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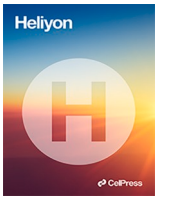

Research article

Comprehensive characterization of the chemical constituents of Lianhua Qingwen capsule by ultra high performance liquid chromatography coupled with Fourier transform ion cyclotron resonance mass spectrometry

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ABSTRACT

Lianhua Qingwen capsule is a famous traditional Chinese medicine (TCM) prescription that is widely used for the treatment of respiratory diseases in China. To facilitate in-depth and global characterization of the chemical constituents of Lianhua Qingwen capsule, a profiling method based on ultra-high performance liquid chromatography coupled with Fourier transform ion cyclotron resonance mass spectrometry (UHPLC-FT-ICR-MS) was applied in both positive and negative ion modes for the comprehensive characterization of the chemical profiles of Lianhua Qingwen capsule. A total of 596 compounds were identified or tentatively characterized, including 137 flavonoids, 46 phenylpropanoids, 43 phenylethanoid glycosides, 145 terpenoids, 83 organic acids and their derivatives, 15 quinones, 39 alkaloids, 32 alcohol glycosides and 56 other compounds. Thus, this results widely extended and enriched the chemical constituents of Lianhua Qingwen capsule, which will provide comprehensive and valuable information for its quality control and further pharmacological study, facilitate understanding the effective substance and pharmacodynamic material basis, thereby providing a solid foundation for further development of the Lianhuaqingwen capsule.

1. Introduction

Lianhua Qingwen capsule is based on two traditional Chinese medicine prescriptions (TCMPs) named Maxingshigan decoction (as recorded in ShangHanLun in the Han Dynasty) and Yinqiao powder (as recorded in WenBingTiaoBian in the Qing Dynasty) of Chinese history, respectively [1]. Lianhua Qingwen capsule is composed of 13 herbal medicines [1]: Forsythiae Fructus (Lianqiao), Lonicerae Japonicae Flos (Jinyinhua), Ephedrae Herba Praeparata Cum Melle (Zhimahuang), Armeniacae Semen Amarum Tostum (Chaokuxingren), Gypsum Fibrosum (Shigao), Isatidis Radix (Banlangen), Dryopteridis Crassirhizomatis Rhizoma (Mianmaguanzhong), Houttuyniae Herba (Yuxingcao), Pogostemonis Herba (Guanghuoxiang), Rhei Radix et Rhizoma (Dahuang), Rhodiolae Crenulatae Radix et Rhizoma (Hongjingtian), Menthol (Bohenao), and Glycyrrhizae Radix et Rhizoma (Gancao). Lianhuaqingwen capsule possesses the functions of clearing away heat and detoxifying the lungs, and it can also be applied clinically to treat patients presenting with the symptoms of fever and respiratory diseases. Lianhua Qingwen capsule possesses anti-inflammatory [2] and anti-influenza

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activities against IBV [2] , H7N9 [3], H1N1 [4], and SARS-CoV-2 [5], which is widely used for the treatment of COVID-19 [6–9]. Owing to its increasing success in the prevention and treatment of respiratory diseases, considerable attention has been paid worldwide to the Lianhua Qingwen capsule.

Traditional Chinese medicine (TCM) plays a non-negligible role in the prevention and treatment of diseases. The TCM formula has received more attention from researchers due to its remarkable therapeutic effectiveness in recent times. The TCM formula is composed of different herbal medicines with complex chemical compositions and presents synergistic effects via multi-components and multi-target mechanism. Therefore, it has become crucial to comprehensively characterize its chemical profile so as to elucidate the effective material basis. According to past reports on the analysis of the Lianhua Qingwen capsule, 61 compounds [10], 104 compounds [11] and 185 compounds [12] were unambiguously or tentatively identified, respectively. As a complicated prescription consisting of 13 herbal medicines, the actual chemical constituents of the Lianhua Qingwen capsule remain to be elucidated, albeit the inherent variety of compounds presents significant challenges in terms of separation and detection techniques for the rapid characterization of the chemical constituents. Thus, a rapid, sensitive, and accurate analytical method is necessary and urgent for the comprehensive chemical composition characterization of the Lianhua Qingwen capsule.

Modern analytical techniques have been applied to investigate the chemical constituents of TCM prescriptions. Ultra-high performance liquid chromatography-high-resolution mass spectrometry (UHPLC-HRMS) stands out from the other techniques in terms of the analysis of chemical components in TCM, due to the advantages of separation time, sensitivity, mass accuracy, resolution, and abundant information. To date, Fourier-transformed ion cyclotron resonance mass spectrometry (FT-ICR-MS) with a high resolution and unsurpassed mass measurement accuracy is a powerful and representative instrument in the mass spectrum fields [13–17]. UHPLC combined with FT-ICR-MS (UHPLC-FT-ICR-MS) is a powerful analytical technique for detecting and tentatively characterizing multi-components owing to its rapid elution, high sensitivity, high mass accuracy, high resolution, and abundance information [18–21].

In the present study, a method based on UHPLC-FT-ICR-MS/MS was applied for the rapid, sensitive, and accurate characterization of various chemical components of the Lianhua Qingwen capsule. A total of 596 compounds were identified or tentatively characterized. Results of this investigation were expected to improve the quality control, promote the pharmacological study and expand the clinical applications of the Lianhua Qingwen capsule.

2. Materials and methods

2.1. Chemicals and reagents

Lianhua Qingwen capsule (Lot No. B2008172) were obtained from Yiling Pharmaceutical Co., Ltd. (Shijiazhuang, China). Reference compounds (purity>98 %) of chlorogenic acid, esculetin, caffeic acid, luteolin, apigenin, liquiritigenin, isoliquiritigenin, liquiritin, isoliquiritin, glycyrrhizic acid and glycyrrhetinic acid were purchased from Chengdu Must Bio-Technology Co., Ltd (Chengdu, China). Acetonitrile and formic acid of HPLC grade were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Purified water was provided from Hangzhou Wahaha Corporation (Hangzhou, China).

2.2. Sample preparation

0.35 g of Lianhua Qingwen capsule was accurately measured, then respectively added into 7 mL water and methanol with ultrasonic treatment for 0.5 h, the water and methanol extract of Lianhua Qingwen capsule was prepared by diluting to a final concentration of 0.05 g/mL, subsequently the water and methanol extract of Lianhua Qingwen capsule were filtered through a 0.22 μm filter membrane for further analysis.

The standard stock solutions were prepared by dissolving chlorogenic acid, esculetin, caffeic acid, luteolin, apigenin, liquiritigenin, isoliquiritigenin, liquiritin, isoliquiritin, glycyrrhizic acid and glycyrrhetinic acid in methanol, respectively. And then the proper amount of stock solution of each reference substance was taken, mixed and finally diluted to an appropriate concentration which was stored at 4 °C for the following analysis.

2.3. Instruments and analytical conditions

Liquid chromatography analysis was carried out on an Agilent 1260 UPLC system (Agilent, USA). An ACQUITY UPLC HSS T3 column (2.1 mm × 100 mm, 1.8 μm, Waters, Ireland) being protected by an ACQUITY UPLC HSS T3 VanGuard Pre-Column (2.1 mm × 5 mm, 1.8 μm, Waters, Ireland) was utilized at 35 °C. The mobile phase system was composed of 0.1% formic acid in water (A) and acetonitrile (B). The gradient condition of the mobile phase was as following: 8% to 20%B (0–2 min); 20% to 50%B (2–20 min); 50% to 98%B (20–26 min); an isocratic elution of B (26–33 min), at a flow rate of 0.30 mL/min. The injection volume was 10 μL.

The UHPLC-FT-ICR-MS/MS detection was carried out on a Bruker Solarix 7.0T FT-ICR mass pectrometer coupled with an ESI interface. The ESI source was operated in positive-ionization and negative-ionization mode. The capillary voltage is set at 4.5 kV, the endplate offset is set at 500 V, dry gas flow is set at 8 L/min, dry gas temperature is set at 200 °C, nebulizer gas pressure is set at 4 bar. The collision gas and nebulizing gas were high-purity argon (Ar) and high-purity nitrogen (N_2), respectively. Full-scan analysis was scanned from a mass range of m/z 100–1200. And the collision energy was initially set at 5 eV and then modified to obtain the

representative fragment ions. Bruker Compass Hystar (version 4.1, Bruker Daltonics, Germany) and Fourier Transform Mass Spectrometer Control (version 2.1, Bruker Daltonics, Germany) were used for instrument control and data acquisition. Data Analysis Software (version 4.4; Bruker Daltonics, Germany) was used for data analysis.

3. Results and discussion

3.1. Chemical profiling of Lianhua Qingwen capsule

The representative base peak intensity chromatograms in positive and negative modes of Lianhua Qingwen capsule water and methanol extract were shown in Figs. 1 and 2. The difference between water extract and methanol extract is mainly in the contents of compounds. Water and methanol extract of Lianhua Qingwen capsule were both used to get comprehensive information of chemical compounds in Lianhua Qingwen capsule. In total, 596 chemical constituents, including 137 flavonoids, 46 phenylpropanoids, 43 phenylethanoid glycosides, 145 terpenoids, 83 organic acids and their derivatives, 15 quinones, 39 alkaloids, 32 alcohol glycosides and 56 other phytochemicals, were unambiguously identified or tentatively characterized in Lianhua Qingwen capsule by UHPLC-FT-ICR-MS method. Among them, chlorogenic acid, esculetin, caffeic acid, luteolin, apigenin, liquiritigenin, isoliquiritigenin, liquiritin, isoliquiritin, glycyrrhizic acid and glycyrrhetinic acid were unambiguously identified based on data comparing with the reference compounds. Besides, the chemical constituents were tentatively characterized based on retention time, accurate molecular mass and MS^2 data [11–13,18–30]. The retention time, accurate mass weights of the precursor negative and positive ions, predicted molecular formula, mass error and fragment ions are summarized in Table 1. The chemical structures of major constituents are shown in Fig. S1.

3.1.1. Flavonoids

Flavonoids, for example, isoliquiritigenin possesses effectiveness of anti-inflammatory [31]. Flavonoids in Lianhua Qingwen capsule mainly include flavones, isoflavones, flavonols, flavanones, chalcones, and isoflavans.

The identifications of rutin and kaempferol were taking as the examples of flavonols for illustration. Compound 199 with a retention time of 7.81 min generated the precursor ion of $[M+H]^+$ at *m/z* 611.16097, indicating the molecular formula of $C_{27}H_{30}O_{16}$. The characteristic fragments *m/z* 465.10267 and *m/z* 303.04947 corresponding to fragment ions [M + H-Rha (Rhamnosyl group, $C_6H_{10}O_4$)]$^+$ and [M + H-Rha-Glc (Glucosyl group, $C_6H_{10}O_5$)]$^+$ were observed. were observed. It was putatively characterized as rutin. Compound 392 with a retention time of 15.56 min generated the precursor ion of $[M+H]^+$ at *m/z* 287.05511 in positive ion mode, indicating the molecular formula of $C_{15}H_{10}O_6$. The characteristic fragments at *m/z* 269.04370, *m/z* 258.05152, *m/z* 241.04887, *m/z* 231.06472, *m/z* 213.05426 *m/z* 185.05875, *m/z* 165.01764, and *m/z* 153.01757 corresponded to $[M + H–H_2O]^+$, $[M + H–CHO]^+$, $[M + H–H_2O–CO]^+$, $[M + H–2CO]^+$, $[M + H–2CO–H_2O]^+$, $[M + H–3CO–H_2O]^+$, $[M + H–C_7H_6O_2]^+$, and $[M + H–C_8H_6O_2]^+$. It was putatively characterized as kaempferol.

The identifications of isoviolanthin and luteolin were taking as the examples of flavones for illustration. Compound 197 with a retention time of 7.76 min generated the precursor ion of $[M - H]^-$ at *m/z* 577.15506, indicating the molecular formula of $C_{27}H_{30}O_{14}$.

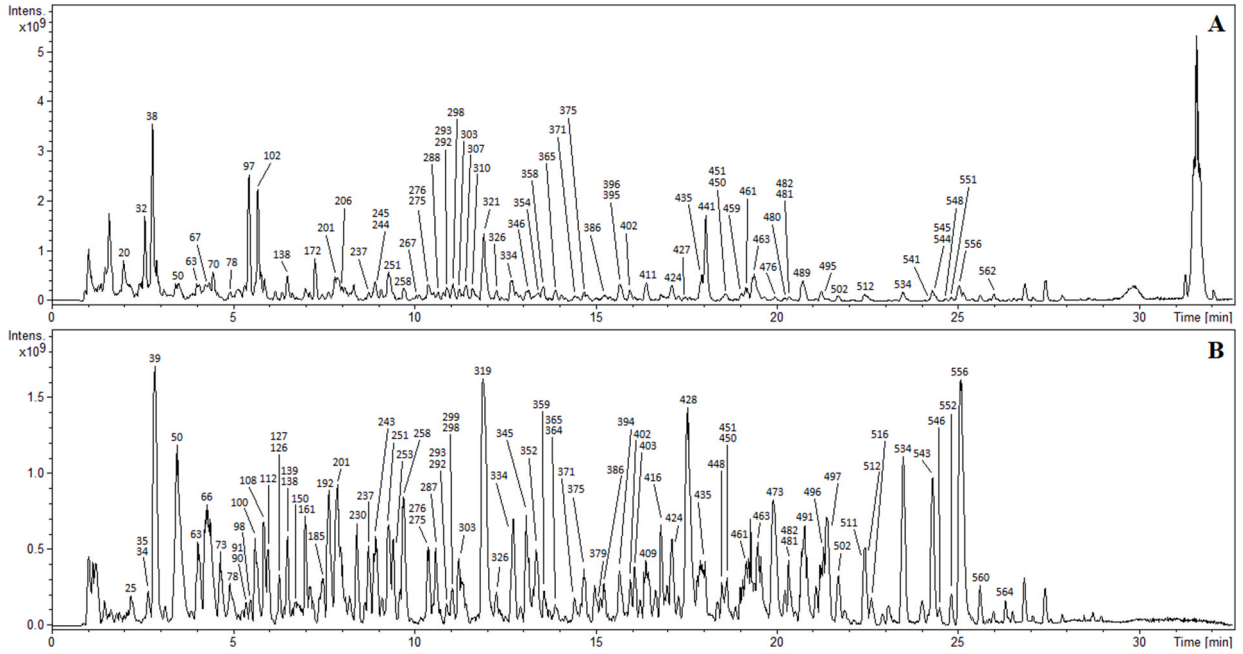

Fig. 1. UHPLC-FT-ICR-MS base peak intensity chromatograms in positive (A) and negative (B) modes of Lianhua Qingwen capsule water extract.

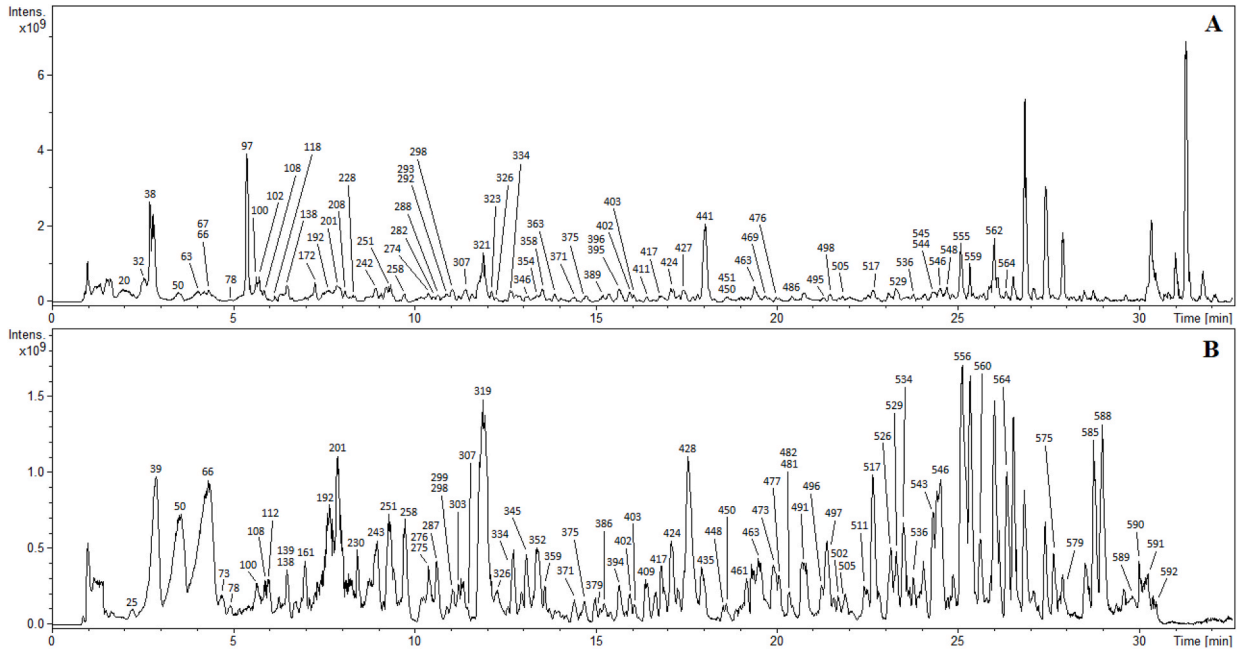

Fig. 2. UHPLC-FT-ICR-MS base peak intensity chromatograms in positive (A) and negative (B) modes of Lianhua Qingwen capsule methanol extract.

The fragments at *m/z* 457.11433 $[M\text{-}H\text{-}120]^-$, *m/z* 439.10370 $[M\text{-}H\text{-}120\text{-}18]^-$, *m/z* 413.08700, $[M\text{-}H\text{-}164]^-$ *m/z* 395.07664 $[M\text{-}H\text{-}164\text{-}18]^-$, *m/z* 383.07676 $[M\text{-}H\text{-}194]^-$, *m/z* 365.06635 $[M\text{-}H\text{-}194\text{-}18]^-$, *m/z* 353.06635 $[M\text{-}H\text{-}224]^-$, *m/z* 337.07184 $[M\text{-}H\text{-}194\text{-}18\text{-}28]^-$, *m/z* 325.07209 $[M\text{-}H\text{-}224\text{-}28]^-$, *m/z* 311.05522 $[M\text{-}H\text{-}266]^-$ and *m/z* 297.07643 $[M\text{-}H\text{-}224\text{-}56]^-$ corresponded to $[M\text{-}H\text{-}C_4H_8O_4]^-$, $[M\text{-}H\text{–}C_4H_8O_4\text{–}H_2O]^-$, $[M\text{-}H\text{-}C_6H_{12}O_5]^-$, $[M\text{-}H\text{–}C_6H_{12}O_5\text{–}H_2O]^-$, $[M\text{-}H\text{-}C_7H_{14}O_6]^-$, $[M\text{-}H\text{–}C_7H_{14}O_6\text{–}H_2O]^-$, $[M\text{-}H\text{-}C_8H_{16}O_7]^-$, $[M\text{-}H\text{–}C_7H_{14}O_6\text{–}H_2O\text{–}CO]^-$, $[M\text{-}H\text{–}C_8H_{16}O_7\text{–}CO]^-$, $[M\text{-}H\text{-}C_{10}H_{18}O_8]^-$, and $[M\text{-}H\text{–}C_8H_{16}O_7\text{–}2CO]^-$. It was putatively characterized as isoviolanthin. Compound 338 with a retention time of 12.82 min generated the precursor ion of $[M-H]^-$ at *m/z* 285.04038, indicating the molecular formula of $C_{15}H_{10}O_6$. The fragments at *m/z* 268.03756, *m/z* 267.02963, *m/z* 243.02957, *m/z* 241.05043, *m/z* 239.03480, *m/z* 223.03996, *m/z* 217.05046, *m/z* 215.03451, *m/z* 213.05547, *m/z* 211.03995, *m/z* 201.01930, *m/z* 199.03991, *m/z* 197.06068, *m/z* 195.04506, *m/z* 185.06059, *m/z* 183.04495, *m/z* 175.03994, *m/z* 171.04510, *m/z* 151.00357, *m/z* 149.02429 and *m/z* 133.02935 corresponded to $[M\text{-}H\text{-}OH]^-$, $[M\text{-}H\text{-}H_2O]^-$, $[M\text{-}H\text{-}C_2H_2O]^-$, $[M\text{-}H\text{-}CO_2]^-$, $[M\text{-}H\text{-}CH_2O_2]^-$, $[M\text{-}H\text{-}CH_2O_3]^-$, $[M\text{-}H\text{-}C_3O_2]^-$, $[M\text{-}H\text{-}C_3H_2O_2]^-$, $[M\text{-}H\text{-}C_2O_3]^-$, $[M\text{-}H\text{-}C_2H_2O_3]^-$, $[M\text{-}H\text{-}C_4H_4O_2]^-$, $[M\text{-}H\text{-}C_3H_2O_3]^-$, $[M\text{-}H\text{-}C_2O_4]^-$, $[M\text{-}H\text{-}C_2H_2O_4]^-$, $[M\text{-}H\text{-}C_3O_4]^-$, $[M\text{-}H\text{-}C_3H_2O_4]^-$, $[M\text{-}H\text{-}C_5H_2O_3]^-$, $[M\text{-}H\text{-}C_4H_2O_4]^-$, $[M\text{-}H\text{-}C_8H_6O_2]^-$, $[M\text{-}H\text{-}C_7H_4O_3]^-$, and $[M\text{-}H\text{-}C_7H_4O_4]^-$. It was identified as luteolin.

The identifications of ononin and formononetin were taking as the examples of isoflavones for illustration. Compound 301 with a retention time of 11.06 min generated the precursor ion of $[M+H]^+$ at *m/z* 431.13390, indicating the molecular formula of $C_{22}H_{22}O_9$. The fragment ion at *m/z* 269.08043 $[M + H\text{-glucose}]^+$ was observed. It was putatively characterized as ononin. Compound 432 with a retention time of 17.84 min generated the precursor ion of $[M+H]^+$ at *m/z* 269.08085 in positive ion mode, indicating the formation of $C_{16}H_{12}O_4$. The characteristic fragments at *m/z* 254.05685, *m/z* 253.04903, *m/z* 237.05400, *m/z* 226.06187, *m/z* 225.05375, *m/z* 213.09037, and *m/z* 197.05929 corresponded to $[M + H\text{–}CH_3]^+$, $[M + H\text{–}CH_4]^+$, $[M + H\text{–}CH_4O]^+$, $[M + H\text{–}C_2H_3O]^+$, $[M + H\text{–}C_2H_4O]^+$, $[M + H\text{–}2CO]^+$, and $[M + H\text{–}C_3H_4O_2]^+$. It was putatively characterized as formononetin.

The identifications of liquiritigenin, licorice glycoside B and naringenin were taking as the examples of flavanones, and isoliquiritigenin, licorice glycoside D1/D2, echinatin, and licochalcone A were taking as the examples of chalcones for illustration. Chalcones possess an open and unsaturated 3-C chain rather than a heterocycle C. Chalcones with C-2′-OH such as isoliquiritigenin, licorice glycoside D1/D2, and the corresponding flavanone such as liquiritigenin, licorice glycoside B were isomers, have quite similar MS/MS fragment ions, and it is arduous to distinguish one from the other by means of MS/MS data. But retention time will also provide a reference for identifying compounds.

