>H<sub>24</sub>O<sub>13</sub> | 555.1115              | 555.1107            | -1.44            | 37.72    | [M + Na]<sup>+</sup>   | 555.1107, 285.0729 |
| 77  | Apigenin-7,4’-di-O-rhamnoside<sup>b</sup>                                      | C<sub>27</sub>H<sub>30</sub>O<sub>13</sub> | 561.1614              | 561.1620            | 1.07             | 38.12    | [M - H]<sup>−</sup>     | 561.1620, 415.1063, 268.0400 |
| 78  | Genistein<sup>a</sup>                                                           | C<sub>15</sub>H<sub>10</sub>O<sub>5</sub>  | 271.0601              | 271.0597            | -1.48            | 38.46    | [M + H]<sup>+</sup>     | 271.0601 |
| 79  | Apigenin-7-O-α-L-mannopyranosyl (1→3)-α-L-rhamnopyranoside<sup>b</sup>         | C<sub>27</sub>H<sub>30</sub>O<sub>13</sub> | 561.1614              | 561.1620            | 1.07             | 38.58    | [M - H]<sup>−</sup>     | 561.1692, 415.1063, 397.0893, 269.0484 |
| 80  | Diosmetin                                                                       | C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>  | 299.0561              | 299.0570            | 3.01             | 39.69    | [M - H]<sup>−</sup>     | 299.0570, 284.0320, 255.0295 |
| 81  | Acacetin                                                                        | C<sub>15</sub>H<sub>10</sub>O<sub>5</sub>  | 283.0612              | 283.0600            | -4.24            | 40.36    | [M - H]<sup>−</sup>     | 283.0600, 255.0295, 242.9433 |
| 82  | Kaempferol<sup>a</sup>                                                          | C<sub>15</sub>H<sub>10</sub>O<sub>5</sub>  | 287.0550              | 287.0559            | 3.14             | 40.71    | [M + H]<sup>+</sup>     | 287.0559 |
| 83  | Baicailein<sup>a</sup>                                                          | C<sub>15</sub>H<sub>10</sub>O<sub>5</sub>  | 269.0455              | 269.0450            | -1.86            | 41.11    | [M - H]<sup>−</sup>     | 269.0450 |
| 84  | Apigenin<sup>a</sup>                                                            | C<sub>15</sub>H<sub>10</sub>O<sub>5</sub>  | 269.0455              | 269.0450            | -1.86            | 41.41    | [M - H]<sup>−</sup>     | 269.0450 |

<sup>a</sup>Compared with reference substance.
<sup>b</sup>Be first found in Sophora.
| No. | Component name                                              | Formula                     | RT (min) | Adducts                        | Mass (m/z) | Calculated mass (m/z) | Measured mass (m/z) | Mass error (ppm) | Fragment ions (m/z, ESP/ESI) |
|-----|-------------------------------------------------------------|-----------------------------|----------|--------------------------------|------------|-----------------------|--------------------|------------------|-------------------------------|
| 85  | Gallic acid-O-glucoside (isomer)                           | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 86  | Gallic acid-O-diglucoside                                  | C_{17}H_{14}O_{16}           | 3.45     | -M–H+                         | 277.0511   | 276.0511              | 277.0511           | 10.95            | [M–H]+ 185.0134, 149.0050, 103.0063 |
| 87  | 5-Hydroxybenzoic acid–glucoside                           | C_{17}H_{14}O_{17}           | 3.52     | -M–H, [M+Na]+                 | 347.0545   | 347.0577              | 347.0545           | 2.97             | [M+Na]+ 211.0100, 171.0097, 125.0021 |
| 88  | 1-p-Nitro-phenyl-3,4,5-trihydroxybenzoyl acid              | C_{17}H_{16}O_{18}           | 3.58     | -M–H+                         | 347.0545   | 347.0577              | 347.0545           | 2.97             | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 89  | 3,5-Dihydroxy-4-(3,4,5-trihydroxybenzoyl)                 | C_{17}H_{16}O_{18}           | 3.58     | -M–H+                         | 347.0545   | 347.0577              | 347.0545           | 2.97             | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 90  | Gallic acid-O-glucoside (isomer)                           | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 91  | Digallic acid                                              | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 92  | 3,5-Dihydroxy-4-(3,4,5-trihydroxybenzoyl)                 | C_{17}H_{16}O_{18}           | 3.58     | -M–H+                         | 347.0545   | 347.0577              | 347.0545           | 2.97             | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 93  | Amygdalinic acid                                           | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 94  | 2,3-Dihydroxy-4-(3,4,5-trihydroxybenzoyl)                 | C_{17}H_{16}O_{18}           | 3.58     | -M–H+                         | 347.0545   | 347.0577              | 347.0545           | 2.97             | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 95  | Everlastoside B                                           | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 96  | Everlastoside B                                           | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 97  | Pothabanoside C                                            | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 98  | Tabernosine D                                             | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 99  | Dr-Gal-O-galactopyranosyl-(1-4)–O-glucopyranosyl-(1-4)–D-  | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 100 | Isoflavone 1                                               | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 101 | Isoflavone 1                                               | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 102 | Isoflavone 1                                               | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |
| 103 | Polybosaponin A                                           | C_{17}H_{14}O_{15}           | 3.41     | -M–H+                         | 288.0589   | 287.0589              | 288.0589           | 10.66            | [M–H]+ 211.0100, 171.0097, 125.0021 |