Compound 427 (t_R = 17.46 min) showed deprotonated ion $[M+H]^+$ at *m/z* 257.08088, corresponding to a molecular formula of $C_{15}H_{12}O_4$. In the MS^2 spectrum, the characteristic fragments at *m/z* 239.06994, *m/z* 211.07504, *m/z* 147.04390 and *m/z* 137.02309 corresponded to $[M + H\text{–}H_2O]^+$, $[M + H\text{–}CO\text{–}H_2O]^+$, $[M + H\text{–}C_6H_6O_2]^+$ and $[M + H\text{–}C_8H_8O]^+$. The product ion at *m/z* 137.02309 was generated through RDA cleavage. It was identified as isoliquiritigenin. Compound 323 (t_R = 12.14 min) showed deprotonated ion $[M+H]^+$ at *m/z* 257.08100, with similar fragment behaviors to that of isoliquiritigenin. It was identified as liquiritigenin. Compound 311 (t_R = 11.63 min) showed deprotonated ion $[M-H]^-$ at *m/z* 695.19746, corresponding to a molecular formula of $C_{35}H_{36}O_{15}$. In the MS^2 spectrum, the characteristic fragments at *m/z* 549.16094, *m/z* 531.15018, *m/z* 417.11811, *m/z* 399.10799 and *m/z* 255.06610 corresponded to $[M\text{-}H\text{-}C_9H_6O_2]^-$, $[M\text{-}H\text{–}C_9H_6O_2\text{–}H_2O]^-$, $[M\text{-}H\text{–}C_9H_6O_2\text{–}Api$ (Apiosyl group, $C_5H_8O_4)]^-$, $[M\text{-}H\text{–}C_9H_6O_2\text{–}Api\text{-}H_2O]^-$, and $[M\text{-}H\text{–}C_9H_6O_2\text{–}Api\text{-}Glc]^-$. It was temporarily deduced as licorice glycoside D1/D2. And the MS/MS spectrum is shown in Fig. 3.

Table 1
Compounds identified in Lianhua Qingwen capsule by UHPLC-FT-ICR MS.

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
1	0.90	Arginine	175.11845	175.11895	2.86	–	–	–	$C_6H_{14}N_4O_2$	(+): 158
2	0.97	Quinic acid	–	–	–	191.05594	191.05611	0.91	$C_7H_{12}O_6$	(−): 173, 127
3	1.14	Cytidine	244.09304	244.09280	−1.01	–	–	–	$C_9H_{13}N_3O_5$	(+): 112
4	1.21	Heterodendrin	262.12879	262.12851	−1.07	–	–	–	$C_{11}H_{19}NO_6$	(+): 216, 178, 157
5	1.36	Uridine	–	–	–	243.06208	243.06226	0.74	$C_9H_{12}N_2O_6$	(−): 110
6	1.39	Adenosine	268.10448	268.10403	−1.69	–	–	–	$C_{10}H_{13}N_5O_4$	(+): 136
7	1.40	Guanosine	284.09945	284.09894	−1.78	282.08422	282.08439	0.63	$C_{10}H_{13}N_5O_5$	(+): 152
8	1.46	Cornoside	317.12390	317.12309	−2.55	315.10845	315.10854	0.29	$C_{14}H_{20}O_8$	(−): 153
9	1.48	Succinic acid	–	–	–	117.01922	117.01933	1.00	$C_4H_6O_4$	–
10	1.48	Gallic acid-4-*O*-β-D-glucoside	–	–	–	331.06709	331.06707	−0.05	$C_{13}H_{16}O_{10}$	(−): 169
11	1.55	Rengyoside B	321.15544	321.15439	−3.26	319.13978	319.13984	0.20	$C_{14}H_{24}O_8$	(−): 157, 139
12	1.61	Rengynic acid-1′-*O*-β-D-glucoside	–	–	–	335.13456	335.13476	0.59	$C_{14}H_{24}O_9$	(−): 173
13	1.64	Norephedrine-rhamnose-glucose	460.21913	460.21772	−3.05	–	–	–	$C_{21}H_{33}NO_{10}$	(+): 298
14	1.72	Ephedrine-rhamnose-glucose	474.23490	474.23337	−3.22	–	–	–	$C_{22}H_{35}NO_{10}$	(+): 312, 166
15	1.78	Gallic acid	–	–	–	169.01406	169.01425	1.11	$C_7H_6O_5$	(−): 125
16	1.80	Citraconic acid	–	–	–	129.01917	129.01933	1.27	$C_5H_6O_4$	–
17	1.89	Caffeoylshikimic acid	337.09074	337.09179	3.13	335.07705	335.07724	0.56	$C_{16}H_{16}O_8$	(−): 179, 135
18	1.90	Vanillic acid	–	–	–	167.03481	167.03498	1.05	$C_8H_8O_4$	(−): 152, 123
19	1.95	Gallic acid-3-*O*-β-D-glucoside	–	–	–	331.06699	331.06707	0.23	$C_{13}H_{16}O_{10}$	(−): 169
20	1.96	Phenylalanine hexose	328.13953	328.13908	−1.39	326.12446	326.12453	0.19	$C_{15}H_{21}NO_7$	(−): 164
21	2.00	Hydroxytyrosol glucoside	317.12384	317.12309	−2.35	315.10841	315.10854	0.41	$C_{14}H_{20}O_8$	(−): 179, 153, 135
22	2.02	Hydroxyphenyl glycol gentiobioside	–	–	–	477.16102	477.16136	0.72	$C_{20}H_{30}O_{13}$	(−): 315
23	2.07	Deacetylasperulosidic acid	391.12465	391.12349	−2.98	389.10885	389.10894	0.22	$C_{16}H_{22}O_{11}$	(−):227
24	2.14	6-*O*-Galloylglucose	–	–	–	331.06695	331.06707	0.36	$C_{13}H_{16}O_{10}$	(−): 169
25	2.20	Amygdalin amide	476.17776	476.17625	−3.16	520.16691	520.16718	0.52[c]	$C_{20}H_{29}NO_{12}$	(−): 474, 312
26	2.26	Dihydroxybenzoic acid glucoside	–	–	–	315.07201	315.07216	0.46[c]	$C_{12}H_{16}O_7$	(−): 153, 109
27	2.31	Vanillic acid hexose	331.10343	331.10236	−3.24	329.08769	329.08781	0.36	$C_{14}H_{18}O_9$	(−): 167
28	2.34	Unknown	314.12402	314.12343	−1.88	312.10888	312.10888	0.00	$C_{14}H_{19}NO_7$	–
29	2.34	Geniposidic acid	–	–	–	373.11395	373.11402	0.20	$C_{16}H_{22}O_{10}$	(−): 211
30	2.46	Norephedrine-glucose isomer	314.16028	314.15981	−1.47	–	–	–	$C_{15}H_{23}NO_6$	(+): 152, 134
31	2.56	Hydroxytyrosol glucoside isomer	317.12381	317.12309	−2.26	315.10840	315.10854	0.44	$C_{14}H_{20}O_8$	(−): 179, 153, 135
32	2.57	Ephedrine-glucose isomer	328.17536	328.17546	0.33	–	–	–	$C_{16}H_{25}NO_6$	(+): 166, 148
33	2.58	(−)-5-*O*-(4-*O*-β-D-glucopyranosylcaffeoyl) quinic acid	517.15662	517.15518	−2.78	515.14023	515.14063	0.77	$C_{22}H_{28}O_{14}$	(−): 191, 179, 135
34	2.65	Dihydroxybenzoic acid glucoside	–	–	–	315.07194	315.07216	0.67	$C_{13}H_{16}O_9$	(−): 153, 109
35	2.65	Amygdalinic acid isomer	–	–	–	475.14533	475.14571	0.82	$C_{20}H_{28}O_{13}$	(−): 269
36	2.68	Norephedrine-glucose	314.16020	314.15981	−1.23	–	–	–	$C_{15}H_{23}NO_6$	(+): 152, 134
37	2.73	Hydroxyphenyl glycol gentiobioside	–	–	–	477.16127	477.16136	0.19	$C_{20}H_{30}O_{13}$	(−): 315
38	2.78	Ephedrine-glucose	328.17512	328.17546	1.04	–	–	–	$C_{16}H_{25}NO_6$	(+): 166, 148
39	2.84	8-Epiloganic acid	399.12672	399.12617	−1.39[a]	375.12950	375.12967	0.47	$C_{16}H_{24}O_{10}$	(−): 213
40	2.97	Syringic acid-*O*-glucoside	–	–	–	359.09846	359.09837	−0.25	$C_{15}H_{20}O_{10}$	(−): 197
41	3.00	(−)-3-*O*-(4-*O*-β-D-glucopyranosylcaffeoyl) quinic acid	517.15555	517.15518	−0.71	515.14061	515.14063	0.03	$C_{22}H_{28}O_{14}$	(−): 353, 191, 179, 135
42	3.04	Gallocatechin	–	–	–	305.06666	305.06668	0.06	$C_{15}H_{14}O_7$	(−): 137, 125
43	3.15	Ephedrine or pseudoephedrine	166.12289	166.12264	−1.48	–	–	–	$C_{10}H_{15}NO$	(+): 148
44	3.19	Pyrocatechol	–	–	–	153.01918	153.01933	1.01[c]	$C_6H_6O_2$	(−): 109
45	3.20	Phaseoloidin	–	–	–	329.08776	329.08781	0.13	$C_{14}H_{18}O_9$	–
46	3.24	Syringic acid-*O*-glucoside	–	–	–	359.09842	359.09837	−0.15	$C_{15}H_{20}O_{10}$	(−): 197

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
47	3.24	Caffeoyl quinic acid butyl ester	–	–	–	409.15078	409.15041	−0.91	$C_{20}H_{26}O_9$	(−): 353, 191, 179, 135
48	3.37	Amygdalinic acid	499.14266	499.14221	−0.91[a]	475.14551	475.14571	0.43	$C_{20}H_{28}O_{13}$	(−): 269
49	3.38	Forsythoside E isomer	463.18144	463.18100	−0.94	461.16627	461.16645	0.39	$C_{20}H_{30}O_{12}$	(−): 315
50	3.46	Neochlorogenic acid	355.10241	355.10236	−0.15	353.08758	353.08781	0.64	$C_{16}H_{18}O_9$	(−): 191, 179, 173, 135
51	3.51	Rebouoside B	449.16546	449.16535	−0.24	447.15069	447.15080	0.25	$C_{19}H_{28}O_{12}$	(−): 315, 297, 191, 135
52	3.59	Caffeic acid-glucoside	–	–	–	341.08777	341.08781	0.10	$C_{15}H_{18}O_9$	(−): 179, 161, 135
53	3.60	Dihydrosecologanic acid	–	–	–	375.12954	375.12967	0.35	$C_{16}H_{24}O_{10}$	–
54	3.60	Campneoside	655.22301	655.22326	0.38	653.20845	653.20871	0.40	$C_{30}H_{38}O_{16}$	(−): 179
55	3.62	Coniferinoside	–	–	–	549.18227	549.18249	0.41[c]	$C_{22}H_{32}O_{13}$	(−): 503, 341
56	3.65	Benzyl 3-(hydroxymethyl)-1-piperidinecarboxylate	250.14403	250.14377	−1.03	–	–	–	$C_{14}H_{19}NO_3$	–
57	3.68	P-Hydroxyphenacyl-β-D-glucopyranoside	315.10778	315.10744	−1.08	313.09285	313.09289	0.13	$C_{14}H_{18}O_8$	(−): 161, 151
58	3.75	Unknown	–	–	–	371.09839	371.09837	−0.06	$C_{16}H_{20}O_{10}$	(−): 163
59	3.76	Tryptophan	205.09747	205.09715	−1.55	–	–	–	$C_{11}H_{12}N_2O_2$	(+):188
60	3.76	P-Coumaric acid-*O*-glycoside	327.10793	327.10744	−1.49	325.09290	325.09289	−0.03	$C_{15}H_{18}O_8$	(−): 163, 119
61	3.76	(−)-4-*O*-(4-*O*-β-D-glucopyranosylcaffeoyl) quinic acid	517.15614	517.15518	−1.86	515.14053	515.14063	0.19	$C_{22}H_{28}O_{14}$	(−): 191, 179, 135
62	3.90	P-Hydroxyphenacyl-β-*D*-glucopyranoside	315.10773	315.10744	−0.91	313.09281	313.09289	0.26	$C_{14}H_{18}O_8$	(−): 161, 151
63	4.03	Salidroside	323.11030	323.11012	−0.53[a]	299.11371	299.11363	−0.27	$C_{14}H_{20}O_7$	(+): 301
64	4.07	Aucubin	–	–	–	345.11894	345.11911	0.49	$C_{15}H_{22}O_9$	(−): 183
65	4.14	Methylephedrine or methylpseudoephedrine	180.13858	180.13829	−1.63	–	–	–	$C_{11}H_{17}NO$	(+): 162
66	4.28	Forsythoside E	463.18165	463.18100	−1.39	461.16594	461.16645	1.11	$C_{20}H_{30}O_{12}$	(−): 315
67	4.29	Ephedrine-glucose isomer	328.17548	328.17546	−0.03	–	–	–	$C_{16}H_{25}NO_6$	(+): 166, 148
68	4.41	Esculin	341.08698	341.08671	−0.80	339.07203	339.07216	0.36	$C_{15}H_{16}O_9$	(+): 179
69	4.42	P-Coumaric acid-*O*-glycoside isomer	–	–	–	325.09277	325.09289	0.36	$C_{15}H_{18}O_8$	(−): 163
70	4.45	Crenulatanoside B	519.24300	519.24360	1.17	517.22860	517.22905	0.87	$C_{24}H_{38}O_{12}$	(+): 271
71	4.46	Crenulatin	249.13365	249.13326	−1.55	293.12399	293.12419	0.69[c]	$C_{11}H_{20}O_6$	(−): 247
72	4.53	Amygdalin amide isomer	–	–	–	474.16161	474.16170	0.19	$C_{20}H_{29}NO_{12}$	–
73	4.64	Loganic acid	399.12662	399.12617	−1.14[a]	375.12957	375.12967	0.27	$C_{16}H_{24}O_{10}$	(−): 213
74	4.66	Benzyl-4-(hydroxymethyl)piperidin-1-carboxylate	250.14408	250.14377	−1.23	–	–	–	$C_{14}H_{19}NO_3$	–
75	4.69	Syringinoside	557.18518	557.18408	−1.99[a]	579.19288	579.19306	0.30[c]	$C_{23}H_{34}O_{14}$	(−): 533
76	4.74	Dopacetic acid-*O*-rutinoside	–	–	–	475.14562	475.14571	0.20	$C_{20}H_{28}O_{13}$	–
77	4.76	Salicin or isomer	–	–	–	285.09793	285.09798	0.16	$C_{13}H_{18}O_7$	–
78	4.91	Kingiside	405.13961	405.13914	−1.17	449.12964	449.13006	0.94[c]	$C_{17}H_{24}O_{11}$	(−): 403, 241
79	4.92	Dihydromelilotoside or isomer	–	–	–	327.10854	327.10854	0.00	$C_{15}H_{20}O_8$	(−): 165
80	4.94	Protocatechualdehyde	–	–	–	137.02429	137.02442	0.95	$C_7H_6O_3$	–
81	4.98	Suspensaside C isomer	461.16624	461.16535	−1.92	459.15073	459.15080	0.15	$C_{20}H_{28}O_{12}$	–
82	5.01	Isaindigodione isomer	327.13433	327.13393	−1.22	–	–	–	$C_{18}H_{18}N_2O_4$	(+): 201
83	5.02	Coniferin	365.12113	365.12069	−1.21[a]	387.12956	387.12967	0.29[c]	$C_{16}H_{22}O_8$	(−): 341, 179
84	5.05	4-Methoxyphenethyl β-D-glucopyranoside	–	–	–	313.12920	313.12928	0.24	$C_{15}H_{22}O_7$	–
85	5.16	Darendoside A	–	–	–	431.15564	431.15589	0.56	$C_{19}H_{28}O_{11}$	(−): 387, 299, 251, 191, 149
86	5.17	Suspensaside C	461.16627	461.16535	−1.99	459.15068	459.15080	0.26	$C_{20}H_{28}O_{12}$	(−): 205, 163, 151
87	5.27	P-Coumaric acid-*O*-glycoside isomer	–	–	–	325.09266	325.09289	0.71	$C_{15}H_{18}O_8$	(−): 163
88	5.30	Morroniside	429.13789	429.13673	−2.69[a]	451.14532	451.14571	0.87[c]	$C_{17}H_{26}O_{11}$	(−): 405, 243, 225, 179
89	5.31	3-p-Coumaroylquinic acid	339.10802	339.10744	−1.68	337.09270	337.09289	0.56	$C_{16}H_{18}O_8$	(−): 191, 163
90	5.35	Ferruginoside B	479.17609	479.17592	−0.36	477.16092	477.16136	0.94	$C_{20}H_{30}O_{13}$	(−): 431, 269
91	5.35	Darendoside A isomer	433.16975	433.17044	1.59	431.15558	431.15589	0.70	$C_{19}H_{28}O_{11}$	(−): 387, 299, 251, 191, 149, 101
92	5.37	Isaindigodione	327.13449	327.13393	−1.71	–	–	–	$C_{18}H_{18}N_2O_4$	(+): 201
93	5.38	P-Coumaroyltartaric acid	–	–	–	295.04555	295.04594	1.31	$C_{13}H_{12}O_8$	(−): 163

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Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
94	5.38	Di-galloyl-*O*-glucose	–	–	–	483.07769	483.07803	0.70	$C_{20}H_{20}O_{14}$	–
95	5.41	7-Epiloganin	–	–	–	389.14512	389.14532	0.52	$C_{17}H_{26}O_{10}$	(−): 181, 166
96	5.42	P-Anisic acid	–	–	–	151.03990	151.04007	1.09	$C_8H_8O_3$	–
97	5.44	Unknown	354.19096	354.19111	0.43	–	–	–	$C_{18}H_{27}NO_6$	(+): 192, 174
98	5.48	P-coumaroyl-shikimaroylquinic acid	–	–	–	511.14534	511.14571	0.74	$C_{23}H_{28}O_{13}$	(−): 337
99	5.56	Syringin	390.17627	390.17586	−1.06[b]	417.13989	417.14024	0.82[c]	$C_{17}H_{24}O_9$	(−): 371, 209
100	5.59	Chlorogenic acid[d]	355.10244	355.10236	−0.24	353.08750	353.08781	0.87	$C_{16}H_{18}O_9$	(−): 191, 179, 173, 135
101	5.65	Unknown	–	–	–	743.20283	743.20402	1.59	$C_{32}H_{40}O_{20}$	(−): 191
102	5.68	Unknown	395.21739	395.21766	0.70	–	–	–	$C_{20}H_{30}N_2O_6$	(+): 377, 359, 267, 252, 216
103	5.69	Secologanoside	391.12424	391.12349	−1.92	389.10856	389.10894	0.96	$C_{16}H_{22}O_{11}$	(−): 345, 183
104	5.71	Indican	296.11362	296.11286	−2.55	340.10341	340.10379	1.12[c]	$C_{14}H_{17}NO_6$	(−): 294, 132
105	5.72	Catechin	–	–	–	289.07182	289.07176	−0.20	$C_{15}H_{14}O_6$	(−): 245, 203
106	5.75	Norisoboldine isomer	314.13933	314.13868	−2.05	–	–	–	$C_{18}H_{19}NO_4$	–
107	5.78	Creoside I	305.15990	305.15948	−1.38	349.15011	349.15041	0.85[c]	$C_{14}H_{24}O_7$	(−): 303
108	5.82	Cryptochlorogenic acid	355.10282	355.10236	−1.30	353.08754	353.08781	0.75	$C_{16}H_{18}O_9$	(−): 191, 179, 173, 135
109	5.82	Secologanic acid	375.12955	375.12857	−2.60	373.11355	373.11402	1.27	$C_{16}H_{22}O_{10}$	(−): 193, 149
110	5.90	Phthalic acid	–	–	–	165.01917	165.01933	1.01	$C_8H_6O_4$	–
111	5.91	5-*O*-Feruloylquinic acid	–	–	–	367.10296	367.10346	1.36	$C_{17}H_{20}O_9$	(−): 193, 173, 149
112	5.96	Amygdalin	475.19349	475.19224	−2.64[b]	456.15077	456.15113	0.81	$C_{20}H_{27}NO_{11}$	(−): 323
113	5.98	Secoxyloganin	405.14006	405.13914	−2.29	449.12935	449.13006	1.59[c]	$C_{17}H_{24}O_{11}$	–
114	6.04	Creoside I isomer	305.15946	305.15948	0.06	349.15010	349.15041	0.87[c]	$C_{14}H_{24}O_7$	(−): 303
115	6.04	Licoagroside B	433.13518	433.13405	−2.61	431.11917	431.11950	0.76	$C_{18}H_{24}O_{12}$	(+): 127
116	6.05	3,4-Dihydroxy cinnamic acid glycerol ester	255.08678	255.08631	−1.83	253.07155	253.07176	0.85	$C_{12}H_{14}O_6$	–
117	6.09	Rhodioloside D	373.18408	373.18329	−2.12[a]	395.19190	395.19227	0.95[c]	$C_{16}H_{30}O_8$	(−): 349
118	6.13	Norisoboldine	314.13928	314.13868	−1.89	–	–	–	$C_{18}H_{19}NO_4$	(+): 297, 265, 237
119	6.17	Esculetin[d]	–	–	–	177.01912	177.01933	1.21	$C_9H_6O_4$	(−): 149, 133
120	6.19	Dihydromelilotoside or isomer	–	–	–	327.10834	327.10854	0.63	$C_{15}H_{20}O_8$	(−): 165
121	6.19	8-Epiloganin	–	–	–	435.15055	435.15080	0.58[c]	$C_{17}H_{26}O_{10}$	(−): 389
122	6.19	Clemastanin B	685.27192	685.27021	−2.49	729.25947	729.26114	2.29[c]	$C_{32}H_{44}O_{16}$	(−): 521
123	6.21	Caffeic acid[d]	–	–	–	179.03477	179.03498	1.17	$C_9H_8O_4$	(−):135
124	6.21	Coclaurine	286.14416	286.14377	−1.37	–	–	–	$C_{17}H_{20}NO_3$	(+): 107
125	6.24	Quercetin-*O*-rhamnoside-glucoside	611.16310	611.16066	−3.99	609.14535	609.14611	1.24	$C_{27}H_{30}O_{16}$	(−): 447, 301
126	6.25	Benzyl β-primeveroside	403.16021	403.15987	−0.83	401.14506	401.14532	0.65	$C_{18}H_{26}O_{10}$	(−): 269
127	6.25	Dai-tunicamine	–	–	–	431.19187	431.19227	0.92	$C_{20}H_{32}O_{10}$	–
128	6.28	Unknown	–	–	–	447.15013	447.15080	1.51	$C_{19}H_{28}O_{12}$	(−): 285
129	6.35	Creoside II	–	–	–	351.16588	351.16606	0.51[c]	$C_{14}H_{26}O_7$	(−): 305, 179
130	6.36	Luteolin-*O*-arabinopyranosyl-glucopyranoside	–	–	–	579.13504	579.13554	0.87	$C_{26}H_{28}O_{15}$	–
131	6.39	Loganin	–	–	–	435.15045	435.15080	0.79[c]	$C_{17}H_{26}O_{10}$	(−): 389, 227
132	6.42	L-Stepholidine	328.15500	328.15433	−2.02	–	–	–	$C_{19}H_{22}NO_4$	(+): 297
133	6.42	Kaempferol-3-*O*-rutinoside isomer	595.16807	595.16575	−3.90	593.15080	593.15119	0.67	$C_{27}H_{30}O_{15}$	–
134	6.43	Geniposide	411.12688	411.12617	−1.73[a]	433.13507	433.13515	0.19[c]	$C_{17}H_{24}O_{10}$	(−): 225, 207
135	6.44	Lariciresinol-4′-*O*-β-D-glucoside	–	–	–	521.20278	521.20284	0.10	$C_{26}H_{34}O_{11}$	(−): 359
136	6.46	Roseoside	387.20223	387.20134	−2.28	431.19199	431.19227	0.66[c]	$C_{19}H_{30}O_8$	(−): 385
137	6.48	1-Phenyl-1-propen-2-amine-xylose	264.12346	264.12303	−1.59	–	–	–	$C_{14}H_{17}NO_4$	–
138	6.50	Sweroside	359.13412	359.13366	−1.30	403.12418	403.12459	1.01[c]	$C_{16}H_{22}O_9$	(+): 197, 179, 127
139	6.50	(R)-Suspensaside	–	–	–	639.19244	639.19306	0.97	$C_{29}H_{36}O_{16}$	(−): 459
140	6.52	Purpureaside C	–	–	–	785.25062	785.25097	0.44	$C_{35}H_{46}O_{20}$	(−): 623

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Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
141	6.58	Magnoflorine	342.17084	342.16998	−2.50	–	–	–	$C_{20}H_{24}NO_4^+$	(+): 297, 265
142	6.58	Norephedrine-glucose-malonyl	400.16113	400.16021	−2.29	–	–	–	$C_{18}H_{25}NO_9$	(+): 152, 134
143	6.59	4-p-Coumaroylquinic acid	339.10810	339.10744	−1.94	337.09270	337.09289	0.58	$C_{16}H_{18}O_8$	(−): 191, 163
144	6.65	Caffeoylmalic acid	–	–	–	295.04558	295.04594	1.22	$C_{13}H_{12}O_8$	(−): 179, 133
145	6.65	Anthranilic acid-7-*O*-β-D-glucopyranose ester	300.10827	300.10778	−1.64	298.09300	298.09323	0.76	$C_{13}H_{17}NO_7$	(−): 280, 262, 244, 136
146	6.66	3,4-Dicaffeoyl quinic acid isomer	517.13521	517.13405	−2.24	515.11896	515.11950	1.04	$C_{25}H_{24}O_{12}$	(−): 353, 191, 179, 135
147	6.69	2-Hydroxy-1,4-phthalic acid	–	–	–	181.01403	181.01425	1.19	$C_8H_6O_5$	(−): 137
148	6.71	Pinoresinol diglucoside	–	–	–	681.23921	681.24001	1.17	$C_{32}H_{42}O_{16}$	(−): 519, 357
149	6.76	Echinacoside	–	–	–	785.25007	785.25097	1.14	$C_{35}H_{46}O_{20}$	(−): 623, 477, 461, 315, 179, 161
150	6.78	Forsythoside C	–	–	–	639.19250	639.19306	0.87	$C_{29}H_{36}O_{16}$	(−): 161, 135
151	6.78	Prunasin	296.11321	296.11286	−1.17	340.10353	340.10379	0.77[c]	$C_{14}H_{17}NO_6$	(−): 161
152	6.79	Pyrocatechol	–	–	–	153.01913	153.01933	1.33[c]	$C_6H_6O_2$	(−): 109
153	6.89	Lugrandoside	641.20954	641.20761	−3.01	639.19223	639.19306	1.30	$C_{29}H_{36}O_{16}$	(−): 179, 161
154	6.92	P-Coumaric acid-*O*-glycoside isomer	–	–	–	325.09285	325.09289	0.13	$C_{15}H_{18}O_8$	(−): 163
155	6.92	6′-*O*-galloylsalidroside or isomer	453.13833	453.13914	1.78	451.12420	451.12459	0.85	$C_{21}H_{24}O_{11}$	–
156	6.93	7-Deoxyloganin	–	–	–	373.15005	373.15041	0.96	$C_{17}H_{26}O_9$	–
157	6.93	Schaftoside	565.15698	565.15518	−3.18	563.13990	563.14063	1.30	$C_{26}H_{28}O_{14}$	(−): 503, 473, 443, 413, 383, 353
158	6.94	Rhododendrol-2-*O*-β-D-glucopyranoside	–	–	–	327.14468	327.14493	0.76	$C_{16}H_{24}O_7$	(−): 165
159	6.96	3-*O*-Feruloylquinic acid	369.11856	369.11801	−1.50	367.10316	367.10346	0.80	$C_{17}H_{20}O_9$	(−): 193, 173, 149
160	6.98	Epicatechin gallate	443.09653	443.09727	1.68	–	–	–	$C_{22}H_{18}O_{10}$	(+): 291, 255
161	6.99	Secologanoside-7-methyl ester	405.13994	405.13914	−1.98	403.12417	403.12459	1.03	$C_{17}H_{24}O_{11}$	(−): 371, 223, 121
162	7.04	β-Hydroxyacteoside	–	–	–	639.19195	639.19306	1.73	$C_{29}H_{36}O_{16}$	(−): 477, 315, 179, 161, 135
163	7.05	Unknown	–	–	–	459.09286	459.09329	0.92	$C_{22}H_{20}O_{11}$	(−): 253
164	7.07	Glucoliquiritin apioside	713.23070	713.22874	−2.75	711.21234	711.21419	2.60	$C_{32}H_{40}O_{18}$	(−): 255
165	7.09	Liriodendrin	–	–	–	787.26449	787.26662	2.71[c]	$C_{34}H_{46}O_{18}$	(−): 741
166	7.17	(S)-Suspensaside	–	–	–	639.19262	639.19306	0.68	$C_{29}H_{36}O_{16}$	(−): 477, 179, 161, 135
167	7.18	Isoschaftoside	565.15689	565.15518	−3.02	563.13976	563.14063	1.55	$C_{26}H_{28}O_{14}$	(−): 503, 473, 443, 413, 383, 353
168	7.19	2-Phenylethyl-6-*O*-α-L-arabinofuranosyl-β-D-glucopyranoside	417.17446	417.17552	2.55	461.16598	461.16645	1.03[c]	$C_{19}H_{28}O_{10}$	(−): 415
169	7.20	Caffeoylshikimic acid	–	–	–	335.07694	335.07724	0.90	$C_{16}H_{16}O_8$	(−): 179, 135
170	7.23	Vogeloside	–	–	–	387.12966	387.12967	0.03	$C_{17}H_{24}O_{10}$	–
171	7.24	Plantainoside A	479.15572	479.15479	−1.94	477.13984	477.14024	0.82	$C_{23}H_{26}O_{11}$	(−): 179, 161, 135
172	7.26	L-Phenylalaninosecologanin	538.22822	538.22829	0.12	536.21316	536.21373	1.08	$C_{26}H_{35}NO_{11}$	(+): 376, 358
173	7.21	Liquiritigenin-7-O-apiosyl (1–2)-glucoside	551.17709	551.17592	−2.13	–	–	–	$C_{26}H_{30}O_{13}$	(+): 257
174	7.29	8′-Hydroxypionresinol-4′-*O*-glucoside	537.19843	537.19665	−3.32	535.18169	535.18210	0.76	$C_{26}H_{32}O_{12}$	(−): 343
175	7.30	Deoxyvasicinone	187.08634	187.08659	1.31	–	–	–	$C_{11}H_{10}N_2O$	(+): 146
176	7.30	2-Phenylethyl-1-β-D-glucoside	285.13355	285.13326	−0.99	329.12397	329.12419	0.66[c]	$C_{14}H_{20}O_6$	–
177	7.32	Caffeoylshikimic acid	337.09228	337.09179	−1.45	335.07698	335.07724	0.77	$C_{16}H_{16}O_8$	(−): 179, 135
178	7.36	Dimethyl secologanoside	–	–	–	417.13986	417.14024	0.91	$C_{18}H_{26}O_{11}$	(−): 255
179	7.37	2-*O*-(α-L-arabinose)-1-*O*-hexanoyl-β-D-rhamnose	–	–	–	393.17632	393.17662	0.77	$C_{17}H_{30}O_{10}$	(−): 347, 261, 149
180	7.38	Hydroxyluteolin-*O*-arabinopyranosyl-glucopyranoside	597.14677	597.14501	−2.95	595.12926	595.13046	2.01	$C_{26}H_{28}O_{16}$	(−): 301
181	7.42	Sachalinoside B	333.19129	333.19078	−1.53	377.18137	377.18171	0.88[c]	$C_{16}H_{28}O_7$	–
182	7.40	Secoisolariciresinol 4-*O*-β-D-glucopyranoside	–	–	–	523.21791	523.21849	1.09	$C_{26}H_{36}O_{11}$	(−): 361, 346, 165
183	7.42	Isolugrandoside	–	–	–	639.19237	639.19306	1.08	$C_{29}H_{36}O_{16}$	(−): 477, 315, 179, 161, 135
184	7.45	Darendroside B	–	–	–	475.18112	475.18210	2.06	$C_{21}H_{32}O_{12}$	(−): 329
185	7.45	Calceolarioside C	611.19912	611.19705	−3.39	609.18145	609.18249	1.71	$C_{28}H_{34}O_{15}$	(−): 179, 161

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
186	7.51	Ethyl gallate	–	–	–	197.04536	197.04555	0.96	$C_9H_{10}O_5$	(−): 169, 125
187	7.51	Caffeoylshikimic acid	337.09236	337.09179	−1.68	335.07691	335.07724	1.00	$C_{16}H_{16}O_8$	(−): 179, 135
188	7.52	Plantainoside B	479.15511	479.15479	−0.67	477.13973	477.14024	1.07	$C_{23}H_{26}O_{11}$	(−): 179, 161, 135
189	7.53	4-*O*-Feruloylquinic acid	369.11849	369.11801	−1.30	367.10344	367.10346	0.04	$C_{17}H_{20}O_9$	(−): 193, 173, 149
190	7.53	Demethyldihydrophillygenin glucuronide	537.19757	537.19665	−1.71	535.18148	535.18210	1.17	$C_{26}H_{32}O_{12}$	(−): 373
191	7.56	Forsythoside B	779.23975	779.23690	−3.66[a]	755.23923	755.24040	1.55	$C_{34}H_{44}O_{19}$	(−): 593, 461, 447, 161
192	7.64	Forsythoside H	625.21341	625.21270	−1.14	623.19692	623.19814	1.96	$C_{29}H_{36}O_{15}$	(−): 477, 461, 443, 315, 297, 179, 161, 135, 133
193	7.70	Calceolarioside B isomer	479.15508	479.15479	−0.62	477.13956	477.14024	1.41	$C_{23}H_{26}O_{11}$	(−): 179, 161
194	7.71	5′-Methoxy-8′-hydroxyl-(+)-isolariciresinol-4′-*O*-β-D-glucopyranoside	–	–	–	567.20728	567.20831	1.82	$C_{27}H_{36}O_{13}$	(−): 359, 329
195	7.73	Neoliquiritin	419.13446	419.13366	−1.91	417.11946	417.11911	−0.84	$C_{21}H_{22}O_9$	(+): 257
196	7.76	5-Carboxymethyl-7-hydroxy-2-methyl-chromone	235.06002	235.06010	0.33	233.04532	233.04555	0.98	$C_{12}H_{10}O_5$	–
197	7.76	Isoviolanthin	579.17150	579.17083	−1.16	577.15506	577.15628	2.12	$C_{27}H_{30}O_{14}$	(−): 457, 439, 413, 395, 383, 365, 353, 337, 325, 311, 297
198	7.79	Norjuziphine	286.14397	286.14377	−0.70	–	–	–	$C_{17}H_{20}NO_3$	(+): 107
199	7.81	Rutin	611.16097	611.16066	−0.50	609.14530	609.14611	1.32	$C_{27}H_{30}O_{16}$	(+): 465, 303
200	7.84	Calycosin-7-glucoside	447.12918	447.12857	−1.36	–	–	–	$C_{22}H_{22}O_{10}$	(+): 285
201	7.87	Forsythoside I	625.21340	625.21270	−1.13	623.19775	623.19814	0.63	$C_{29}H_{36}O_{15}$	(−): 477, 461, 443, 315, 297, 179, 161, 135, 133
202	7.89	4-Hydroxycoumarin	163.03923	163.03897	−1.58	161.02417	161.02442	1.54	$C_9H_6O_3$	–
203	7.97	Liquiritin apioside	551.17709	551.17592	−2.13	549.16066	549.16136	1.27	$C_{26}H_{30}O_{13}$	(+): 257
204	7.99	Isovitexin	433.11335	433.11292	−0.98	431.09759	431.09837	1.81	$C_{21}H_{20}O_{10}$	(+): 415, 397, 379, 367, 361, 351, 349, 337, 323, 313, 309, 295, 283
205	7.99	Lariciresinol-4-*O*-glucoside	545.20051	545.19933	−2.17[a]	521.20241	521.20284	0.82	$C_{26}H_{34}O_{11}$	(−): 359
206	8.00	Unknown	398.18129	398.18094	−0.87	396.16601	396.16639	0.97	$C_{19}H_{27}NO_8$	(+): 236, 218, 190
207	8.05	Liquiritin	419.13402	419.13366	−0.86	417.11940	417.11911	−0.71	$C_{21}H_{22}O_9$	(+): 257
208	8.07	Isoquercitrin	465.10349	465.10275	−1.59	463.08760	463.08820	1.30	$C_{21}H_{20}O_{12}$	(+): 303
209	8.07	Liquiritigenin-7,4′-diglucoside	581.18785	581.18648	−2.36	579.17011	579.17193	3.14	$C_{27}H_{32}O_{14}$	(+): 239
210	8.08	Forsythoside G	–	–	–	769.25389	769.25605	2.81	$C_{35}H_{46}O_{19}$	(−): 607
211	8.10	Calceolarioside A	479.15525	479.15479	−0.97	477.13974	477.14024	1.04	$C_{23}H_{26}O_{11}$	(−): 179, 161
212	8.13	Neoamygdalin	–	–	–	456.15079	456.15113	0.75	$C_{20}H_{27}NO_{11}$	(−): 323
213	8.17	Ferulic acid	–	–	–	193.05044	193.05063	0.99	$C_{10}H_{10}O_4$	(−): 149
214	8.18	1-*O*-trans-Cinnamoyl-beta-D-glucopyranose	311.11285	311.11253	−1.03	355.10311	355.10346	0.97[c]	$C_{15}H_{18}O_7$	(−): 189, 161, 147
215	8.18	Resveratrol 4′-*O*-glucoside	–	–	–	389.12361	389.12419	1.49	$C_{20}H_{22}O_8$	(−): 227
216	8.14	Rhein-8-*O*-β-D-glucoside	–	–	–	445.07800	445.07763	−0.82	$C_{21}H_{18}O_{11}$	(−): 283, 239
217	8.19	Strychoside A	745.25615	745.25496	−1.60	743.23879	743.24040	2.17	$C_{33}H_{44}O_{19}$	(−): 511, 479
218	8.20	Acteoside isomer	647.19644	647.19464	−2.78[a]	623.19694	623.19814	1.93	$C_{29}H_{36}O_{15}$	(−): 461, 315, 179, 161, 135
219	8.21	Hyperin	465.10365	465.10275	−1.92	463.08777	463.08820	0.94	$C_{21}H_{20}O_{12}$	(+): 303
220	8.21	Kaempferol-3-*O*-rhamnose-7-*O*-glucose	595.16731	595.16575	−2.63	593.14994	593.15119	2.11	$C_{27}H_{30}O_{15}$	(−): 285
221	8.22	Conicaoside	–	–	–	551.21249	551.21340	1.65	$C_{27}H_{36}O_{12}$	–
222	8.26	Rosiridin	333.19129	333.19078	−1.53	377.18125	377.18171	1.20[c]	$C_{16}H_{28}O_7$	–
223	8.26	Scutellarin	463.08802	463.08710	−1.98	461.07191	461.07255	1.39	$C_{21}H_{18}O_{12}$	(+): 287
224	8.27	Suspensaside A isomer	623.19945	623.19705	−3.86	621.18146	621.18249	1.67	$C_{29}H_{34}O_{15}$	(−): 161
225	8.28	Cynaroside	449.10878	449.10784	−2.10	447.09286	447.09329	0.96	$C_{21}H_{20}O_{11}$	(−): 285
226	8.30	1-Methoxyindole-3-acetamide	205.09741	205.09715	−1.25	–	–	–	$C_{11}H_{12}N_2O_2$	(+):188
227	8.34	Creoside IV	397.20694	397.20682	−0.29	395.19202	395.19227	0.63	$C_{17}H_{32}O_{10}$	–

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
228	8.38	Luteolin-7-*O*-rutinoside	595.16734	595.16575	−2.68	593.15031	593.15119	1.49	$C_{27}H_{30}O_{15}$	(−): 285
229	8.39	Rosavin	–	–	–	473.16680	473.16645	−0.74[c]	$C_{20}H_{28}O_{10}$	(−): 427, 293, 233, 191, 149, 131
230	8.41	Calceolarioside B	479.15560	479.15479	−1.69	477.13966	477.14024	1.20	$C_{23}H_{26}O_{11}$	(+): 325, 163
231	8.43	Rhodioloside E	–	–	–	511.23891	511.23961	1.38[c]	$C_{21}H_{38}O_{11}$	–
232	8.51	Isaindigodione isomer	327.13412	327.13393	−0.57	–	–	–	$C_{18}H_{18}N_2O_4$	(+): 201
233	8.53	Forsythenside K isomer	609.21958	609.21778	−2.95	607.20230	607.20323	1.53	$C_{29}H_{36}O_{14}$	(−): 461
234	8.64	Suspensaside A	623.19760	623.19705	−0.89	621.18152	621.18249	1.58	$C_{29}H_{34}O_{15}$	(−): 161
235	8.66	Forsythoside A	647.19663	647.19464	−3.07[a]	623.19737	623.19814	1.25	$C_{29}H_{36}O_{15}$	(−): 461, 315, 297, 179, 161, 135
236	8.72	Nicotiflorin	595.16730	595.16575	−2.61	593.15034	593.15119	1.44	$C_{27}H_{30}O_{15}$	(+): 287
237	8.73	3,4-Dicaffeoyl quinic acid	517.13515	517.13405	−2.12	515.11892	515.11950	1.13	$C_{25}H_{24}O_{12}$	(−): 353, 191, 179, 135
238	8.82	Isolariciresinol	361.16492	361.16456	−0.98	405.15504	405.15549	1.12[c]	$C_{20}H_{24}O_6$	(−): 359, 344, 313
239	8.82	Acteoside	625.21423	625.21270	−2.45	623.19642	623.19814	2.77	$C_{29}H_{36}O_{15}$	(−): 461, 315, 297, 179, 161, 135, 133
240	8.83	Luteolin-5-*O*-glucoside	449.10877	449.10784	−2.09	447.09290	447.09329	0.86	$C_{21}H_{20}O_{11}$	(+): 287
241	8.85	Forsythenside K	609.21862	609.21778	−1.38	607.20233	607.20323	1.48	$C_{29}H_{36}O_{14}$	(−): 461
242	8.91	Licoflavanone isomer	341.13847	341.13835	−0.35	–	–	–	$C_{20}H_{20}O_5$	(+): 291, 263
243	8.93	Pinoresinol-4-*O*-glucoside	543.18472	543.18368	−1.91[a]	519.18642	519.18719	1.48	$C_{26}H_{32}O_{11}$	(−): 357, 342, 151
244	8.95	Rhodioloside A	371.16804	371.16764	−1.08[a]	347.17090	347.17114	0.69	$C_{16}H_{28}O_8$	(+): 203
245	8.96	Rhodiolgin	465.10353	465.10275	−1.67	463.08778	463.08820	0.91	$C_{21}H_{20}O_{12}$	(−): 317, 303
246	9.02	n-Hexyl-*β*-D-glucopyranoside	287.14678	287.14651	−0.96[a]	309.15531	309.15549	0.59[c]	$C_{12}H_{24}O_6$	–
247	9.08	Leucosceptoside A	639.23032	639.22835	−3.09	637.21288	637.21379	1.43	$C_{30}H_{38}O_{15}$	(−): 461, 175
248	9.10	3,5-Dicaffeoyl quinic acid	517.13509	517.13405	−2.01	515.11886	515.11950	1.23	$C_{25}H_{24}O_{12}$	(−): 353, 191, 179, 135
249	9.14	Acanthoside B	603.20614	603.20481	−2.21[a]	579.20778	579.20831	0.93	$C_{28}H_{36}O_{13}$	(−): 417, 402
250	9.26	Rhoifolin	579.17222	579.17083	−2.40	577.15722	577.15628	−1.63	$C_{27}H_{30}O_{14}$	(+): 271
251	9.30	Quercitrin	449.10818	449.10784	−0.77	447.09270	447.09329	1.30	$C_{21}H_{20}O_{11}$	(−): 301, 285, 284, 271, 255
252	9.37	Centauroside	759.27302	759.27061	−3.18	757.25408	757.25605	2.61	$C_{34}H_{46}O_{19}$	(−): 595, 525, 493
253	9.45	Isorhamnetin-3-*O*-glucoside	479.11912	479.11840	−1.50	477.10325	477.10385	1.26	$C_{22}H_{22}O_{12}$	(+): 317
254	9.49	Choerospondin	435.12890	435.12857	−0.75	433.11374	433.11402	0.65	$C_{21}H_{22}O_{10}$	(+): 273
255	9.52	Apigenin-7-*O*-glucoside	433.11352	433.11292	−1.37	431.09768	431.09837	1.61	$C_{21}H_{20}O_{10}$	(+): 271
256	9.60	Hesperidin	–	–	–	609.18085	609.18249	2.70	$C_{28}H_{34}O_{15}$	(−): 301
257	9.64	Acacetin-6,8-di-*C*-glucoside	609.18290	609.18140	−2.47	607.16628	607.16684	0.93	$C_{28}H_{32}O_{15}$	–
258	9.68	4,5-Dicaffeoyl quinic acid	517.13470	517.13405	−1.24	515.11866	515.11950	1.64	$C_{25}H_{24}O_{12}$	(−): 353, 191, 179, 135
259	9.73	Indole-3-acetonitrile-2-*S*-β-D-glucopyranoside	351.10150	351.10092	−1.65	349.08603	349.08637	0.96	$C_{16}H_{18}N_2O_5S$	(−): 187, 160
260	9.81	(7R,8S,7′R,8′S)-5-Methoxyprinsepiol-4-*O*-β-D-glucose	583.20347	583.20213	−2.29	581.18690	581.18758	1.16	$C_{27}H_{34}O_{14}$	(−): 419, 371, 223
261	9.82	Azelaic acid	189.11208	189.11214	0.29	187.09736	187.09758	1.18	$C_9H_{16}O_4$	(−): 125
262	9.85	Salicylic acid	–	–	–	137.02428	137.02442	1.02	$C_7H_6O_3$	–
263	9.88	Pratensein-7-*O*-glucoside isomer	463.12422	463.12349	−1.58	461.10903	461.10894	−0.21	$C_{22}H_{22}O_{11}$	(+): 301
264	9.88	(E)-Aldosecologanin	759.27028	759.27061	0.43	757.25436	757.25605	2.24	$C_{34}H_{46}O_{19}$	(−): 595, 525, 493
265	10.00	Rosin	–	–	–	341.12382	341.12419	1.09[c]	$C_{15}H_{20}O_6$	–
266	10.02	Kaempferol-3-*O*-rutinoside isomer	595.16699	595.16575	−2.10	593.15050	593.15119	1.17	$C_{27}H_{30}O_{15}$	(−): 285
267	10.06	Unknown	506.23943	506.23846	−1.93	–	–	–	$C_{26}H_{35}NO_9$	(+): 344, 326
268	10.08	6-Hydroxymusizin-8-*O*-β-D-glucopyranoside	395.13394	395.13366	−0.71	393.11872	393.11911	0.99	$C_{19}H_{22}O_9$	(−): 231
269	10.13	Rhododendrol-2-*O*-β-D-glucopyranoside isomer	329.15996	329.15948	−1.46	327.14463	327.14493	0.90	$C_{16}H_{24}O_7$	–
270	10.16	P-Coumarin caffeoylquinic acid	501.14029	501.13914	−2.30	499.12405	499.12459	1.08	$C_{25}H_{24}O_{11}$	(−): 353, 337, 191, 179
271	10.26	Rhapontin	–	–	–	419.13439	419.13476	0.88	$C_{21}H_{24}O_9$	–
272	10.26	Crenatoside	623.19760	623.19705	−0.89	621.18149	621.18249	1.62	$C_{29}H_{34}O_{15}$	(−): 161
273	10.30	8-Hydroxypinoresinol	375.14425	375.14383	−1.13	373.12900	373.12928	0.74	$C_{20}H_{22}O_7$	(−): 313
274	10.36	Epi-pinoresinol	359.14922	359.14891	−0.85	357.13402	357.13436	0.96	$C_{20}H_{22}O_6$	(−): 342