(Continued)
| No. | Component name | Formula | Calculated mass (m/z) | Measured mass (m/z) | Mass error (ppm) | RT (min) | Adducts | Fragment ions (m/z, ESI+/ESI−) |
|-----|----------------|---------|----------------------|-------------------|-----------------|----------|---------|-------------------------------|
| 104 | Azukisaponin V  | C48H76O18 | 941.5115           | 941.5151         | 3.83            | 19.01    | [M − H]− | 941.5151, 795.4539, 615.3890, 457.3663, 441.3744, 423.3672, 405.3513 |
| 105 | Azukisaponin II | C42H68O14 | 795.4536           | 795.4539         | 0.38            | 19.33    | [M − H]− | 795.4539, 633.1541, 617.4020, 441.3744, 423.3627, 405.3471, 395.0494 |
| 106 | Dehydrosoyasaponin I | C48H76O18 | 941.5104           | 941.5088         | −1.70           | 19.67    | [M + H]⁺ | 941.5088, 795.4539, 633.3990, 457.3667, 439.3549, 421.3438, 403.3315, 395.0746 |
| 107 | Abrisaponin I   | C48H74O20 | 971.4846           | 971.4894         | 4.94            | 19.87    | [M + H]⁺ | 971.4894, 825.4259, 649.4018, 469.3304, 451.3204, 433.1133, 405.3430 |
| 108 | Umbellatoside A  | C48H76O19 | 979.4878           | 979.4835         | −4.39           | 19.96    | [M + Na]⁺ | 979.4835, 819.4411, 649.3965, 473.3636, 455.3542, 437.3389, 421.3444, 391.1188 |
| 109 | Astragaloside VIII | C47H76O17 | 935.4980           | 935.4990         | 1.07            | 20.23    | [M + Na]⁺ | 935.4990, 789.4240, 633.1387, 441.3744, 423.3627, 405.3513 |
| 110 | Putranoside C    | C47H72O19 | 963.4929           | 963.4963         | 3.53            | 20.65    | [M + Na]⁺ | 963.4963, 779.4532, 633.4012, 457.3692, 439.3565, 421.3480, 391.1228 |
| 111 | Yunganoside D1   | C48H74O19 | 977.4722           | 977.4739         | 1.74            | 21.03    | [M + Na]⁺ | 977.4739, 831.4089, 633.4012, 453.3394, 435.3260 |
| 112 | Soyasaponin Bg   | C47H74O17 | 933.4824           | 933.4748         | −8.15           | 21.08    | [M + Na]⁺ | 933.4788, 765.4444, 633.4012, 453.3455, 439.3565 |
| 113 | (3β,4β)-23-hydroxy-22-oxoolean-12-en-3-yl-O-6-deoxy-a-L-mannopyranosyl-(1→2)-O-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosiduronic acid | C48H76O18 | 963.4929           | 963.4900         | −3.01           | 21.14    | [M + Na]⁺ | 963.4900, 817.4276, 633.4012, 439.3565, 421.3486 |
| 114 | Soybean phenol A  | C42H66O14 | 793.4380           | 793.4404         | 3.03            | 21.25    | [M − H]− | 793.4404, 631.3856, 455.0141 |
| 115 | Glycryrrhetic acid-3-O-Glucopyranosiduronic acid-29-O-glucoside | C42H66O15 | 831.4143           | 831.4148         | 0.61            | 21.62    | [M + Na]⁺ | 831.4148, 647.4064, 471.3449, 453.3351, 435.3260, 424.1924, 407.3350 |
| 116 | Uralisaponin X    | C50H142O22 | 1,049.4569         | 1,049.4613       | 4.19            | 21.81    | [M + Na]⁺ | 1049.4613, 741.3734, 704.2580, 565.3466, 525.1416, 507.1360, 481.0825, 457.2379, 439.3565, 421.3444, 403.3354 |
| 117 | (3β,4β,22β)-22,23-Dihydroxy-11-oxoolean-12-en-3-yl-O-6-deoxy-a-L-mannopyranosyl-(1→2)-O-β-D-galactopyranosyl-(1→2)-β-D-glucopyranosiduronic acid | C48H76O19 | 979.4878           | 979.4835         | −4.39           | 22.23    | [M + Na]⁺ | 979.4835, 833.4841, 671.3387, 455.3542, 445.1306, 423.3585, 409.1622 |
| 118 | Wistariasaponin D | C47H74O17 | 909.4853           | 909.4829         | −2.64           | 22.46    | [M − H]− | 909.4829, 763.4296, 631.3805, 455.3504 |
| 119 | Glycryrrhizoside B | C47H72O18 | 947.4616           | 947.4581         | −3.70           | 22.95    | [M + Na]⁺ | 947.4581, 801.3914, 669.3496, 471.3449, 453.3351, 435.3260 |
| 120 | (3β,4α,22β)-22,23-Dihydroxyolean-12-en-3-yl-O-β-D-arabinofuranosyl-(1→2)-O-6-deoxy- | C47H76O17 | 935.4980           | 935.4927         | −5.67           | 23.84    | [M + Na]⁺ | 935.4927, 781.4766, 635.3337, 441.3658, 423.3585, 405.3471 |
### Table 4 (Continued)

| No. | Component name                                                                 | Formula      | Calculated mass (m/z) | Measured mass (m/z) | Mass error (ppm) | RT (min) | Adducts          | Fragment ions (m/z, ESI⁻/ESI⁺) |
|-----|---------------------------------------------------------------------------------|--------------|-----------------------|---------------------|------------------|----------|------------------|--------------------------------|
| 121 | Soyasaponin I                                                                   | C₄₈H₇₈O₁₈   | 943.5261              | 943.5261            | 0                | 23.99    | [M + H]⁺        | 943.5261, 797.4693, 635.4162, 441.3781, 423.3627 |
| 122 | Soyasaponin III                                                                 | C₄₂H₆₈O₁₄   | 795.4536              | 795.4539            | 0.38             | 24.69    | [M - H]⁻        | 795.4539, 633.3983, 455.3504 |
| 123 | Kaikasaponin III                                                                | C₄₈H₇₈O₁₇   | 949.5137              | 949.5123            | -1.48            | 25.42    | [M + Na]⁺       | 949.5123, 803.4489, 601.4117, 425.3773, 407.3681 |
| 124 | β-D-glucopyranosiduronic acid deriv-oleanane                                    | C₄₈H₇₈O₁₇   | 949.5137              | 949.5123            | -1.48            | 25.87    | [M + Na]⁺       | 949.5123, 803.4431, 657.3563, 633.4012, 457.3648, 437.1935, 425.3773, 407.3681 |
| 125 | Pisumsaponin II                                                                 | C₄₈H₇₈O₁₈   | 939.4959              | 939.4937            | -2.34            | 25.97    | [M - H]⁻        | 939.4937, 793.4346, 631.3856, 455.3504 |
| 126 | Kaikasaponin I                                                                  | C₄₂H₆₈O₁₃   | 803.4558              | 803.4539            | -1.37            | 26.33    | [M + Na]⁺       | 803.4547, 641.2833, 425.3773, 405.3513 |
| 127 | Azukisaponin I                                                                  | C₄₂H₆₈O₁₃   | 779.4587              | 779.4567            | -2.57            | 26.65    | [M - H]⁻        | 779.4567, 617.4016, 441.3724 |
| 128 | Kakkasaponin I                                                                  | C₄₂H₆₈O₁₃   | 895.5061              | 895.5054            | -0.78            | 26.92    | [M - H]⁻        | 895.5054, 749.4451, 599.3972, 441.3724 |
| 129 | Phaseoside IV                                                                   | C₄₈H₇₈O₁₇   | 947.4980              | 947.4958            | -2.32            | 27.09    | [M + Na]⁺       | 947.4958, 803.4025, 641.4025, 617.4020, 441.3744, 423.3627, 405.3513 |
| 130 | Kakasaponin II                                                                  | C₄₂H₆₈O₁₃   | 777.4431              | 777.4463            | 4.12             | 27.91    | [M - H]⁻        | 777.4463, 615.3941, 437.3435 |
| 131 | Zygophyloside M⁺                                                                 | C₄₀H₆₂O₁₃   | 795.4536              | 795.4539            | 0.38             | 28.16    | [M + HCOO]⁻     | 795.4539, 793.4346, 631.3856, 455.3504 |
| 132 | Kakkasaponin III                                                                | C₄₂H₆₂O₁₆   | 917.4875              | 917.4889            | 1.53             | 28.39    | [M + Na]⁺       | 917.4889, 749.4507, 617.4071, 441.3701, 423.3627, 405.3471 |
| 133 | Paradoxoside E⁺                                                                  | C₃₇H₅₂O₁₁   | 699.3720              | 699.3745            | 3.58             | 28.64    | [M + Na]⁺       | 699.3582, 471, 453.1652, 437.2020, 407.3681 |
| 134 | Presenegenin                                                                     | C₃₀H₄₆O₇    | 563.3226              | 563.3226            | 0                | 29.44    | [M + HCOO]⁻     | 563.3226, 502.2917, 311.1677, 265.1462 |
| 135 | Paritriside C⁺                                                                   | C₄₁H₆₄O₁₂   | 771.4295              | 771.4313            | 2.33             | 29.59    | [M + Na]⁺       | 771.4313, 609.3352, 441.3701, 423.3627, 405.3471 |
| 136 | Aspacochinoside O⁺                                                               | C₃₃H₅₂O₁₂   | 641.3532              | 641.3506            | -4.06            | 29.95    | [M + H]⁺        | 641.3506, 479.2936, 317.1825, 301.0718, 279.2312 |
| 137 | Coronaric acid                                                                   | C₁₈H₃₂O₃    | 295.2279              | 295.2259            | -0.78            | 30.31    | [M - H]⁻        | 295.2259, 265.1462 |
| 138 | Δ⁵-Pregnen-20β-ol-3-one glucoside⁺                                                | C₂₁H₂₄O₇    | 479.3003              | 479.2981            | -0.49            | 30.40    | [M + H]⁺        | 479.2981, 318.2985, 301.0789, 281.2932 |
| 139 | Oleanonic acid                                                                  | C₃₁H₅₂O₃    | 453.3374              | 453.3346            | -0.86            | 31.03    | [M - H]⁻        | 453.3316, 325.1842, 285.1703 |
| 140 | Linolenic acid                                                                  | C₁₈H₃₂O₂    | 277.2173              | 277.2166            | -0.32            | 32.56    | [M - H]⁻        | 277.2166, 251.1630, 99.9244 |
| 141 | Oleanolic acidb                                                                  | C₃₀H₄₈O₃    | 455.3531              | 455.3548            | 0.74             | 32.65    | [M - H]⁻        | 455.3548, 325.1842, 271.2271 |
| 142 | Methyl 9-hexadecenoate                                                          | C₁₃H₂₂O₂    | 269.2475              | 269.2500            | 9.29             | 32.96    | [M + H]⁺        | 269.2500, 255.2637, 184.0740 |