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
275	10.39	8-Hydroxysyringaresinol	435.16555	435.16496	−1.35	433.15040	433.15041	0.01	$C_{22}H_{26}O_9$	(−): 403, 385, 373, 358, 343, 325
276	10.39	Pinoresinol-4-*O*-glucoside isomer	543.18459	543.18368	−1.67[a]	519.18658	519.18719	1.16	$C_{26}H_{32}O_{11}$	(−): 357, 342
277	10.43	Secoisolariciresinol	–	–	–	361.16522	361.16566	1.21	$C_{20}H_{26}O_6$	(−): 346, 165
278	10.43	Sachaloside II	469.20530	469.20442	−1.88[a]	491.21283	491.21340	1.15[c]	$C_{21}H_{34}O_{10}$	(−): 445
279	10.48	Luteolin-7-*O*-α-L-rhamnoside	–	–	–	431.09793	431.09837	1.03	$C_{21}H_{20}O_{10}$	(−): 285
280	10.49	3,5-*O*-dicaffeoylquinic acid methyl ester	531.14933	531.14970	0.70	529.13459	529.13515	1.05	$C_{26}H_{26}O_{12}$	(−): 191, 173
281	10.50	Hydroxymedioresinol	405.15482	405.15439	−1.04	403.13953	403.13984	0.77	$C_{21}H_{24}O_8$	(−): 343
282	10.53	Isoliquiritin apioside	551.17675	551.17592	−1.51	549.16082	549.16136	0.99	$C_{26}H_{30}O_{13}$	(+): 257
283	10.54	Glycyroside	563.17681	563.17592	−1.58	561.16086	561.16136	0.90	$C_{27}H_{30}O_{13}$	(+): 269
284	10.55	Chrysoeriol-7-*O*-neohesperidoside	–	–	–	607.16565	607.16684	1.97	$C_{28}H_{32}O_{15}$	–
285	10.57	7-*O*-ethyl-sweroside	–	–	–	401.14496	401.14532	0.89	$C_{18}H_{26}O_{10}$	(−): 233, 215, 197, 175
286	10.57	Leucosceptoside A or isomer	639.22838	639.22835	−0.05	637.21287	637.21379	1.46	$C_{30}H_{38}O_{15}$	(−): 461
287	10.59	Pratensein-7-*O*-glucoside	463.12435	463.12349	−1.86	461.10846	461.10894	1.04	$C_{22}H_{22}O_{11}$	(−): 299, 284
288	10.66	Genistin	433.11338	433.11292	−1.06	431.09800	431.09837	0.86	$C_{21}H_{20}O_{10}$	(−): 269
289	10.66	Oleuropein	–	–	–	539.17665	539.17701	0.68	$C_{25}H_{32}O_{13}$	(−): 377, 345, 327, 307, 275
290	10.67	Tricin 7-*O*-glucoside	493.13463	493.13405	−1.17	491.11918	491.11950	0.65	$C_{23}H_{24}O_{12}$	–
291	10.73	Indole-3-acetonitrile-4-methoxy-2-*S*-β-D-glucopyranoside or N-Methoxyindole-3-acetonitrile-2-*S*-β-D-glucopyranoside	381.11204	381.11148	−1.46	379.09664	379.09693	0.76	$C_{17}H_{20}N_2O_6S$	(+): 219
292	10.88	Isoliquiritin apioside isomer	551.17690	551.17592	−1.78	549.16083	549.16136	0.97	$C_{26}H_{30}O_{13}$	(+): 257
293	10.88	Rhodiosin	611.16141	611.16066	−1.23	609.14512	609.14611	1.63	$C_{27}H_{30}O_{16}$	(−): 301
294	10.91	8-*O*-Methylretusin-7-*O*-β-D-glucopyranoside	461.14485	461.14422	−1.36	459.12925	459.12967	0.91	$C_{23}H_{24}O_{10}$	(+): 299
295	10.96	Lariciresinol	361.16492	361.16456	−0.98	405.15509	405.15549	1.00[c]	$C_{20}H_{24}O_6$	(−): 329.13917
296	10.96	Unknown	–	–	–	459.09293	459.09329	0.78	$C_{22}H_{20}O_{11}$	(−): 253
297	11.03	4,5-*O*-dicaffeoylquinic acid methyl ester	–	–	–	529.13432	529.13515	1.57	$C_{26}H_{26}O_{12}$	(−): 179, 173
298	11.04	Isoliquiritin	419.13408	419.13366	−1.01	417.11866	417.11911	1.08	$C_{21}H_{22}O_9$	(+): 257
299	11.04	Pratensein-7-*O*-glucoside isomer	–	–	–	461.10848	461.10894	1.00	$C_{22}H_{22}O_{11}$	(−): 299, 284
300	11.05	Flavoyadorinin B	–	–	–	475.12417	475.12459	0.88	$C_{23}H_{24}O_{11}$	(−): 283
301	11.06	Ononin	431.13390	431.13366	−0.55	429.11941	429.11911	−0.71	$C_{22}H_{22}O_9$	(+): 269
302	11.18	Lonijapospiroside A	–	–	–	560.17670	560.17735	1.15	$C_{27}H_{31}NO_{12}$	(−): 296
303	11.22	Arctiin isomer	557.20019	557.19933	−1.53[a]	579.20762	579.20831	1.20[c]	$C_{27}H_{34}O_{11}$	(−): 371
304	11.25	3-(2′-Hydroxyphenyl)-4-(3H)-quinazolinone	239.08175	239.08150	−1.03	–	–	–	$C_{14}H_{10}N_2O_2$	–
305	11.28	*N*-p-Coumaroyltyramine	284.12839	284.12812	−0.95	–	–	–	$C_{17}H_{17}NO_3$	(+): 147
306	11.29	7,4′-Dihydroxyflavone	255.06527	255.06519	−0.35	253.05057	253.05063	0.25	$C_{15}H_{10}O_4$	(+): 137
307	11.43	Rhodiolatuntoside	449.10804	449.10784	−0.45	447.09289	447.09329	0.88	$C_{21}H_{20}O_{11}$	(−): 151
308	11.44	Neoisoliquiritin	419.13413	419.13366	−1.12	417.11881	417.11911	0.71	$C_{21}H_{22}O_9$	(+): 257
309	11.58	3,4-*O*-dicaffeoylquinic acid methyl ester	531.15067	531.14970	−1.82	529.13454	529.13515	1.15	$C_{26}H_{26}O_{12}$	(−): 191, 179, 173
310	11.60	Unknown	553.19237	553.19157	−1.46	551.17597	551.17701	1.90	$C_{26}H_{32}O_{13}$	(+): 391, 373, 347
311	11.63	Licorice glycoside D1/D2	697.21387	697.21270	−1.68	695.19746	695.19814	0.99	$C_{35}H_{36}O_{15}$	(−): 549, 531, 417, 399, 255
312	11.70	1-*O*-Galloy1-2-*O*-cinnamoylglucose	–	–	–	461.10849	461.10894	0.97	$C_{22}H_{22}O_{11}$	(−): 313, 169
313	11.70	Crenuloside	595.16654	595.16575	−1.34	593.15061	593.15119	0.98	$C_{27}H_{30}O_{15}$	(+): 287
314	11.75	Licorice glycoside C1/C2	727.22455	727.22326	−1.77	725.20724	725.20871	2.03	$C_{36}H_{38}O_{16}$	(−): 255
315	11.82	Licochalcone B	287.09170	287.09140	−1.04	285.07669	285.07685	0.55	$C_{16}H_{14}O_5$	(−): 270, 177, 150
316	11.83	N-transferuloyltyramine	314.13899	314.13868	−0.99	312.12388	312.12413	0.82	$C_{18}H_{19}NO_4$	(+): 177
317	11.83	Dryocrassin ABBA	821.30122	821.30151	0.36	819.28569	819.28696	1.55	$C_{43}H_{48}O_{16}$	(−): 611, 403
318	11.85	Daidzein	255.06551	255.06519	−1.27	253.05027	253.05063	1.43	$C_{15}H_{10}O_4$	(+): 227, 199
319	11.89	Phillyrin	557.20015	557.19933	−1.47[a]	579.20726	579.20831	1.83[c]	$C_{27}H_{34}O_{11}$	(+): 395, 373, 355, 337, 305

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
320	11.90	Unknown	745.32360	745.32319	−0.55	–	–	–	$C_{43}H_{44}N_4O_8$	(+): 322, 219, 201, 189
321	11.91	4′-*O*-methyl glabridin isomer	355.15397	355.15400	0.09	–	–	–	$C_{21}H_{22}O_5$	(+): 337, 322, 306, 305, 290, 285, 284, 254
322	12.01	Herbacetin	303.05025	303.04993	−1.06	301.03510	301.03538	0.92	$C_{15}H_{10}O_7$	(−): 283
323	12.14	Liquiritigenin	257.08100	257.08084	−0.65	255.06610	255.06628	0.72	$C_{15}H_{12}O_4$	(+): 239, 211, 147, 137
324	12.15	Lonijapospiroside A isomer	562.19303	562.19190	−2.01	560.17675	560.17735	1.08	$C_{27}H_{31}NO_{12}$	(−): 296
325	12.20	Chrysoeriol 7-*O*-glucoside	463.12431	463.12349	−1.78	461.10867	461.10894	0.57	$C_{22}H_{22}O_{11}$	(−): 256
326	12.25	Arctiin	557.20005	557.19933	−1.28[a]	579.20736	579.20831	1.64[c]	$C_{27}H_{34}O_{11}$	(+): 395, 355, 337, 323, 305, 295, 277, 273, 263, 245, 237, 219
327	12.26	Rhamnetin	317.06599	317.06558	−1.30	315.05155	315.05103	−1.66	$C_{16}H_{12}O_7$	(−): 300
328	12.38	Eriodictyol	289.07088	289.07066	−0.75	287.05590	287.05611	0.73	$C_{15}H_{12}O_6$	(+): 153
329	12.38	Linarin	593.18730	593.18648	−1.39	–	–	–	$C_{28}H_{32}O_{14}$	(+): 447, 285
330	12.50	Chrysoeriol	301.07091	301.07066	−0.82	299.05600	299.05611	0.36	$C_{16}H_{12}O_6$	(−): 284
331	12.50	Sebacic acid	203.12807	203.12779	−1.40	201.11295	201.11323	1.41	$C_{10}H_{18}O_4$	–
332	12.55	1,6-Di-*O*-galloyl-2-*O*-cinnamoyl-β-D-glucose	–	–	–	613.11880	613.11989	1.78	$C_{29}H_{26}O_{15}$	(−): 461, 169
333	12.55	Licorice saponin O4	–	–	–	1115.52753	1115.52798	0.40	$C_{54}H_{84}O_{24}$	–
334	12.65	L-phenylalaninosecologanin B	506.20241	506.20207	−0.67	504.18704	504.18752	0.96	$C_{25}H_{31}NO_{10}$	(−): 342, 324, 314, 272
335	12.70	1-*O*-Galloy1-6-*O*-cinnamoylglucose	–	–	–	461.10906	461.10894	−0.27	$C_{22}H_{22}O_{11}$	(−): 313, 169
336	12.71	Matairesinoside	–	–	–	519.18734	519.18719	−0.30	$C_{26}H_{32}O_{11}$	(−): 357
337	12.75	*Erythro*-dihydroguaiacylglycerol-*O*-4′-dehydrodisinapyl ether	–	–	–	585.23417	585.23414	−0.05	$C_{31}H_{38}O_{11}$	–
338	12.82	Luteolin[d]	287.05523	287.05501	−0.74	285.04038	285.04046	0.29	$C_{15}H_{10}O_6$	(−): 268, 267, 243, 241, 239, 223, 217, 215, 213, 211, 201, 199, 197, 195, 185, 183, 175, 171, 151, 149, 133
339	12.84	Kaempferin	433.11331	433.11292	−0.88	431.09817	431.09837	0.45	$C_{21}H_{20}O_{10}$	(+): 287
340	12.87	Sachalinoside A or isomer	485.20051	485.20174	2.53	483.18711	483.18719	0.17	$C_{23}H_{32}O_{11}$	–
341	12.89	Quercetin	303.05017	303.04993	−0.80	301.03529	301.03538	0.30	$C_{15}H_{10}O_7$	(−): 151
342	12.90	Kenposide A	–	–	–	447.22336	447.22357	0.48	$C_{21}H_{36}O_{10}$	–
343	12.94	Calycosin	285.07596	285.07575	−0.72	283.06112	283.06120	0.28	$C_{16}H_{12}O_5$	(+): 270
344	13.07	Rhamnoliquiritin	565.19252	565.19157	−1.68	563.17653	563.17701	0.86	$C_{27}H_{32}O_{13}$	–
345	13.08	Rhodiooctanoside	425.23899	425.23812	−2.04	423.22330	423.22357	0.65	$C_{19}H_{36}O_{10}$	(−): 291,
346	13.10	Torachrysone 8-*O*-glucoside	409.14968	409.14931	−0.91	407.13463	407.13476	0.32	$C_{20}H_{24}O_9$	(−): 245
347	13.14	Rhodioloside C	–	–	–	493.22872	493.22905	0.67	$C_{22}H_{38}O_{12}$	(−): 447
348	13.14	Licorice glycoside E	694.21415	694.21303	−1.61	692.19904	692.19848	−0.81	$C_{35}H_{35}NO_{14}$	(−): 549, 531, 399, 255
349	13.16	Chrysophanol-1-*O*-glucoside	439.10043	439.09995	−1.09[a]	415.10322	415.10346	0.58	$C_{21}H_{20}O_9$	(−): 253, 225
350	13.22	Emodin-glucoside	433.11268	433.11292	0.56	431.09808	431.09837	0.68	$C_{21}H_{20}O_{10}$	(−): 269
351	13.33	Ethyl caffeate	209.08104	209.08084	−0.96	207.06611	207.06628	0.85	$C_{11}H_{12}O_4$	(−): 179, 161, 135
352	13.34	Kaempferol-7-*O*-α-L-rhamnoside	433.11357	433.11292	−1.49	431.09799	431.09837	0.88	$C_{21}H_{20}O_{10}$	(−): 285
353	13.37	Myrciacitrin I	479.15535	479.15479	−1.17	477.14006	477.14024	0.36	$C_{23}H_{26}O_{11}$	(−): 269
354	13.40	Unknown	590.26036	590.25959	−1.32	588.24591	588.24503	−1.49	$C_{30}H_{39}NO_{11}$	(+): 428, 282
355	13.41	Rhodioloside B	–	–	–	493.22864	493.22905	0.83	$C_{22}H_{38}O_{12}$	(−): 311
356	13.45	Uralsaponin C isomer	825.42822	825.42671	−1.82	823.41124	823.41216	1.11	$C_{42}H_{64}O_{16}$	(+): 455
357	13.53	Pinoresinol	359.14933	359.14891	−1.15	357.13430	357.13436	0.17	$C_{20}H_{22}O_6$	(−): 342, 151, 136
358	13.55	Licoflavanone isomer	341.13856	341.13835	−0.63	–	–	–	$C_{20}H_{20}O_5$	(+): 263
359	13.58	Chrysophanol-8-*O*-glucoside	439.10037	439.09995	−0.96[a]	415.10336	415.10346	0.23	$C_{21}H_{20}O_9$	(−): 253, 225
360	13.66	Wogonoside	461.10819	461.10784	−0.76	459.09377	459.09329	−1.06	$C_{22}H_{20}O_{11}$	(+): 285

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
361	13.81	Di-*O*-galloyl-*O*-cinnamoyl-β-D-glucose	–	–	–	613.11922	613.11989	1.09	$C_{29}H_{26}O_{15}$	(−): 461, 169
362	13.81	Licorice glycoside B	697.21341	697.21270	−1.02	695.19785	695.19814	0.43	$C_{35}H_{36}O_{15}$	(−): 549, 531, 417, 399, 255
363	13.83	Licorice glycoside A	727.22367	727.22326	−0.56	725.20767	725.20871	1.43	$C_{36}H_{38}O_{16}$	(−): 255
364	13.88	Neohesperidin dihydrochalcone	–	–	–	611.19743	611.19814	1.16	$C_{28}H_{36}O_{15}$	(−): 565
365	13.88	24-Hydroxy-licoricesaponin A3	1001.45919	1001.45880	−0.39	999.44190	999.44425	2.34	$C_{48}H_{72}O_{22}$	(+): 825, 649, 631, 487, 469, 451
366	13.91	Laccaic acid D	315.05015	315.04993	−0.72	313.03522	313.03538	0.49	$C_{16}H_{10}O_7$	(−): 269, 241, 225
367	13.99	*Erythro*-guaiacylglycerol-*O*-4′-dehydrodisinapyl ether	585.23441	585.23304	−2.34	583.21807	583.21849	0.71	$C_{31}H_{36}O_{11}$	(−): 535
368	14.14	Di-*O*-galloyl-*O*-cinnamoyl-β-D-glucose	–	–	–	613.11929	613.11989	0.98	$C_{29}H_{26}O_{15}$	(−): 461 443, 169
369	14.14	Syringlyglycerol-β-syringaresinol ether	–	–	–	643.23901	643.23961	0.93	$C_{33}H_{40}O_{13}$	(−): 595, 417, 387
370	14.37	24-Hydroxy-licoricesaponin A3 isomer	1001.45939	1001.45880	−0.58	999.44143	999.44425	2.82	$C_{48}H_{72}O_{22}$	(−): 351
371	14.41	Unknown	685.24873	685.24908	0.52	729.23869	729.24001	1.81[c]	$C_{35}H_{40}O_{14}$	(−): 371, 149
372	14.50	Uralsaponin F	897.41308	897.41146	−1.81	895.39620	895.39690	0.79	$C_{44}H_{64}O_{19}$	(+): 545, 527
373	14.59	Emodin-*O*-(6-carboxyacetyl)-β-D-glucopyranoside	519.11381	519.11332	−0.94	517.09827	517.09876	0.96	$C_{24}H_{22}O_{13}$	(−): 269
374	14.60	Uralsaponin T	955.49216	955.48971	−2.57	953.47433	953.47515	0.86	$C_{48}H_{74}O_{19}$	(−): 351
375	14.67	22-Hydroxyl licorice saponin G2	855.40216	855.40089	−1.48	853.38505	853.38634	1.51	$C_{42}H_{62}O_{18}$	(+): 679, 661, 643, 503, 485, 467
376	14.75	*Erythro*-guaiacylglycerol-*O*-4′-dehydrodisinapyl ether isomer	–	–	–	583.21820	583.21849	0.48	$C_{31}H_{36}O_{11}$	(−): 535
377	14.83	4,5-Dioxodehydroasimilobine	294.07638	294.07608	−1.02	292.06147	292.06153	0.21	$C_{17}H_{11}NO_4$	–
378	14.87	Naringenin	273.07596	273.07575	−0.76	271.06109	271.06120	0.39	$C_{15}H_{12}O_5$	(−): 177, 165, 151, 119, 107
379	15.02	Amorfrutin 2	307.19061	307.19039	−0.72	305.17575	305.17583	0.28	$C_{18}H_{26}O_4$	(−): 261, 243, 191
380	15.05	Prunetrin	–	–	–	445.11408	445.11402	−0.13	$C_{22}H_{22}O_{10}$	(−): 283
381	15.06	Echinatin	271.09663	271.09649	−0.55	–	–	–	$C_{16}H_{14}O_4$	(+): 229, 177
382	15.08	Glyzaglabrin	299.05512	299.05501	−0.35	297.04049	297.04046	−0.11	$C_{16}H_{10}O_6$	–
383	15.08	Uralsaponin F isomer	897.41292	897.41146	−1.63	895.39611	895.39690	0.88	$C_{44}H_{64}O_{19}$	(−): 351
384	15.09	Apigenin[d]	271.06023	271.06010	−0.47	269.04547	269.04555	0.29	$C_{15}H_{10}O_5$	(−): 237, 225, 201, 175, 151, 149
385	15.18	Matairesinol	359.14899	359.14891	−0.21	357.13426	357.13436	0.27	$C_{20}H_{22}O_6$	(+): 323, 305, 291
386	15.23	Licorice saponin A3	985.46490	985.46389	−1.03	983.44717	983.44933	2.20	$C_{48}H_{72}O_{21}$	(−): 821
387	15.32	Herbacetin-8-methyl ether	317.06585	317.06558	−0.87	315.05108	315.05103	−0.17	$C_{16}H_{12}O_7$	–
388	15.37	Uralsaponin D	851.37053	851.36959	−1.10	849.35583	849.35504	−0.93	$C_{42}H_{58}O_{18}$	(+): 499
389	15.39	Matairesinol isomer	359.14901	359.14891	−0.26	357.13429	357.13436	0.21	$C_{20}H_{22}O_6$	(−): 342
390	15.45	Emodin-glucoside	433.11357	433.11292	−1.49	431.09831	431.09837	0.15	$C_{21}H_{20}O_{10}$	(−): 269
391	15.47	Genistein	271.06031	271.06010	−0.79	269.04562	269.04555	−0.27	$C_{15}H_{10}O_5$	(+): 243
392	15.56	Kaempferol	287.05511	287.05501	−0.33	285.04045	285.04046	0.02	$C_{15}H_{10}O_6$	(+): 269, 258, 241, 231, 213, 185, 165, 153
393	15.61	Quercetin 3,4'-dimethyl ether or isomer	331.08144	331.08123	−0.63	329.06678	329.06668	−0.32	$C_{17}H_{14}O_7$	–
394	15.63	Emodin methyl ether-8-*O*-glucoside	469.11082	469.11052	−0.65[a]	445.11405	445.11402	−0.06	$C_{22}H_{22}O_{10}$	(−): 283
395	15.66	Physcion isomer	285.07592	285.07575	−0.60	283.06119	283.06120	0.03	$C_{16}H_{12}O_5$	(−): 240
396	15.66	9,12-Dihydroxy-13-oxooctadec-14-enoic acid	351.21417	351.21419	0.08[a]	327.21741	327.21770	0.89	$C_{18}H_{32}O_5$	(−): 229, 211, 183, 171
397	15.69	Unknown	543.19786	543.19732	−1.00	–	–	–	$C_{27}H_{31}N_2O_{10}$	(+): 381, 363, 335, 311
398	15.75	Kaempferide	301.07102	301.07066	−1.19	299.05633	299.05611	−0.73	$C_{16}H_{12}O_6$	(−): 284, 255, 240, 228
399	15.78	22-Hydroxyl licorice saponin G2 isomer	855.40178	855.40089	−1.03	853.38571	853.38634	0.73	$C_{42}H_{62}O_{18}$	(−): 351
400	15.87	Amorfrutin 2 isomer	307.19056	307.19039	−0.55	305.17585	305.17583	−0.05	$C_{18}H_{26}O_4$	(−): 261, 243, 191
401	15.87	Uralsaponin R isomer	971.48609	971.48462	−1.52	969.46932	969.47007	0.77	$C_{48}H_{74}O_{20}$	(+): 439
402	15.94	9,12-Dihydroxy-13-oxooctadec-14-enoic acid isomer	351.21414	351.21419	0.15[a]	327.21745	327.21770	0.77	$C_{18}H_{32}O_5$	(−): 229, 211, 183, 171
403	16.06	22β-Acetoxylglycyrrhizin	881.41716	881.41654	−0.71	879.40042	879.40199	1.78	$C_{44}H_{64}O_{18}$	(−): 351
404	16.13	Isorhamnetin	317.06551	317.06558	0.22	315.05089	315.05103	0.44	$C_{16}H_{12}O_7$	(−): 300, 283, 271, 255, 243, 227, 151
405	16.17	24-Hydroxy-licorice-saponin E2	837.39098	837.39033	−0.78	835.37446	835.37577	1.58	$C_{42}H_{60}O_{17}$	(+): 485, 469, 467

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
406	16.18	Uralsaponin X	1027.47405	1027.47445	0.39	1025.45807	1025.45990	1.78	$C_{50}H_{74}O_{22}$	–
407	16.21	Licorice saponin A3 isomer	985.46418	985.46389	−0.30	983.44730	983.44933	2.06	$C_{48}H_{72}O_{21}$	(+): 647,453
408	16.35	Uralsaponin R	971.48605	971.48462	−1.47	969.46925	969.47007	0.85	$C_{48}H_{74}O_{20}$	(+): 439
409	16.37	Yunganoside K2	839.40595	839.40598	0.03	837.39094	837.39142	0.58	$C_{42}H_{62}O_{17}$	(−): 661, 485, 351
410	16.38	Glabric acid isomer	487.34218	487.34180	−0.78	–	–	–	$C_{30}H_{46}O_5$	(+): 469, 451
411	16.40	Glabrolide	469.33124	469.33124	0.00	–	–	–	$C_{30}H_{44}O_4$	(+): 451
412	16.42	Baicalein	271.06018	271.06010	−0.31	269.04562	269.04555	−0.27	$C_{15}H_{10}O_5$	(+): 253
413	16.49	Dihydrolicorice saponin A3 isomer	987.48093	987.47954	−1.41	985.46372	985.46498	1.28	$C_{48}H_{74}O_{21}$	(−): 823, 351
414	16.57	Aristolactam AII/F1	266.08121	266.08117	−0.14	264.06661	264.06662	0.01	$C_{16}H_{11}NO_3$	–
415	16.68	Licorice saponin B2 isomer	809.43232	809.43180	−0.65	807.41673	807.41724	0.64	$C_{42}H_{64}O_{15}$	–
416	16.72	Uralsaponin R isomer	971.48469	971.48462	−0.07	969.46953	969.47007	0.55	$C_{48}H_{74}O_{20}$	(+): 439
417	16.82	Unknown	349.20099	349.20095	−0.11	347.18606	347.18640	0.97	$C_{20}H_{28}O_5$	(−): 303, 285, 259, 243
418	16.94	Licorice saponin A3 isomer	985.46436	985.46389	−0.48	983.44753	983.44933	1.83	$C_{48}H_{72}O_{21}$	(+): 647, 453
419	16.98	Glabrolide isomer	469.33145	469.33124	−0.45	–	–	–	$C_{30}H_{44}O_4$	(+): 451
420	16.98	Licorice saponin G2 isomer	839.40663	839.40598	−0.78	837.39080	837.39142	0.74	$C_{42}H_{62}O_{17}$	(+): 487
421	17.03	22β-Acetoxyl Uralsaponin C	867.43747	867.43728	−0.22	865.42218	865.42272	0.63	$C_{44}H_{66}O_{17}$	(+): 691
422	17.03	Uralsaponin R isomer	971.48596	971.48462	−1.37	969.46968	969.47007	0.40	$C_{48}H_{74}O_{20}$	(+): 439
423	17.12	Uralsaponin Q	941.47497	941.47406	−0.97	939.45817	939.45950	1.41	$C_{47}H_{72}O_{19}$	(+): 647, 471
424	17.14	9,12-Dihydroxy-13-oxooctadecanoic acid	353.22983	353.22984	0.04[a]	329.23309	329.23335	0.77	$C_{18}H_{34}O_5$	(−): 311, 229, 211
425	17.17	Uralsaponin T isomer	955.49150	955.48971	−1.88	953.47509	953.47515	0.07	$C_{48}H_{74}O_{19}$	(−): 351
426	17.22	Aristolactam AII/F1	266.08131	266.08117	−0.53	264.06657	264.06662	0.17	$C_{16}H_{11}NO_3$	–
427	17.46	Isoliquiritigenin	257.08088	257.08084	−0.17	255.06616	255.06628	0.47	$C_{15}H_{12}O_4$	(+): 239, 211, 147, 137
428	17.55	Glyzaglabrin isomer	299.05503	299.05501	−0.07	297.04020	297.04046	0.87	$C_{16}H_{10}O_6$	–
429	17.62	Bourneioside B	–	–	–	957.50662	957.50645	−0.17	$C_{48}H_{78}O_{19}$	(−): 911, 791, 645, 603
430	17.71	22β-Acetoxyl Licorice saponin J2	883.43315	883.43219	−1.09	881.41509	881.41764	2.89	$C_{44}H_{66}O_{18}$	(+): 707
431	17.82	Licorice saponin E2	821.39590	821.39541	−0.59	819.37984	819.38086	1.24	$C_{42}H_{60}O_{16}$	(+): 645, 469, 451
432	17.84	Formononetin	269.08085	269.08084	−0.07	267.06619	267.06628	0.34	$C_{16}H_{12}O_4$	(+): 254, 253, 237, 226, 225, 213, 197
433	17.92	Glabrolide isomer	469.33161	469.33124	−0.80	–	–	–	$C_{30}H_{44}O_4$	(+): 451
434	17.93	Glabric acid	487.34215	487.34180	−0.73	–	–	–	$C_{30}H_{46}O_5$	(+):469, 451
435	17.96	Licorice saponin G2	839.40696	839.40598	−1.17	837.39081	837.39142	0.73	$C_{42}H_{62}O_{17}$	(+): 487, 469
436	17.97	Norcepharadione B	308.09206	308.09173	−1.06	–	–	–	$C_{18}H_{13}NO_4$	–
437	18.04	Phillygenin	373.16478	373.16456	−0.58	371.15018	371.15001	−0.46	$C_{21}H_{24}O_6$	(+): 355, 337, 306, 305, 284, 269
438	18.04	Licorice saponin B2 isomer	–	–	–	807.41600	807.41724	1.55	$C_{42}H_{64}O_{15}$	–
439	18.05	Glycyuralin E	371.14932	371.14891	−1.09	–	–	–	$C_{21}H_{22}O_6$	–
440	18.05	Uralsaponin O	821.39785	821.39541	−2.97	819.37964	819.38086	1.49	$C_{42}H_{60}O_{16}$	(+): 645, 469, 451
441	18.06	4′-*O*-methyl glabridin	355.15395	355.15400	0.15	–	–	–	$C_{21}H_{22}O_5$	–
442	18.12	10,16-Dihydroxy-palmitic acid	289.23760	289.23734	−0.91	287.22276	287.22278	0.07	$C_{16}H_{32}O_4$	(−): 269, 241
443	18.23	Clinodiside A or Bourneioside B	–	–	–	957.50479	957.50645	1.74	$C_{48}H_{78}O_{19}$	(−): 911
444	18.24	Yunganoside J1/L1 isomer	969.46673	969.46897	2.32	967.45147	967.45442	3.05	$C_{48}H_{72}O_{20}$	(−): 803, 645, 497
445	18.30	Amentoflavone	539.09838	539.09727	−2.05	537.08306	537.08272	−0.63	$C_{30}H_{18}O_{10}$	(−): 375
446	18.35	Uralsaponin T isomer	955.48929	955.48971	0.44	953.47373	953.47515	1.49	$C_{48}H_{74}O_{19}$	(−): 351
447	18.38	22β-Acetoxyl-glycyrrhaldehyde	887.40429	887.40357	−0.81[a]	863.40441	863.40707	3.09	$C_{44}H_{64}O_{17}$	(+): 865, 689
448	18.49	Yunganoside J1/L1	969.46957	969.46897	−0.62	967.45405	967.45442	0.38	$C_{48}H_{72}O_{20}$	(−): 803, 645, 497
449	18.56	Glycyrrhizic acid isomer	823.41153	823.41106	−0.57	821.39558	821.39651	1.13	$C_{42}H_{62}O_{16}$	(+): 647, 471
450	18.64	Licorice saponin G2 isomer	839.40623	839.40598	−0.30	837.39103	837.39142	0.47	$C_{42}H_{62}O_{17}$	(+): 487
451	18.64	Licorice saponin A3 isomer	985.46469	985.46389	−0.81	983.44646	983.44933	2.92	$C_{48}H_{72}O_{21}$	(−): 821
452	18.72	9,12-Dihydroxy-13-oxooctadecanoic acid isomer	353.22977	353.22984	0.22[a]	329.23323	329.23335	0.35	$C_{18}H_{34}O_5$	(−): 311, 229, 211

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
453	18.78	Uralsaponin T isomer	955.49075	955.48971	−1.09	953.47336	953.47515	1.88	$C_{48}H_{74}O_{19}$	(−): 351
454	18.87	Retusin	–	–	–	357.09779	357.09798	0.51	$C_{19}H_{18}O_7$	–
455	18.88	Aloe emodin	271.06015	271.06010	−0.20	269.04540	269.04555	0.54	$C_{15}H_{10}O_5$	(−): 240, 223, 211
456	18.89	Licorice saponin J2 isomer	825.42742	825.42671	−0.86	823.41107	823.41216	1.33	$C_{42}H_{64}O_{16}$	(+): 455
457	19.00	9,12-Dihydroxy-13-oxooctadecanoic acid isomer	353.22975	353.22984	0.27[a]	329.23333	329.23335	0.06	$C_{18}H_{34}O_5$	(−): 311, 229, 211
458	19.02	Irisolidone	–	–	–	313.07162	313.07176	0.46	$C_{17}H_{14}O_6$	–
459	19.06	Dihydrolicorice saponin A3 isomer	987.48014	987.47954	−0.61	985.46561	985.46498	−0.63	$C_{48}H_{74}O_{21}$	(+): 629, 471, 453
460	19.11	Norcepharadione B isomer	308.09176	308.09173	−0.09	–	–	–	$C_{18}H_{13}NO_4$	–
461	19.17	Uralsaponin N	839.40620	839.40598	−0.26	837.39101	837.39142	0.49	$C_{42}H_{62}O_{17}$	(+): 487
462	19.35	Glycyrrhetic acid 3-*O*-glucuronide	647.37926	647.37897	−0.43	–	–	–	$C_{36}H_{54}O_{10}$	(+): 453, 435, 407
463	19.49	Glycyrrhizic acid[d]	823.41127	823.41106	−0.25	821.39607	821.39651	0.53	$C_{42}H_{62}O_{16}$	(+): 647, 471, 453
464	19.57	22β-Acetoxyl-glycyrrhaldehyde isomer	887.40351	887.40357	0.07[a]	863.40508	863.40707	2.31	$C_{44}H_{64}O_{17}$	(+): 865, 689
465	19.61	Cepharadione B	322.10739	322.10738	−0.03	–	–	–	$C_{19}H_{15}NO_4$	(+): 292
466	19.61	Uralsaponin T isomer	955.48943	955.48971	0.29	953.47476	953.47515	0.41	$C_{48}H_{74}O_{19}$	(−): 351
467	19.65	Licorice saponin B2 isomer	809.43122	809.43180	0.71	807.41529	807.41724	2.42	$C_{42}H_{64}O_{15}$	(+): 453
468	19.67	Quercetin 3,4'-dimethyl ether or isomer	331.08124	331.08123	−0.02	329.06671	329.06668	−0.09	$C_{17}H_{14}O_7$	(−): 314, 299
469	19.68	9,12-Dihydroxy-13-oxooctadecanoic acid isomer	353.22979	353.22984	0.15[a]	329.23325	329.23335	0.29	$C_{18}H_{34}O_5$	(−): 311, 229, 211
470	19.72	Glycyrrhetinic acid rhamnosyl diglucuronide or isomer	973.50145	973.50027	−1.21	–	–	–	$C_{48}H_{76}O_{20}$	(+): 471, 453
471	19.78	Yunganoside J1/L1 isomer	969.46972	969.46897	−0.77	967.45159	967.45442	2.93	$C_{48}H_{72}O_{20}$	(−): 803, 645, 497
472	19.82	Dihydrolicorice saponin A3 isomer	987.48065	987.47954	−1.13	985.46146	985.46498	3.58	$C_{48}H_{74}O_{21}$	(+): 629, 471, 453
473	19.91	Rhein	285.03941	285.03936	−0.17	283.02465	283.02481	0.55	$C_{15}H_8O_6$	(−): 255, 239, 211, 183
474	19.92	Antrapurol	–	–	–	239.03490	239.03498	0.34	$C_{14}H_8O_4$	(−): 211
475	19.95	Licorice saponin B2 isomer	809.43191	809.43180	−0.14	807.41581	807.41724	1.78	$C_{42}H_{64}O_{15}$	(−): 631, 351
476	19.97	Glycyrrhetinic acid monoglucuronide or isomer	647.37929	647.37897	−0.48	–	–	–	$C_{36}H_{54}O_{10}$	(+): 453, 435, 407
477	20.06	Unknown	–	–	–	607.18122	607.18210	1.46	$C_{32}H_{32}O_{12}$	(−): 443
478	20.14	Echinatin isomer	271.09652	271.09649	−0.13	–	–	–	$C_{16}H_{14}O_4$	(+): 239
479	20.18	Uralsaponin O isomer	821.39595	821.39541	−0.66	819.37883	819.38086	2.47	$C_{42}H_{60}O_{16}$	(+): 469
480	20.23	Licorice saponin G2 isomer	839.40665	839.40598	−0.80	837.39002	837.39142	1.67	$C_{42}H_{62}O_{17}$	(+): 487
481	20.34	Licorice saponin B2	809.43231	809.43180	−0.64	807.41544	807.41724	2.23	$C_{42}H_{64}O_{15}$	(−): 631, 455, 351
482	20.34	Licorice saponin J2 isomer	825.42845	825.42671	−2.11	823.41058	823.41216	1.92	$C_{42}H_{64}O_{16}$	(+): 487, 469
483	20.37	Uralsaponin R isomer	971.48545	971.48462	−0.86	969.46829	969.47007	1.84	$C_{48}H_{74}O_{20}$	(−): 497
484	20.41	Yunganoside J1/L1	969.47038	969.46897	−1.45	967.45266	967.45442	1.82	$C_{48}H_{72}O_{20}$	(−): 803, 645, 497
485	20.42	Wogonin	285.07579	285.07575	−0.14	283.06112	283.06120	0.28	$C_{16}H_{12}O_5$	(+): 270
486	20.42	Yunganoside A1	957.50618	957.50536	−0.86	955.48997	955.49080	0.87	$C_{48}H_{76}O_{19}$	(+): 811
487	20.46	Uralsaponin T isomer	955.49226	955.48971	−2.67	953.47267	953.47515	2.60	$C_{48}H_{74}O_{19}$	(−): 351
488	20.63	9,12-Dihydroxy-13-oxooctadecanoic acid isomer	353.22973	353.22984	0.32[a]	329.23317	329.23335	0.55	$C_{18}H_{34}O_5$	(−): 311, 229, 211
489	20.72	Glycyrrhetinic acid monoglucuronide or isomer	647.37932	647.37897	−0.53	–	–	–	$C_{36}H_{54}O_{10}$	(+): 453, 435, 407
490	20.74	Chrysin	255.06551	255.06519	−1.27	253.05084	253.05063	−0.81	$C_{15}H_{10}O_4$	(−): 209
491	20.77	Licorice saponin H2	823.41114	823.41106	−0.10	821.39529	821.39651	1.48	$C_{42}H_{62}O_{16}$	(+): 647, 471
492	20.85	Uralsaponin T isomer	–	–	–	953.47421	953.47515	0.99	$C_{48}H_{74}O_{19}$	(−): 351
493	20.98	Yunganoside B1	957.50595	957.50536	−0.62	955.48940	955.49080	1.47	$C_{48}H_{76}O_{19}$	(+): 811
494	21.21	Licorice saponin B2 isomer	809.43122	809.43180	0.71	807.41612	807.41724	1.39	$C_{42}H_{64}O_{15}$	(−): 351
495	21.29	Cepharanone B	280.09680	280.09682	0.05	–	–	–	$C_{17}H_{13}NO_3$	(+): 265
496	21.30	Licroice saponin K2	823.41144	823.41106	−0.45	821.39556	821.39651	1.16	$C_{42}H_{62}O_{16}$	(+): 647, 471
497	21.44	Uralsaponin Q isomer	941.47414	941.47406	−0.09	939.45792	939.45950	1.69	$C_{47}H_{72}O_{19}$	(+): 647, 471
498	21.45	Oroxylin A	285.07578	285.07575	−0.12	283.06102	283.06120	0.62	$C_{16}H_{12}O_5$	(+): 270

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Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
499	21.49	Clinodiside A	–	–	–	957.50566	957.50645	0.83	$C_{48}H_{78}O_{19}$	(−): 911, 749, 471
500	21.51	3-*O*-rhamnopyranosyl-(2→1)-arabinopyranosyl-28-*O*-glucopyranosyl hederagenin	913.51412	913.51553	1.54	911.49761	911.50097	3.69	$C_{47}H_{76}O_{17}$	(−): 749, 603, 471
501	21.54	Licorice saponin B2 isomer	–	–	–	807.41490	807.41724	2.91	$C_{42}H_{64}O_{15}$	(−): 351
502	21.71	Licorice saponin J2	825.42726	825.42671	−0.66	823.41044	823.41216	2.09	$C_{42}H_{64}O_{16}$	(+): 455, 437
503	21.77	Glycyrrhetinic acid monoglucuronide or isomer	647.37922	647.37897	−0.37	–	–	–	$C_{36}H_{54}O_{10}$	(+): 453, 435, 407
504	21.77	Araboglycyrrhizin	779.42277	779.42123	−1.97	777.40466	777.40668	2.60	$C_{41}H_{62}O_{14}$	(+): 453
505	21.81	Sophoraisoflavone A	353.10190	353.10196	0.19	351.08794	351.08741	−1.51	$C_{20}H_{16}O_6$	(+): 311
506	21.85	Licoflavonol	355.11802	355.11761	−1.14	353.10281	353.10306	0.70	$C_{20}H_{18}O_6$	(−): 297
507	21.88	Diosmetin	–	–	–	299.05591	299.05611	0.67	$C_{16}H_{12}O_6$	(−): 284, 256
508	21.89	Uralsaponin B	823.41119	823.41106	−0.16	821.39391	821.39651	3.17	$C_{42}H_{62}O_{16}$	(+): 647, 471
509	21.99	Uralsaponin T isomer	–	–	–	953.47362	953.47515	1.61	$C_{48}H_{74}O_{19}$	(−): 351
510	22.13	Dimethoxyluteolin	315.08630	315.08631	0.04	313.07152	313.07176	0.77	$C_{17}H_{14}O_6$	(+): 300
511	22.39	Glycyrrhisoflavone	355.11757	355.11761	0.12	353.10276	353.10306	0.85	$C_{20}H_{18}O_6$	(−): 297
512	22.45	Uralsaponin T isomer	955.48924	955.48971	0.48	953.47302	953.47515	2.23	$C_{48}H_{74}O_{19}$	(−): 351
513	22.49	Cepharadione B isomer	322.10738	322.10738	0.00	–	–	–	$C_{19}H_{15}NO_4$	–
514	22.50	Uralsaponin C	825.42680	825.42671	−0.11	823.41054	823.41216	1.97	$C_{42}H_{64}O_{16}$	(+): 455, 437
515	22.53	Glicophenone	359.14901	359.14891	−0.26	357.13414	357.13436	0.63	$C_{20}H_{22}O_6$	–
516	22.61	Licorice saponin C2	829.39863	829.39809	−0.65[a]	805.39991	805.40159	2.09	$C_{42}H_{62}O_{15}$	(−): 351
517	22.64	Glycycoumarin	369.13218	369.13326	2.93	367.11839	367.11871	0.89	$C_{21}H_{20}O_6$	(+): 313, 285
518	22.66	Carnosic acid isomer	333.20665	333.20604	−1.83	331.19192	331.19148	−1.32	$C_{20}H_{28}O_4$	(−): 287, 271
519	22.73	Licofuranone	357.13365	357.13326	−1.09	355.11903	355.11871	−0.90	$C_{20}H_{20}O_6$	(−): 229, 193
520	22.92	Saikosaponin B2/D	–	–	–	779.45667	779.45872	2.62	$C_{42}H_{68}O_{13}$	–
521	22.92	Uralsaponin W	807.41648	807.41615	−0.41	805.39962	805.40159	2.46	$C_{42}H_{62}O_{15}$	(−): 351
522	22.98	5,3′-Dimethoxyluteolin	315.08622	315.08631	0.29	313.07146	313.07176	0.97	$C_{17}H_{14}O_6$	(−): 298, 283, 255
523	23.08	Glyasperin C	357.16961	357.16965	0.13	355.15478	355.15510	0.88	$C_{21}H_{24}O_5$	–
524	23.09	Semilicoisoflavone B	353.10185	353.10196	0.33	351.08708	351.08741	0.93	$C_{20}H_{16}O_6$	(+): 311
525	23.10	Licorice saponin B2 isomer	–	–	–	807.41423	807.41724	3.73	$C_{42}H_{64}O_{15}$	(−): 351
526	23.14	Licoflavanone	341.13841	341.13835	−0.18	339.12347	339.12380	0.98	$C_{20}H_{20}O_5$	(−): 293, 229, 167
527	23.24	Arjunolic acid	489.35780	489.35745	−0.71	487.34247	487.34290	0.87	$C_{30}H_{48}O_5$	(−): 409
528	23.28	Uralenin	355.11742	355.11761	0.55	353.10281	353.10306	0.72	$C_{20}H_{18}O_6$	–
529	23.32	9-Hydroxy-12-oxo-10-octadecenoic acid	313.23724	313.23734	0.31	311.22251	311.22278	0.87	$C_{18}H_{32}O_4$	(−): 293, 275
530	23.32	Licorice saponin B2 isomer	809.43218	809.43180	−0.48	807.41475	807.41724	3.09	$C_{42}H_{64}O_{15}$	(−): 351
531	23.34	Glabrene	–	–	–	321.11278	321.11323	1.41	$C_{20}H_{18}O_4$	–
532	23.42	Yunganoside C1	957.50565	957.50536	−0.31	955.48971	955.49080	1.14	$C_{48}H_{76}O_{19}$	(+): 811
533	23.43	Uralsaponin R isomer	971.48496	971.48462	−0.35	969.46870	969.47007	1.41	$C_{48}H_{74}O_{20}$	(−): 497
534	23.49	Glycyrrhizic acid isomer	823.41117	823.41106	−0.13	821.39408	821.39651	2.96	$C_{42}H_{62}O_{16}$	(+): 647, 471
535	23.60	Pachypodol	345.09691	345.09688	−0.08	343.08208	343.08233	0.71	$C_{18}H_{16}O_7$	(−): 328, 313, 285, 270, 257, 242
536	23.77	Gancaonin L	355.11757	355.11761	0.13	353.10273	353.10306	0.93	$C_{20}H_{18}O_6$	(+): 299, 287
537	23.88	Hederagenin-3-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside	–	–	–	795.45219	795.45363	1.81[c]	$C_{41}H_{66}O_{12}$	(−): 749
538	23.89	Carnosic acid	333.20618	333.20604	−0.42	331.19121	331.19148	0.82	$C_{20}H_{28}O_4$	(−): 287, 271
539	23.93	Licochalcone D	355.15398	355.15400	0.06	353.13919	353.13945	0.72	$C_{21}H_{22}O_5$	(−): 338
540	23.99	8-*O*-Methylretusin	299.09190	299.09140	−1.66	–	–	–	$C_{17}H_{14}O_5$	–
541	24.17	Licorice saponin J2 isomer	825.42689	825.42671	−0.21	823.41084	823.41216	1.60	$C_{42}H_{64}O_{16}$	(+): 455, 437
542	24.27	(2R,3R)-3,4′,7-Trihydroxy-3′-prenylflavane	341.13882	341.13835	−1.37	339.12441	339.12380	−1.81	$C_{20}H_{20}O_5$	–
543	24.30	Unknown	363.21646	363.21660	0.40	361.20146	361.20205	1.62	$C_{21}H_{30}O_5$	(−): 317, 285