*Be first found in *Sophora*.

*bCompared with reference substance.
819.4528, 617.4071, 441.3744, 423.3627, 405.3513 corresponded to [M + Na]⁺, [M + Na – 146]⁺, [M + H – 146–162–H₂O]⁺, [M + H – 146–162–176–H₂O]⁺, [M + H – 146–162–176–2H₂O]⁺, [M + H – 146–162–176–3H₂O]⁺, according to the above rules of saponins, there are three hydroxyl groups in the parent nucleus. Combined with Scifinder database and related literature, it was speculated that the compound may be azukisaponin V.

Conclusion

In this experiment, the UPLC-Q-TOF-MS/MS method was used to quickly characterize the chemical components of *Sophora Fructus* in positive and negative ion modes. The cracking rules of main flavone glycosides and saponins, which were preliminarily discussed, were helpful to improve the structural analysis efficiency and provide reference for the rapid screening and identification of flavonoids and saponins. From the data presented, 142 compounds were analyzed and inferred, including 67 saponins. From the data presented, 142 compounds were analyzed and inferred, including 67 saponins. From the structural analysis of known compounds by traditional separation and purification methods is avoided, which is conducive to saving resources, increasing the discovery probability of new compounds, and effectively improving work efficiency. It provides ideas and methods for the basic research and new drug development of traditional Chinese medicine and other complex substrates.

Supporting Information

The chemical structures of the 32 reference substances can be seen in the Supporting Information (∗Fig. S1 [online only]).

Conflicts of Interests

None declared.

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