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
544	24.35	Curdione	237.18481	237.18491	0.41	–	–	–	$C_{15}H_{24}O_2$	(+): 219, 135
545	24.35	Unknown	495.34449	495.34420	−0.59	–	–	–	$C_{28}H_{42}N_6O_2$	(+):259
546	24.50	Licoisoflavone A	355.11750	355.11761	0.34	353.10271	353.10306	1.00	$C_{20}H_{18}O_6$	(−): 309, 285, 267, 243
547	24.63	Glycyrin	405.13090	405.13086	−0.10[a]	381.13413	381.13436	0.60	$C_{22}H_{22}O_6$	(−): 366, 351
548	24.68	Aurantiamide acetate	445.21207	445.21218	0.26	443.19719	443.19763	0.99	$C_{27}H_{28}N_2O_4$	(+): 224, 194
549	24.79	Morachalcone A	341.13887	341.13835	−1.53	339.12457	339.12380	−2.26	$C_{20}H_{20}O_5$	–
550	24.79	Licorice saponin C2 isomer	829.39856	829.39809	−0.56[a]	805.40103	805.40159	0.70	$C_{42}H_{62}O_{15}$	(−): 351
551	24.81	Licochalcone A	339.15934	339.15909	−0.75	337.14423	337.14453	0.90	$C_{21}H_{22}O_4$	(+): 297, 283, 271, 245, 229, 219
552	24.82	Glycyrrhetinic acid monoglucuronide or isomer	647.37921	647.37897	−0.36	645.36308	645.36442	2.08	$C_{36}H_{54}O_{10}$	(+): 453, 435, 407
553	24.87	Licoflavone A	–	–	–	321.11396	321.11323	−2.28	$C_{20}H_{18}O_4$	–
554	24.89	Uralsaponin T	–	–	–	953.47459	953.47515	0.60	$C_{48}H_{74}O_{19}$	(−): 351
555	25.07	Octadecanedioic acid or isomer	337.23488	337.23493	0.14[a]	313.23807	313.23843	1.15	$C_{18}H_{34}O_4$	(−): 295, 277
556	25.08	Emodin	271.06011	271.06010	−0.03	269.04543	269.04555	0.44	$C_{15}H_{10}O_5$	(−): 241, 225, 210
557	25.26	Licorice saponin B2 isomer	–	–	–	807.41556	807.41724	2.08	$C_{42}H_{64}O_{15}$	–
558	25.27	Neoglycyrol	367.11745	367.11761	0.45	365.10281	365.10306	0.70	$C_{21}H_{18}O_6$	(+): 339, 311, 296, 283
559	25.34	Octadecanedioic acid or isomer	337.23492	337.23493	0.02[a]	313.23823	313.23843	0.66	$C_{18}H_{34}O_4$	(−): 295
560	25.58	Psoralidin or isomer	337.10695	337.10705	0.30	335.09234	335.09250	0.46	$C_{20}H_{16}O_5$	(−): 320, 307, 291, 213
561	25.69	Glabridin	325.14310	325.14344	1.03	323.12963	323.12888	−2.30	$C_{20}H_{20}O_4$	(−): 305, 279, 253, 213, 201, 187, 175, 147, 135
562	26.00	Kaurenoic acid	303.23181	303.23186	0.17	–	–	–	$C_{20}H_{30}O_2$	(+): 257
563	26.07	Hydroxyglycyrrhetic acid	487.34173	487.34180	0.14	485.32685	485.32725	0.82	$C_{30}H_{46}O_5$	–
564	26.32	Licoisoflavone B	353.10197	353.10196	−0.03	351.08720	351.08741	0.61	$C_{20}H_{16}O_6$	(+): 311
565	26.40	Pogostone	225.11206	225.11214	0.32	223.09741	223.09758	0.79	$C_{12}H_{16}O_4$	(−): 139
566	26.62	Gingerglycolipid B	–	–	–	723.38016	723.38086	0.96[c]	$C_{33}H_{58}O_{14}$	(−): 677
567	26.87	Glabrone	337.10749	337.10705	−1.31	335.09239	335.09250	0.32	$C_{20}H_{16}O_5$	(−): 320, 307, 291
568	26.95	Hispaglabridin A	393.20685	393.20604	−2.08	391.19232	391.19148	−2.13	$C_{25}H_{28}O_4$	–
569	27.08	Glyasperin D	371.18533	371.18530	−0.07	369.17051	369.17075	0.64	$C_{22}H_{26}O_5$	(+): 303
570	27.20	Manglupenone or isomer	437.34145	437.34141	−0.11	–	–	–	$C_{30}H_{44}O_2$	(+): 391
571	27.39	Gancaonin E	425.19602	425.19587	−0.36	423.18112	423.18131	0.46	$C_{25}H_{28}O_6$	(−): 229, 193
572	27.41	Chrysophanol	255.06528	255.06519	−0.39	253.05052	253.05063	0.46	$C_{15}H_{10}O_4$	(−): 225, 210, 197, 182, 181
573	27.46	Hederagenin	473.36332	473.36254	−1.66	471.34753	471.34798	0.96	$C_{30}H_{48}O_4$	(+): 409, 391
574	27.62	3-Hydroxyglabrol	409.20072	409.20095	0.56	407.18743	407.18640	−2.55	$C_{25}H_{28}O_5$	(−): 219
575	27.64	9S-Hyroxy-10E,12E-octadecadienoic acid	297.24268	297.24242	−0.87	295.22816	295.22787	−1.00	$C_{18}H_{32}O_3$	(−): 277, 227, 195, 183, 155, 139
576	27.78	Gancaonin E isomer	425.19688	425.19587	−2.39	423.18199	423.18131	−1.60	$C_{25}H_{28}O_6$	(−): 229, 193
577	27.79	Angustone A	423.18105	423.18022	−1.97	421.16658	421.16566	−2.18	$C_{25}H_{26}O_6$	(−): 309
578	27.93	Isoangustone A	423.18111	423.18022	−2.13	421.16644	421.16566	−1.84	$C_{25}H_{26}O_6$	(−): 309
579	27.93	Glycyrrhetinic acid isomer	471.34746	471.34689	−1.22	469.33234	469.33233	−0.01	$C_{30}H_{46}O_4$	(+): 425, 407
580	28.17	Corosolic acid	473.36226	473.36254	0.58	471.34761	471.34798	0.79	$C_{30}H_{48}O_4$	(+): 437, 409, 313, 205
581	28.40	Glyasperin A	423.18121	423.18022	−2.35	421.16610	421.16566	−1.04	$C_{25}H_{26}O_6$	(−): 379
582	28.40	Physcion	285.07586	285.07575	−0.40	283.06098	283.06120	0.75	$C_{16}H_{12}O_5$	(−): 269, 268, 240
583	28.49	Lupenone isomer	425.37876	425.37779	−2.27	–	–	–	$C_{30}H_{48}O$	–
584	28.55	Glyinflanin C	407.18612	407.18530	−2.01	405.17115	405.17075	−0.99	$C_{25}H_{26}O_5$	(−): 201
585	28.72	Unknown	495.33188	495.33163	−0.50	493.31625	493.31708	1.67	$C_{28}H_{46}O_7$	(+): 477, 459, 441, 431, 413, 399
586	28.79	Glycyrrhetinic acid[d]	471.34712	471.34689	−0.49	469.33310	469.33233	−1.64	$C_{30}H_{46}O_4$	(+): 453, 435, 425, 407, 389
587	28.86	Lupenone	425.37879	425.37779	−2.33	–	–	–	$C_{30}H_{48}O$	–
588	28.96	Unknown	495.33199	495.33163	−0.73	493.31616	493.31708	1.85	$C_{28}H_{46}O_7$	(−): 475
589	29.82	Flavaspidic acid AB	–	–	–	417.15542	417.15549	0.16	$C_{22}H_{26}O_8$	(−): 221, 209, 207, 195

(*continued on next page*)

Table 1 (*continued*)

No.	RT (min)	Identification	$[M+H]^+$			$[M-H]^-$			Formula	Product ion *m/z*
			Observed	Calculated	Error (ppm)	Observed	Calculated	Error (ppm)		
590	29.98	γ-Linolenic acid	279.23235	279.23186	−1.75	277.21689	277.21730	1.48	$C_{18}H_{30}O_2$	(−): 233
591	30.23	Ursolic acid	–	–	–	455.35247	455.35307	1.32	$C_{30}H_{48}O_3$	(−): 407
592	30.45	Betulinic acid	457.36796	457.36762	−0.74	455.35241	455.35307	1.45	$C_{30}H_{48}O_3$	(−): 407, 391
593	30.71	Linoleic acid	–	–	–	279.23247	279.23295	1.73	$C_{18}H_{32}O_2$	(−): 261
594	30.93	Oleanolic acid	457.36747	457.36762	0.33	455.35223	455.35307	1.84	$C_{30}H_{48}O_3$	(−): 407, 391
595	31.42	Hexadecanoic acid	–	–	–	255.23269	255.23295	1.05	$C_{16}H_{32}O_2$	(−): 237
596	31.62	Oleic acid	–	–	–	281.24818	281.24860	1.52	$C_{18}H_{34}O_2$	–

—: not detected.

[a] $[M+Na]^+$.

[b] $[M + NH_4]^+$.

[c] $[M + HCOO]^-$.

[d] Compared with a reference standard.

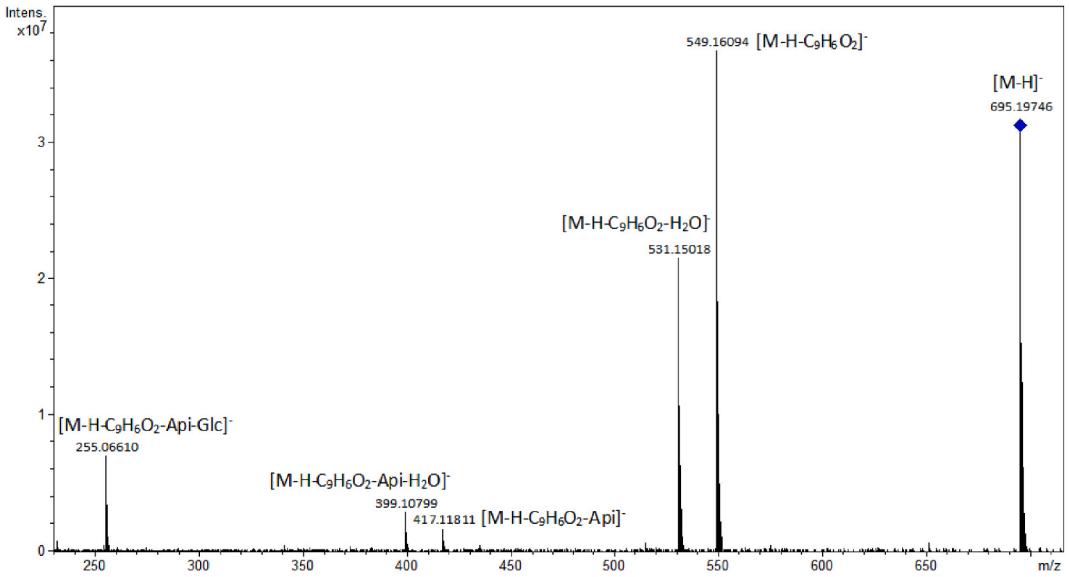

Fig. 3. The MS/MS spectrum of licorice glycoside D1/D2.

Compound 362 (t_R = 13.81 min) showed deprotonated ion $[M-H]^-$ at *m/z* 695.19785, with similar fragment behaviors to that of licorice glycoside D1/D2. It was temporarily deduced as licorice glycoside B.

Compound 378 with a retention time of 14.87 min generated the precursor ion of $[M-H]^-$ at *m/z* 271.06109, indicating the molecular formula of $C_{15}H_{12}O_5$. The characteristic fragments at *m/z* 177.01922, *m/z* 165.01934, *m/z* 151.00363, *m/z* 119.05013, and *m/z* 107.01387 corresponded to $[M-H-C_6H_6O]^-$, $[M-H-C_7H_6O]^-$, $[M-H-C_8H_8O]^-$, $[M-H-C_7H_4O_4]^-$, and $[M-H-C_9H_8O_3]^-$. The precursor ion underwent RDA cleavage, resulted in two complementary product ions at *m/z* 151.00363 and *m/z* 119.05013. It was putatively characterized as naringenin.

The precursor ion $[M+H]^+$ of compound 381 at *m/z* 271.09663 was observed at 15.06 min. The molecular formula was $C_{16}H_{14}O_4$, as predicted by the precursor ion. In the MS/MS spectrum, the fragment ions were at *m/z* 229.08556 and *m/z* 177.05436 corresponded to $[M+H-C_2H_2O]^+$ and $[M+H-C_6H_6O]^+$. The compound was putatively characterized as echinatin. The precursor ion $[M+H]^+$ of compound 551 at *m/z* 339.15934 was observed at 24.81 min. The molecular formula was $C_{21}H_{22}O_4$, as predicted by the precursor ion. In the MS^2 spectrum, the fragment ions were at *m/z* 297.14808, *m/z* 283.09523, *m/z* 271.09615, *m/z* 245.11679, *m/z* 229.08549, and *m/z* 219.10075 corresponded to $[M+H-C_2H_2O]^+$, $[M+H-C_4H_8]^+$, $[M+H-C_5H_8]^+$, $[M+H-C_6H_6O]^+$, $[M+H-C_7H_{10}O_2]^+$, and $[M+H-C_8H_8O]^+$, respectively. The compound was putatively characterized as licochalcone A. Chalcones like echinatin and licochalcone A undergo Nazarov cyclization with loss of a ketene (C_2H_2O, 42 Da).

The identification of glabridin was taking as the example of isoflavans for illustration. Compound 561 with a retention time of 25.69 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 323.12963, corresponding to a molecular formula of $C_{20}H_{20}O_4$. In the MS^2 spectrum, the fragments at *m/z* 305.11823, *m/z* 281.11824, *m/z* 279.13909, *m/z* 253.12331, *m/z* 213.09199, *m/z* 201.09201, *m/z* 187.07632, *m/z* 175.07638, *m/z* 147.0451, and *m/z* 135.04509 corresponded to $[M-H-H_2O]^-$, $[M-H-C_2H_2O]^-$, $[M-H-CO_2]^-$, $[M-H-C_3H_2O_2]^-$, $[M-H-C_6H_6O_2]^-$, $[M-H-C_7H_6O_2]^-$, $[M-H-C_8H_8O_2]^-$, $[M-H-C_9H_8O_2]^-$, $[M-H-C_{11}H_{12}O_2]^-$, and $[M-H-C_{12}H_{12}O_2]^-$. It was putatively characterized as glabridin.

3.1.2. Phenylpropanoids

Phenylpropanoids, for example, pinoresinol shows anti-inflammatory activity [32]. Compound 357 with a retention time of 13.53 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 357.13430, corresponding to a molecular formula of $C_{20}H_{22}O_6$. In the MS^2 spectrum, peaks at *m/z* 342.11064, *m/z* 151.03982, and *m/z* 136.01635 corresponded to $[M-H-CH_3]^-$, $[M-H-C_{12}H_{14}O_3]^-$, and $[M-H-CH_3-C_{12}H_{14}O_3]^-$, respectively. Thus it could be temporarily deduced as pinoresinol. Compound 148 with a retention time of 6.71 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 681.23921, corresponding to a molecular formula of $C_{32}H_{42}O_{16}$. In the MS^2 spectrum, peaks at *m/z* 519.18676 and *m/z* 357.13420 corresponded to $[M-H-Glc]^-$ and $[M-H-2Glc]^-$. Thus it was putatively characterized as pinoresinol diglucoside.

Compound 437 with a retention time of 18.04 min exhibited the precursor ion of $[M+H]^+$ at *m/z* 373.16478, corresponding to a molecular formula of $C_{21}H_{24}O_6$. In the MS^2 spectrum, peaks at *m/z* 355.15517, *m/z* 337.14392, *m/z* 305.11683, *m/z* 284.10392, and *m/z* 269.08038 corresponded to $[M+H-H_2O]^+$, $[M+H-2H_2O]^+$, $[M+H-CH_8O_3]^+$, $[M+H-C_4H_9O_2]^+$, and $[M+H-C_5H_{12}O_2]^+$, respectively. The fragment ion *m/z* 306.12496 was also observed. Thus it could be temporarily deduced as phillygenin. Compound 517 with a retention time of 22.64 min exhibited the precursor ion of $[M+H]^+$ at *m/z* 369.13218, corresponding to a molecular formula of $C_{21}H_{20}O_6$. In the MS^2 spectrum, peaks at *m/z* 313.06983 and *m/z* 285.07497, corresponded to $[M+H-C_4H_8]^+$ and $[M+H-C_4H_8-CO]^+$, respectively. Thus it could be temporarily deduced as glycycoumarin. And the MS/MS spectrum is shown in Fig. 4.

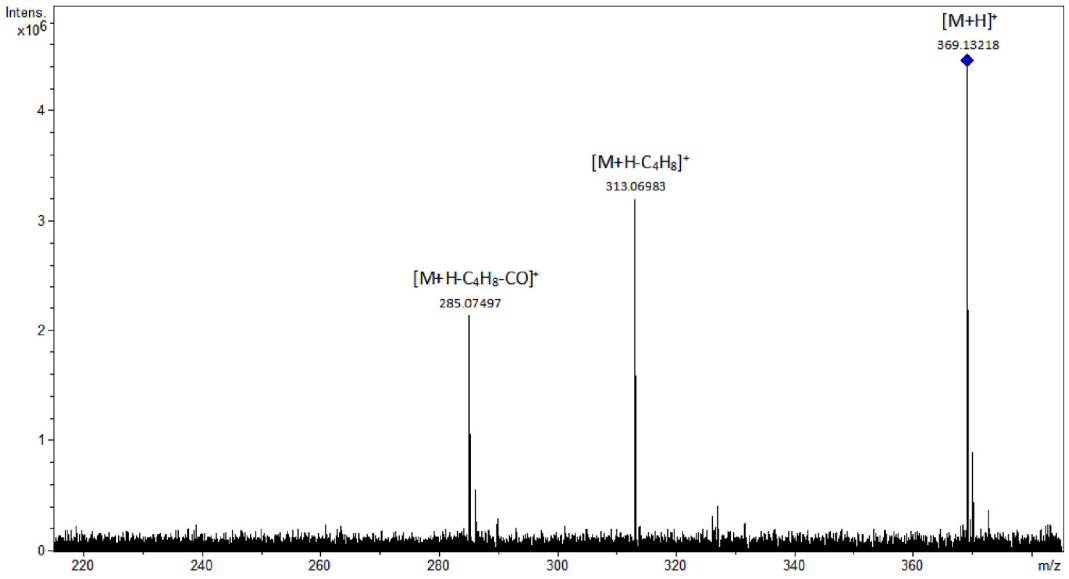

Fig. 4. The MS/MS spectrum of glycycoumarin.

Compound 558 with a retention time of 25.27 min exhibited the precursor ion of $[M+H]^+$ at *m/z* 367.11745, corresponding to a molecular formula of $C_{21}H_{18}O_6$. In the MS^2 spectrum, peaks at *m/z* 339.12218, *m/z* 311.05439, *m/z* 296.03083, and *m/z* 283.05943, corresponded to $[M + H–CO]^+$, $[M + H–C_4H_8]^+$, $[M + H–C_4H_8–CH_3]^+$, and $[M + H–C_4H_8–CO]^+$, respectively. Thus it could be temporarily deduced as neoglycyrol.

3.1.3. Phenylethanoid glycosides

Phenylethanoid glycosides, for example, forsythoside B shows protective effect against lipopolysaccharide-induced acute lung injury [33]. The chemical structures of forsythoside A, forsythoside H, forsythoside I and acteoside all consist of four chemical moieties: caffeoyl, hydroxytyrosol, Rha and Glc. Compound 201 with a retention time of 7.87 min exhibited the precursor ion of $[M - H]^-$ at *m/z* 623.19775, corresponding to a molecular formula of $C_{29}H_{36}O_{15}$. In the MS^2 spectrum, peaks at *m/z* 477.13982, *m/z* 461.16604, *m/z* 443.15545, *m/z* 315.10830, *m/z* 297.09774, *m/z* 179.03475, *m/z* 161.02417, *m/z* 135.04491, *m/z* 133.02926 corresponded to $[M\text{-}H\text{-}C_6H_{10}O_4]^-$, $[M\text{-}H\text{-}C_9H_6O_3]^-$, $[M\text{-}H–C_9H_6O_3–H_2O]^-$, $[M\text{-}H–C_6H_{10}O_4–C_9H_6O_3]^-$, $[M\text{-}H–C_9H_6O_3–H_2O–C_6H_{10}O_4]^-$, $[M\text{-}H–C_6H_{10}O_4–C_6H_{10}O_5–C_8H_8O_2]^-$, $[M\text{-}H–C_6H_{10}O_4–C_6H_{10}O_5–C_8H_8O_2–H_2O]^-$, $[M\text{-}H–C_6H_{10}O_4–C_6H_{10}O_5–C_8H_8O_2–CO_2]^-$, and $[M\text{-}H–C_6H_{10}O_4–C_6H_{10}O_5–C_8H_8O_2–CH_2O_2]^-$, respectively. Fragment ions *m/z* 477.13982 and *m/z* 315.10830 corresponded to successive losses of Rha and caffeoyl groups. Fragment ions *m/z* 461.16604, *m/z* 443.15545, and *m/z* 297.09774 corresponded to successive losses of caffeoyl, H_2O, and Rha groups. Fragment ion *m/z* 179.03475 corresponded to losses of Rha, Glc, and hydroxytyrosol groups, also can be $[M - H]^-$ of caffeic acid, then the eliminations of H_2O, CO_2 and CH_2O_2 from the fragment ion *m/z* 179.03475, respectively, resulting in producting the fragment ions *m/z* 161.02417, *m/z* 135.04491, and *m/z* 133.02926, respectively. The compound was confirmed as forsythoside I. Compound 192 ($t_R = 7.64$ min), compound 235 ($t_R = 8.66$ min) and compound 239 ($t_R =$ 8.82 min) showed deprotonated ions $[M - H]^-$ at *m/z* 623.19692, *m/z* 623.19737 and *m/z* 623.19642, with similar fragment behaviors to that of forsythoside I. They were putatively characterized as forsythoside H, forsythoside A, and acteoside, respectively. The chemical structures of forsythoside B consist of five chemical moieties: caffeoyl, hydroxytyrosol, Api, Rha and Glc. Compound 191 with a retention time of 7.56 min exhibited the precursor ion of $[M - H]^-$ at *m/z* 755.23923, corresponding to a molecular formula of $C_{34}H_{44}O_{19}$. In the MS^2 spectrum, peaks at *m/z* 593.20777, *m/z* 461.16525, *m/z* 447.14973, and *m/z* 161.02423 corresponded to $[M\text{-}H\text{-}C_9H_6O_3]^-$, $[M\text{-}H–C_9H_6O_3–C_5H_8O_4]^-$, $[M\text{-}H–C_9H_6O_3–C_6H_{10}O_4]^-$, and $[M\text{-}H–C_6H_{10}O_4–C_5H_8O_4–C_6H_{10}O_5–C_8H_8O_2–H_2O]^-$, respectively. Fragment ions *m/z* 593.20777 corresponded to loss of caffeoyl group, then the ion further fragmented into two ions at *m/z* 461.16525 and *m/z* 447.14973, owing to losses of Api and Rha groups, respectively. Fragment ion *m/z* 161.02423 corresponded to successive losses of caffeoyl, Api, Rha, Glc, hydroxytyrosol and H_2O. The compound could be temporarily deduced as forsythoside B. And the MS/MS spectrum is shown in Fig. 5.

3.1.4. Terpenoids

Terpenoids, for example, glycyrrhizic acid could ameliorate acute lung injury [34]. Compound 463 with a retention time of 19.49 min exhibited the precursor ion of $[M+H]^+$ at *m/z* 823.41127, indicating the molecular formula of $C_{42}H_{62}O_{16}$. In positive mode, the consequently losses of one and two glucuronic acid produced the fragment ions at *m/z* 647.37690 and *m/z* 471.34606. Fragment ion at *m/z* 453.33547 was corresponded with the losses of diglucuronic acid and H_2O. Fragment ion in negative mode at *m/z* 351.05688 was corresponded with the diglucuronic acid. It was identified as glycyrrhizic acid. Compound 586 with a retention time of 28.79 min exhibited the precursor ion of $[M+H]^+$ at *m/z* 471.34712, indicating the molecular formula of $C_{30}H_{46}O_4$. Peaks at *m/z* 453.33496, *m/z*

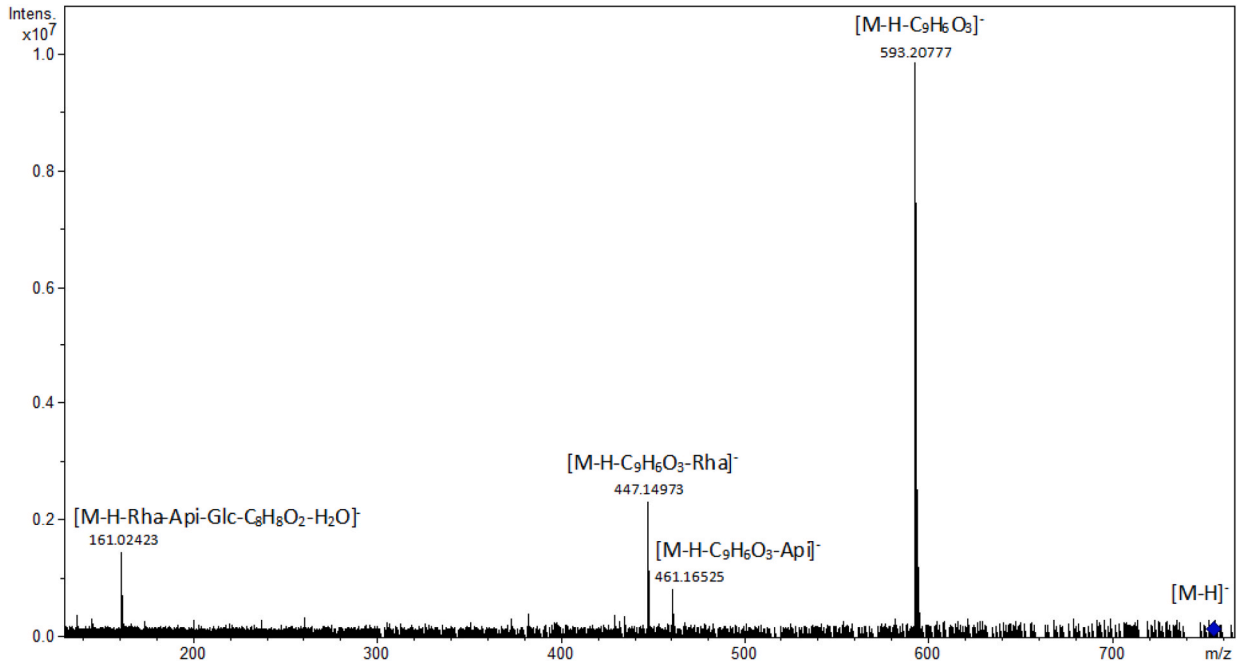

Fig. 5. The MS/MS spectrum of forsythoside B.

435.32485, *m/z* 425.34051, *m/z* 407.32982, and *m/z* 389.31953 can be attributed to $[M + H–H_2O]^+$, $[M + H–2H_2O]^+$, $[M + H–H_2O–CO]^+$, $[M + H–2H_2O–CO]^+$, and $[M + H–3H_2O–CO]^+$, respectively. It was identified as glycyrrhetinic acid.

Compound 138 with a retention time of 6.50 min exhibited the precursor ion of $[M+H]^+$ at *m/z* 359.13412, corresponding to a molecular formula of $C_{16}H_{22}O_9$. In the MS^2 spectrum, the characteristic fragment ions were at *m/z* 197.08054, *m/z* 179.06999, and *m/z* 127.03880 corresponded to $[M + H\text{-Glc}]^+$, $[M + H\text{-Glc-}H_2O]^+$, and $[M + H\text{-Glc-}C_4H_6O]^+$, respectively. The product ion at *m/z* 127.03880 is generated from the precursor ion through RDA cleavage. The compound was putatively characterized as sweroside. Compound 289 with a retention time of 10.66 min exhibited the precursor ion of $[M - H]^-$ at *m/z* 539.17665, corresponding to a molecular formula of $C_{25}H_{32}O_{13}$. In the MS^2 spectrum, peaks at *m/z* 377.12411, *m/z* 345.09810, *m/z* 327.08791, *m/z* 307.08229, and *m/z* 275.09239 corresponded to $[M\text{-H-Glc}]^-$, $[M\text{-H-Glc-}CH_3OH]^-$, $[M\text{-H-Glc–}CH_3OH–H_2O]^-$, $[M\text{-H-Glc-}C_4H_6O]^-$, and $[M\text{-H-Glc-}C_4H_6O_3]^-$, respectively. Thus it was tentatively characterized as oleuropein. Compound 334 with a retention time of 12.65 min exhibited the precursor ion of $[M - H]^-$ at *m/z* 504.18704, corresponding to a molecular formula of $C_{25}H_{31}NO_{10}$. In the MS^2 spectrum,

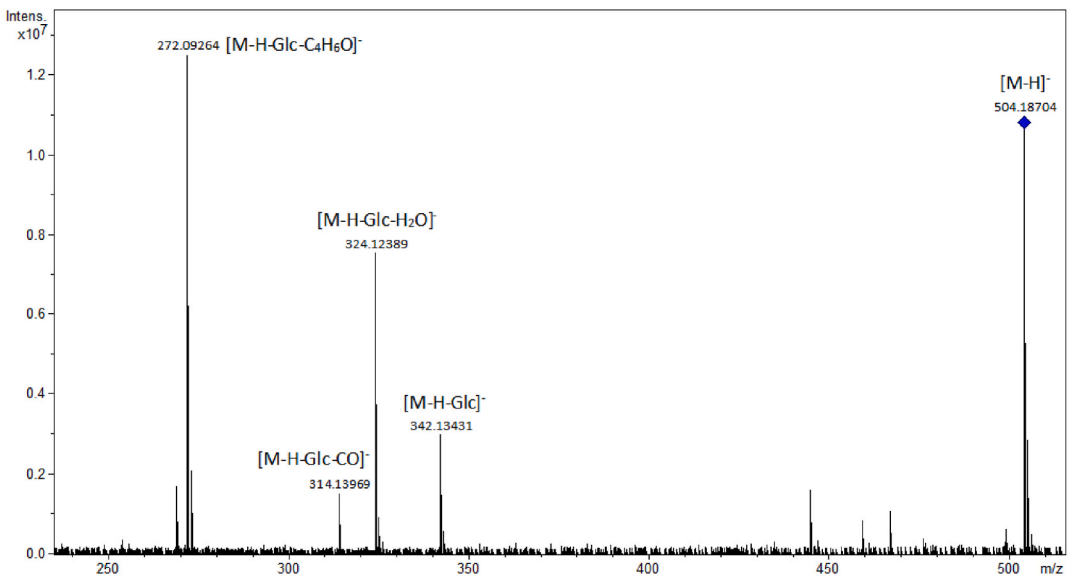

Fig. 6. The MS/MS spectrum of L-phenylalaninosecologanin B.

peaks at *m/z* 342.13431, *m/z* 324.12389, *m/z* 314.13969, and *m/z* 272.09264 corresponded to $[M\text{-}H\text{-}Glc]^-$, $[M\text{-}H\text{-}Glc\text{-}H_2O]^-$, $[M\text{-}H\text{-}Glc\text{-}CO]^-$, and $[M\text{-}H\text{-}Glc\text{-}C_4H_6O]^-$, respectively. Thus it was confirmed as L-phenylalaninosecologanin B. And the MS/MS spectrum is shown in Fig. 6.

3.1.5. Organic acids and their derivatives

A total of 79 organic acids and their derivatives were identified in this study. Organic acid compounds, for example, azelaic acid possesses anti-infective and anti-inflammatory activities [35]. Compound 15 with a retention time of 1.78 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 169.01406, corresponding to a molecular formula of $C_7H_6O_5$. In the MS^2 spectrum, the characteristic fragments at *m/z* 125.02437 corresponded to $[M\text{-}H\text{-}CO_2]^-$. It was putatively characterized as gallic acid. Compound 186 with a retention time of 7.51 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 197.04536, corresponding to a molecular formula of $C_9H_{10}O_5$. In the MS^2 spectrum, the characteristic fragments at *m/z* 169.01417 and *m/z* 125.02437 corresponded to $[M\text{-}H\text{-}C_2H_4]^-$ and $[M\text{-}H\text{-}CO_2]^-$. It was tentatively characterized as ethyl gallate. Compound 18 with a retention time of 1.90 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 167.03481, corresponding to a molecular formula of $C_8H_8O_4$. In the MS^2 spectrum, the characteristic fragments at *m/z* 152.01129 and *m/z* 123.04502 corresponded to $[M\text{-}H\text{-}CH_3]^-$ and $[M\text{-}H\text{-}CO_2]^-$. It was putatively characterized as vanillic acid. Compound 261 with a retention time of 9.82 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 187.09736, corresponding to a molecular formula of $C_9H_{16}O_4$. In the MS^2 spectrum, the characteristic fragments at *m/z* 125.09712 corresponded to $[M\text{–}H\text{–}CO_2\text{–}H_2O]^-$. It was putatively characterized as azelaic acid. Compound 351 with a retention time of 13.33 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 207.06611, corresponding to a molecular formula of $C_{11}H_{12}O_4$. In the MS^2 spectrum, the characteristic fragments at *m/z* 179.03486, *m/z* 161.02430, and *m/z* 135.04505 corresponded to $[M\text{-}H\text{-}C_2H_4]^-$, $[M\text{–}H\text{–}C_2H_4\text{–}H_2O]^-$, and $[M\text{-}H\text{–}C_2H_4\text{–}CO_2]^-$. It was putatively characterized as ethyl caffeate. And the MS/MS spectrum is shown in Fig. 7.

3.1.6. Quinones

Quinones, for example, emodin could alleviate pulmonary inflammation in rats with LPS-induced acute lung injury [36]. Compound 455 (t_R = 18.88 min), and compound 556 (t_R = 25.08 min) were isomers, which showed deprotonated ion $[M-H]^-$ at *m/z* 269.04540, and *m/z* 269.04543. The molecular formula was speculated to be $C_{15}H_{10}O_5$. In the MS^2 spectrum, the characteristic fragment ions of compound 455 produced were at *m/z* 240.04263, *m/z* 223.03987, and *m/z* 211.03980, respectively, corresponding to fragment ions $[M\text{-}H\text{-}CHO]^-$, $[M\text{–}H\text{–}CO\text{–}H_2O]^-$, and $[M\text{-}H\text{-}2CHO]^-$, respectively. The characteristic fragment ions of compound 556 produced were at *m/z* 241.05072, *m/z* 225.05569, and *m/z* 210.03224 respectively, corresponding to fragment ions $[M\text{-}H\text{-}CO]^-$, $[M\text{-}H\text{-}CO_2]^-$, and $[M\text{-}H\text{–}CO_2\text{–}CH_3]^-$, respectively. Compound 455 and compound 556 were tentatively characterized as aloe-emodin and emodin, respectively. And the MS/MS spectrum of compound 556 is shown in Fig. 8.

Compound 473 and peak 582 with a retention time of 19.91 min and 28.40 min yielded the precursor ion of $[M-H]^-$ at *m/z* 283.02465 and *m/z* 283.06098, respectively, corresponding to a molecular formula of $C_{15}H_8O_6$ and $C_{16}H_{12}O_5$. In the MS^2 spectrum, compound 473 showed characteristic fragment ions at *m/z* 255.02976, *m/z* 239.03481, *m/z* 211.03994, and *m/z* 183.04508 corresponded to $[M\text{-}H\text{-}CO]^-$, $[M\text{-}H\text{-}CO_2]^-$, $[M\text{–}H\text{–}CO_2\text{–}CO]^-$, and $[M\text{–}H\text{–}CO_2\text{–}2CO]^-$, respectively. Compound 582 showed characteristic fragment ions at *m/z* 269.04532, *m/z* 268.03751, and *m/z* 240.04258 corresponded to $[M\text{-}H\text{-}CH_2]^-$, $[M\text{-}H\text{-}CH_3]^-$, and $[M\text{–}H\text{–}CH_3\text{–}CO]^-$, respectively. Thus they could be temporarily deduced as rhein and physcion, respectively.

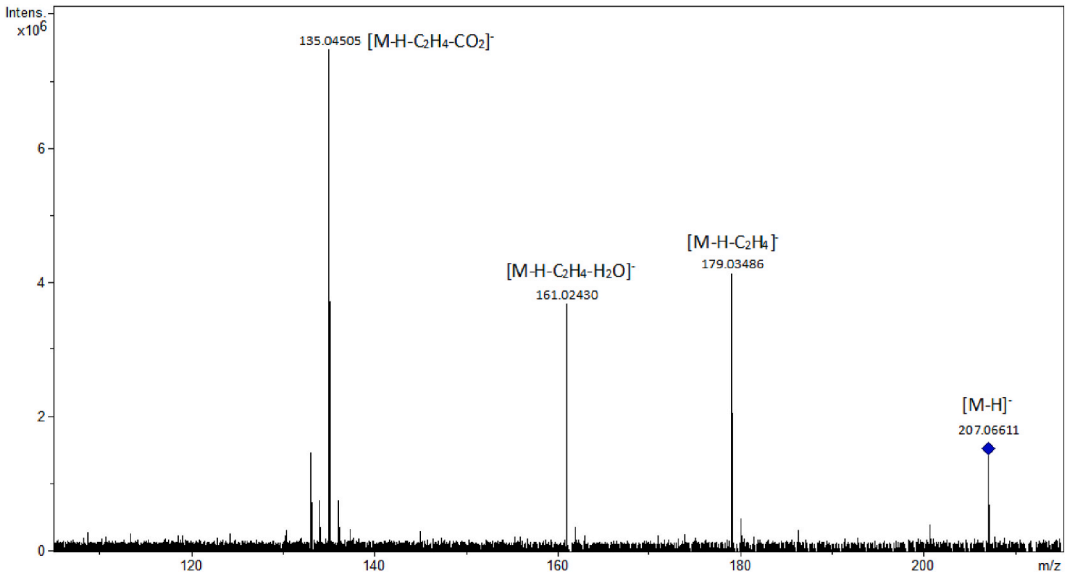

Fig. 7. The MS/MS spectrum of ethyl caffeate.

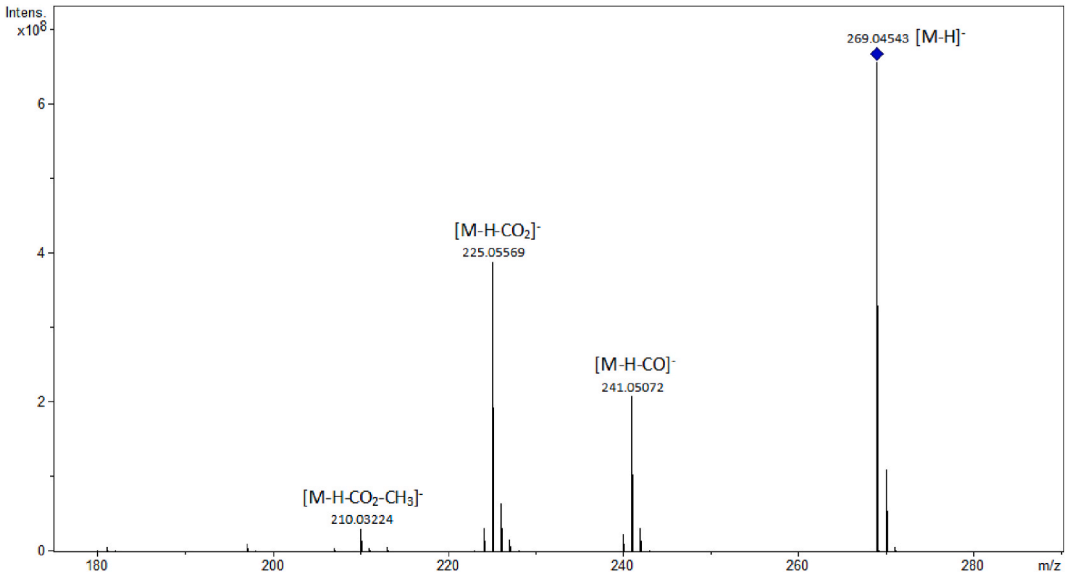

Fig. 8. The MS/MS spectrum of emodin.

Compound 572 with a retention time of 27.41 min exhibited the precursor ion of $[M-H]^-$ at *m/z* 253.05052, corresponding to a molecular formula of $C_{15}H_{10}O_4$. Peaks at *m/z* 225.05551, *m/z* 210.03201, *m/z* 197.06060, *m/z* 182.03707, and *m/z* 181.06569 can be attributed to $[M-H-CO]^-$, $[M-H-CO-CH_3]^-$, $[M-H-2CO]^-$, $[M-H-2CO-CH_3]^-$, and $[M-H-CO-CO_2]^-$, respectively. It was confirmed as chrysophanol.

3.1.7. Alkaloids

Alkaloids, for example, norisoboldine could attenuate sepsis-induced acute lung injury [37]. Compound 43 was found at 3.15 min and exhibited an $[M+H]^+$ ion at *m/z* 166.12289 with a molecular formula of $C_{10}H_{15}NO$. Peak at *m/z* 148.11149 corresponded to $[M-H-H_2O]^+$. It was tentatively confirmed as ephedrine or pseudoephedrine. Compound 65 was found at 4.14 min and exhibited an $[M+H]^+$ ion at *m/z* 180.13858 with a molecular formula of $C_{11}H_{17}NO$. Peak at *m/z* 162.12735 corresponded to $[M-H-H_2O]^+$. It was tentatively confirmed as methylephedrine or methylpseudoephedrine. Compound 118 was found at 6.13 min and exhibited an $[M+H]^+$ ion at *m/z* 314.13928 with a molecular formula of $C_{18}H_{19}NO_4$. Peaks at *m/z* 297.11136, *m/z* 265.08524, and *m/z* 237.09039 corresponded to $[M+H-NH_3]^+$, $[M+H-NH_3-CH_3OH]^+$, and $[M+H-NH_3-CH_3OH-CO]^+$, respectively. It was identified as norisoboldine. And the MS/MS spectrum is shown in Fig. 9. Compound 465 was found at 19.61 min and exhibited an $[M+H]^+$ ion at *m/z*

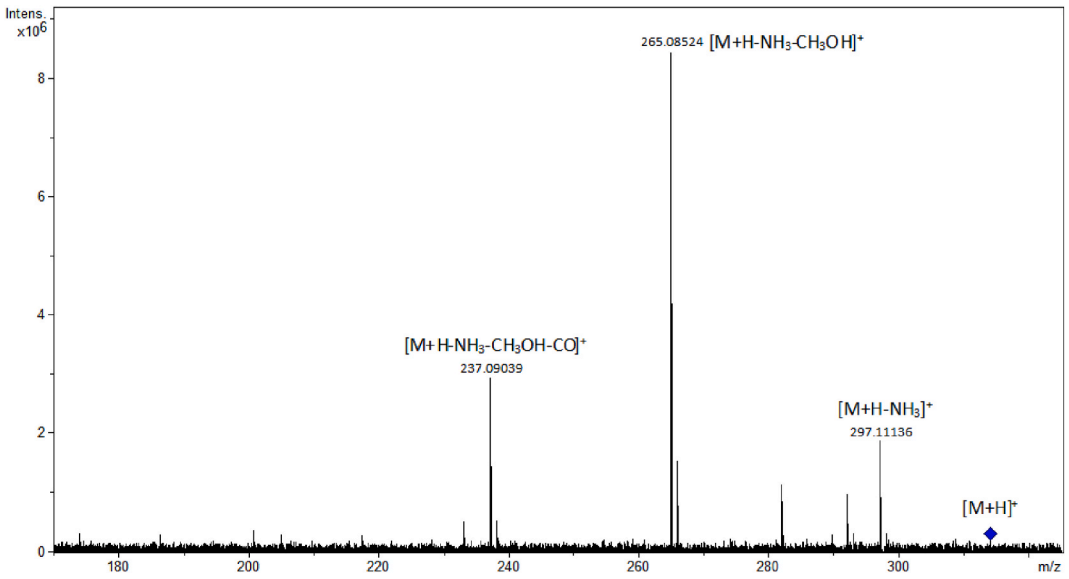

Fig. 9. The MS/MS spectrum of norisoboldine.

322.10739 with a molecular formula of $C_{19}H_{15}NO_4$. Peak at *m/z* 292.05967 corresponded to $[M + H–2CH_3]^+$. It was tentatively characterized as cepharadione B. Compound 548 was found at 24.68 min and exhibited an $[M+H]^+$ ion at *m/z* 445.21207 with a molecular formula of $C_{27}H_{28}N_2O_4$. Peaks at *m/z* 224.10647 and *m/z* 194.11695 corresponded to $[M + H–C_{12}H_{14}NO_3]^+$ and $[M + H–C_{16}H_{12}NO_2]^+$. It was tentatively characterized as aurantiamide acetate.

3.1.8. Alcohol glycosides

Alcohol glycosides, for example, rosavin could show protective effects on bleomycin-induced pulmonary fibrosis [38]. Compound 229 was found at 8.39 min and exhibited an $[M + COOH]^-$ ion at *m/z* 473.16680 with an elemental composition of $C_{20}H_{28}O_{10}$. Peaks at *m/z* 427.16049, *m/z* 293.08757, *m/z* 233.06640, *m/z* 191.05601, *m/z* 149.04540, and *m/z* 131.03490, corresponded to $[M - H]^-$, $[M\text{-}H\text{-}C_9H_{10}O]^-$, $[M\text{-}H\text{-}C_{11}H_{14}O_3]^-$, $[M\text{-}H\text{-}C_{13}H_{16}O_4]^-$, $[M\text{-}H\text{-}C_{15}H_{18}O_5]^-$, and $[M\text{-}H\text{-}C_{15}H_{20}O_6]^-$ fragments, respectively. Compound 229 was confirmed as rosavin. And the MS/MS spectrum is shown in Fig. 10. Compound 347 was found at 13.14 min and exhibited an $[M - H]^-$ ion at *m/z* 493.22872 with an elemental composition of $C_{22}H_{38}O_{12}$. Peak at *m/z* 447.22333 corresponded to $[M\text{-}H\text{-}CH_2O_2]^-$. Compound 347 was confirmed as rhodioloside C.

3.1.9. Others

For example, amygdalin has anti-inflammatory and immunomodulatory properties [39]. The precursor ion $[M - H]^-$ of compound 112 at *m/z* 456.15077 was observed at 5.96 min, the molecular formula was $C_{20}H_{27}NO_{11}$ as predicted by the precursor ion. The characteristic fragment ion found in the MS/MS spectra was at *m/z* 323.09813 corresponded to $[M\text{-}H\text{-}C_8H_7NO]^-$. The compound was tentatively characterized as amygdalin. The precursor ion $[M - H]^-$ of compound 317 at *m/z* 819.28569 was observed at 11.83 min, the molecular formula was $C_{43}H_{48}O_{16}$ as predicted by the precursor ion. The characteristic fragment ion found in the MS/MS spectra was at *m/z* 611.21282 and *m/z* 403.13946, corresponded to $[M\text{-}H\text{-}C_{11}H_{12}O_4]^-$ and $[M\text{-}H\text{-}2C_{11}H_{12}O_4]^-$. The compound was tentatively characterized as dryocrassin ABBA. And the MS/MS spectrum is shown in Fig. 11. The precursor ion $[M - H]^-$ of compound 565 at *m/z* 223.09741 was observed at 26.40 min, the molecular formula was $C_{12}H_{16}O_4$ as predicted by the precursor ion. The characteristic fragment ion found in the MS/MS spectra was at *m/z* 139.07642 corresponded to $[M\text{-}H\text{-}C_4H_4O_2]^-$. The compound was tentatively characterized as pogostone.

This study applied UHPLC-FT-ICR-MS/MS method to identify the chemical components in Lianhua Qingwen capsule, indirectly indicating that UHPLC-FT-ICR-MS/MS method can be efficient, accurate, and sensitive analysis of Lianhua Qingwen capsule chemical profile. According to the above analysis results, 596 compounds in Lianhua Qingwen capsule were identified, mostly have anti-inflammatory, antioxidant, antiviral, antibacterial, and other biological activities, and many studies have reported that they are closely related to the treatment of lung diseases, which correspond with the therapeutic indications.

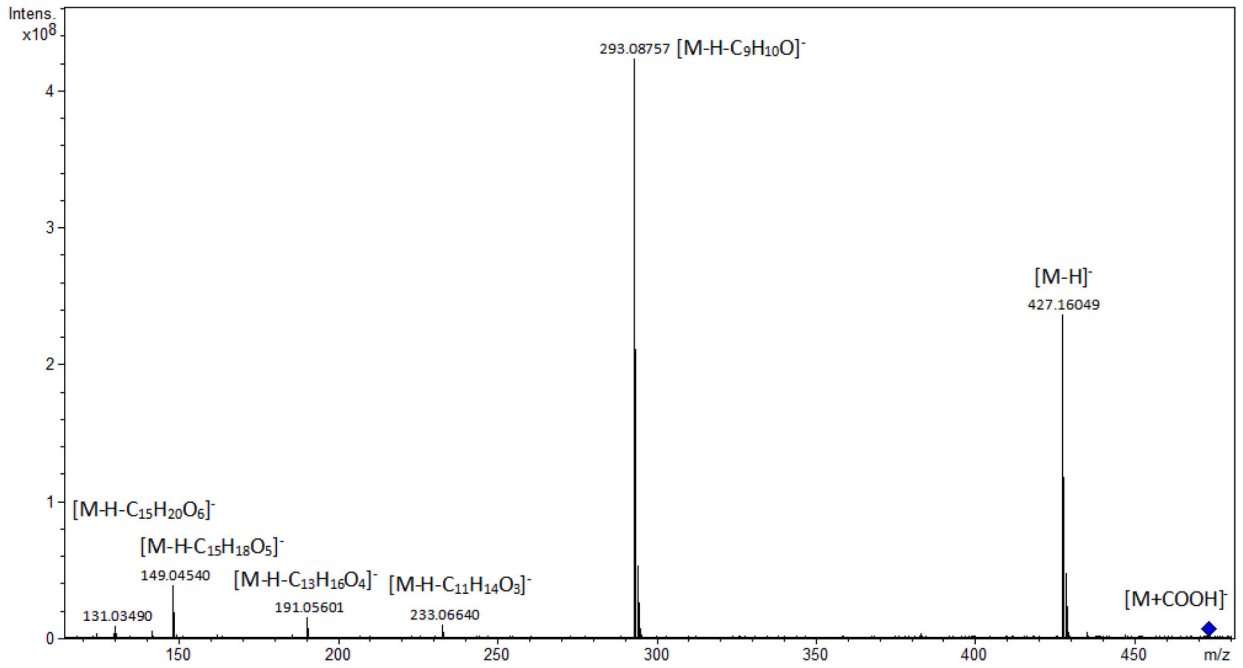

Fig. 10. The MS/MS spectrum of rosavin.

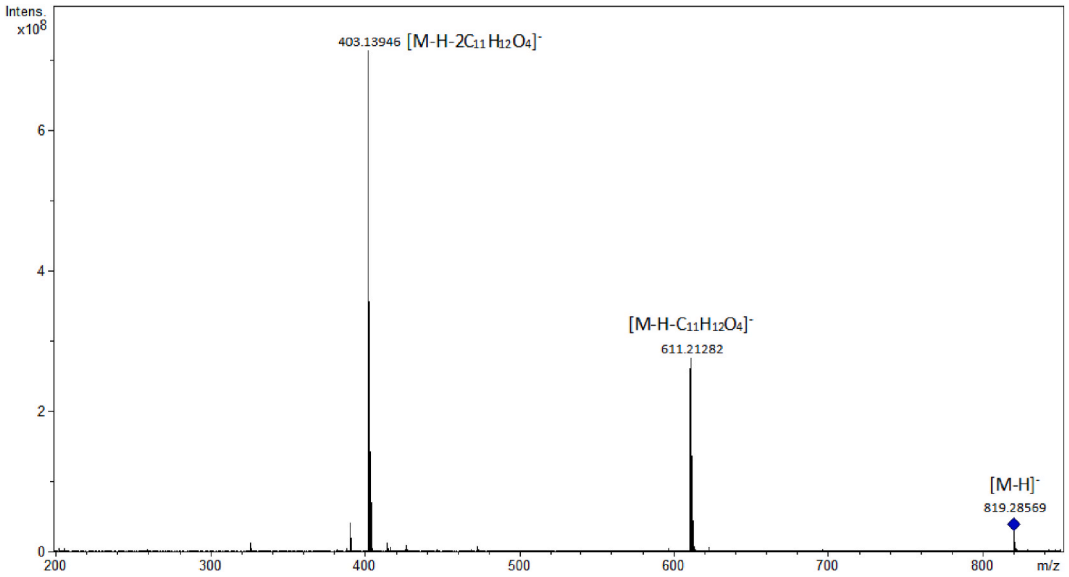

Fig. 11. The MS/MS spectrum of dryocrassin ABBA.

4. Conclusion

In this study, a rapid, sensitive and accurate UHPLC-FT-ICR-MS/MS method was applied for the global profiling of the Lianhua Qingwen capsule, wherein 596 components were appropriately separated and characterized due to the accurate mass fragments and retention time. The profiles of the constituents in the Lianhua Qingwen capsule provided comprehensive chemical information, thereby providing a theoretical foundation for consecutive research on the effective components, its quality control, pharmacology research, and the promotion of future development of the Lianhua Qingwen capsule.

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Data availability statement

The data are contained within the article and supplementary materials.

CRediT authorship contribution statement

Ting Liu: Writing – review & editing, Writing – original draft, Visualization, Supervision, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Shu Lin:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e27352.

References

[1] C.H. Wang, Y. Zhong, Y. Zhang, J.P. Liu, Y.F. Wang, W.N. Jia, G.C. Wang, Z. Li, Y. Zhu, X.M. Gao, A network analysis of the Chinese medicine Lianhua-Qingwen formula to identify its main effective components, Mol. Omics 12 (2) (2016) 606–613.

[2] C. Yang, Y. Wang, J. He, W. Yan, H. Jiang, Q. Chen, L. Li, Z. Yang, Lianhua-Qingwen displays antiviral and anti-Inflammatory activity and synergistic effects with Oseltamivir against influenza B virus infection in the mouse model, Evid. Based Complement Alternat. Med. 2020 (2020) 3196375.

[3] Y.W. Ding, L.J. Zeng, R.F. Li, Q.Y. Chen, B.X. Zhou, Q.L. Chen, P.L. Cheng, W. Yutao, J.P. Zheng, Z.F. Yang, F.X. Zhang, The Chinese prescription lianhuaqingwen capsule exerts anti-influenza activity through the inhibition of viral propagation and impacts immune function, BMC Compl. Alternative Med. 17 (1) (2017) 130.

[4] Z.P. Duan, Z.H. Jia, J. Zhang, S. Liu, Y. Chen, L.C. Liang, C.Q. Zhang, Z. Zhang, Y. Sun, S.Q. Zhang, Y.Y. Wang, Y.L. Wu, Natural herbal medicine Lianhuaqingwen capsule anti-influenza A (H1N1) trial: a randomized, double blind, positive controlled clinical trial, Chin. Med. J. 124 (2011) 2925–2933.

[5] R.F. Li, Y.L. Hou, J.C. Huang, W.Q. Pan, Q.H. Ma, Y.X. Shi, C.F. Li, J. Zhao, Z.H. Jia, H.M. Jiang, K. Zheng, S.X. Huang, J. Dai, X.B. Li, X.T. Hou, L. Wang, N. S. Zhong, Z.F. Yang, Lianhuaqingwen exerts anti-viral and anti-inflammatory activity against novel coronavirus (SARS-CoV-2), Pharmacol. Res. 156 (2020) 104761.

[6] C.Y. Liang, N. Hui, Y. Liu, G.P. Qiao, J. Li, L. Tian, X.K. Ju, M.Y. Jia, H. Liu, W.Q. Cao, P. Yu, H. Li, X.D. Ren, Insights into forsythia honeysuckle (Lianhuaqingwen) capsules: a Chinese herbal medicine repurposed for COVID-19 pandemic, Phytomed. Plus 1 (2) (2021) 100027.

[7] X.W. Gong, B.Y. Yuan, Y.D. Yuan, F.J. Li, Efficacy and safety of lianhuaqingwen capsules for the prevention of coronavirus disease 2019: a Prospective open-Label controlled trial, Evid. Based Complement. Alternat. Med. (2021) 7962630.

[8] P. Shen, J. Li, S.H. Tu, Y.R. Wu, Y.T. Peng, G. Chen, C. Chen, Positive effects of Lianhuaqingwen granules in COVID-19 patients: a retrospective study of 248 cases, J. Ethnopharmacol. 278 (2021) 114220.

[9] M. Liu, Y. Gao, Y. Yuan, K.L. Yang, S.Z. Shi, J.H. Tian, J.H. Zhang, Efficacy and safety of herbal medicine (Lianhuaqingwen) for treating COVID-19: a systematic review and meta-analysis, Integr. Med. Res. 10 (1) (2021) 100644.

[10] W.N. Jia, C.H. Wang, Y.F. Wang, G.X. Pan, M.M. Jiang, Z. Li, Y. Zhu, Qualitative and quantitative analysis of the major constituents in Chinese medical preparation lianhua-qingwen capsule by UPLC-DAD-QTOF-MS, Sci. World J. 2015 (2015) 731–765.

[11] S. Fu, R.R. Cheng, Z.X. Deng, T.G. Liu, Qualitative analysis of chemical components in Lianhua Qingwen capsule by HPLC-Q Exactive-Orbitrap-MS coupled with GC-MS, J Pharm Anal 11 (6) (2021) 709–716.

[12] X.F. Chen, Y.L. Wu, C. Chen, Y.Q. Gu, C.Y. Zhu, S.P. Wang, J.Y. Chen, L. Zhang, L. Lv, G.Q. Zhang, Y.F. Yuan, Y.F. Chai, M.S. Zhu, C.S. Wu, Identifying potential anti-COVID-19 pharmacological components of traditional Chinese medicine Lianhuaqingwen capsule based on human exposure and ACE2 biochromatography screening, Acta Pharm. Sin. B 11 (1) (2021) 222–236.

[13] D.F. Smith, A. Kiss, F.E. Leach III, E.W. Robinson, L. Paša-Tolić, R.M. Heeren, High mass accuracy and high mass resolving power FT-ICR secondary ion mass spectrometry for biological tissue imaging, Anal. Bioanal. Chem. 405 (2013) 6069–6076.

[14] E.N. Nikolaev, Y.I. Kostyukevich, G.N. Vladimirov, Fourier transform ion cyclotron resonance (FT ICR) mass spectrometry: Theory and simulations, Mass Spectrom. Rev. 35 (2) (2016) 219–258.

[15] J.L. Frahm, B.E. Howard, S. Heber, D.C. Muddiman, Accessible proteomics space and its implications for peak capacity for zero-, one- and two-dimensional separations coupled with FT-ICR and TOF mass spectrometry, J. Mass Spectrom. 41 (3) (2006) 281–288.

[16] D. Kim, S. Kim, S. Son, M.J. Jung, S. Kim, Application of online liquid chromatography 7 T FT-ICR mass spectrometer Equipped with Quadrupolar detection for analysis of Natural organic Matter, Anal. Chem. 91 (12) (2019) 7690–7697.

[17] G. Kruppa, P.D. Schnier, K. Tabei, S. Van Orden, M.M. Siegel, Multiple ion isolation applications in FT-ICR MS: exact-mass MSn internal calibration and purification/interrogation of protein-drug complexes, Anal. Chem. 74 (15) (2002) 3877–3886.

[18] T. Liu, Y. Cui, X.M. Tian, S.H. Li, F. Han, B. Ji, Y.L. Zhao, Z.G. Yu, Detection of chemical constituents in Gegenqinlian decoction by ultra-high performance liquid chromatography coupled with Fourier transform ion cyclotron resonance mass spectrometry, Anal. Methods 9 (40) (2017) 5890–5902.

[19] F. Han, Y.T. Li, L. Ma, T.F. Liu, Y.W. Wu, R. Xu, A.H. Song, R. Yin, A rapid and sensitive UHPLC-FT-ICR MS/MS method for identification of chemical constituents in Rhodiola crenulata extract, rat plasma and rat brain after oral administration, Talanta 160 (2016) 183–193.

[20] Z.B. Guan, M. Wang, Y. Cai, H.M. Yang, M. Zhao, C.J. Zhao, Rapid characterization of the chemical constituents of Sijunzi decoction by UHPLC coupled with Fourier transform ion cyclotron resonance mass spectrometry, J. Chromatogr., B: Anal. Technol. Biomed. Life Sci. 1086 (2018) 11–22.

[21] Y. Cui, H.H. Yang, J.X. Jing, T. Liu, R.J. Wang, F.Y. Di, F. Han, Y.L. Zhao, Z.G. Yu, Rapid characterization of chemical constituents of Gansuibanxia decoction by UHPLC-FT-ICR-MS analysis, J. Pharm. Biomed. Anal. 179 (2020) 113029.

[22] J.N. Liu, M. Zhao, S. Zhang, J.N. Liu, C.J. Zhao, M. Wang, Rapid characterization of the chemical constituents of Wangbi Capsule by UPLC coupled with Fourier transform ion cyclotron resonance mass spectrometry, Microchem. J. 180 (2022) 107603.

[23] C.C. Wang, Z.C. Cai, J.J. Shi, S.Y. Chen, M.X. Tan, J.L. Chen, L.H. Chen, L.S. Zou, C.H. Chen, Z.X. Liu, X.H. Liu, Comparative metabolite profiling of wild and cultivated licorice based on ultra-fast liquid chromatography coupled with triple quadrupole-time of flight tandem mass spectrometry, Chem. Pharm. Bull (Tokyo) 67 (10) (2019) 1104–1115.

[24] R.Y. Li, Y.R. Zhu, M.Y. Ma, M. Lei, Y.C. Zhao, T. Liu, M. Yu, Y.L. Zhao, Z.G. Yu, Characterization of chemical constituents in Shuanghuanglian oral dosage forms by ultra-high performance liquid chromatography coupled with time-of-flight mass spectrometry, J. Separ. Sci. 45 (5) (2022) 1020–1030.

[25] L. Chen, C.L. Yao, J.Y. Li, J. Wang, S. Yao, S.J. Shen, L. Yang, J.Q. Zhang, W.L. Wei, Q.R. Bi, D.A. Guo, Systematic characterization of chemical constituents in Mahuang decoction by UHPLC tandem linear ion trap-Orbitrap mass spectrometry coupled with feature-based molecular networking, J. Separ. Sci. 44 (14) (2021) 2717–2727.

[26] X.J. Jiang, Y.H. Lin, Y.L. Wu, C.X. Yuan, X.L. Lang, J.Y. Chen, C.Y. Zhu, X.Y. Yang, Y. Huang, H. Wang, C.S. Wu, Identification of potential anti-pneumonia pharmacological components of Glycyrrhizae Radix et Rhizoma after the treatment with Gan an He Ji oral liquid, J. Pharm. Anal. 12 (6) (2022) 839–851.

[27] S.Y. Xu, X.F. Xu, S.X. Yuan, H. Liu, M.N. Liu, Y. Zhang, H. Zhang, Y. Gao, R.C. Lin, X.R. Li, Identification and analysis of amygdalin, neoamygdalin and amygdalin amide in different processed bitter almonds by HPLC-ESI-MS/MS and HPLC-DAD, Molecules 22 (9) (2017) 1425.

[28] W.W. Tao, J.A. Duan, J.M. Guo, J.P. Li, Y.P. Tang, P. Liu, N.Y. Yang, Simultaneous determination of triterpenoid saponins in dog plasma by a validated UPLC-MS/MS and its application to a pharmacokinetic study after administration of total saponin of licorice, J. Pharm. Biomed. Anal. 75 (2013) 248–255.

[29] Y.M. Ding, Z. Liu, F.Q. Li, Application of a sensitive and accurate LC-MS/MS method for determination of dryocrassin ABBA in rat plasma for a bioavailability study, Biomed. Chromatogr. 28 (9) (2014) 1205–1211.

[30] Y.C. Li, Z.R. Su, S.H. Lin, C.W. Li, Y. Zhao, X. Gao, Y.Q. Lai, X.L. Wu, H.Z. Wu, Z.W. Cai, Characterisation of the metabolism of pogostone in vitro and in vivo using liquid chromatography with mass spectrometry, Phytochem. Anal. 25 (2) (2014) 97–105.

[31] L. Wang, X.H. Wang, L.N. Kong, S.Y. Wang, K. Huang, J.J. Wu, C.Y. Wang, H.J. Sun, K.X. Liu, Q. Meng, Isoliquiritigenin alleviates LPS/D-GalN-induced acute liver failure by activating the PGC-1α/Nrf2 pathway to reduce oxidative stress and inflammatory response, Int. Immunopharm. 100 (2021) 108159.

[32] H.W. Jung, R. Mahesh, J.G. Lee, S.H. Lee, Y.S. Kim, Y.K. Park, Pinoresinol from the fruits of Forsythia koreana inhibits inflammatory responses in LPS-activated microglia, Neurosci. Lett. 480 (3) (2010) 215–220.

[33] J.X. Liu, X. Li, F.G. Yan, Q.J. Pan, C. Yang, M.Y. Wu, G. Li, H.F. Liu, Protective effect of forsythoside B against lipopolysaccharide-induced acute lung injury by attenuating the TLR4/NF-κB pathway, Int. Immunopharm. 66 (2019) 336–346.

[34] L.H. Qu, C. Chen, W. He, Y.Y. Chen, Y. Li, Y. Wen, S.C. Zhou, Y.Q. Jiang, X.P. Yang, R. Zhang, L. Shen, Glycyrrhizic acid ameliorates LPS-induced acute lung injury by regulating autophagy through the PI3K/AKT/mTOR pathway, Am. J. Transl. Res. 11 (4) (2019) 2042–2055.

[35] B.C. Schulte, W. Wu, T. Rosen, Azelaic acid: evidence-based update on mechanism of action and clinical application, J. Drugs Dermatol. JDD 14 (9) (2015) 964–968.
[36] X.Q. Li, C. Shan, Z.H. Wu, H.J. Yu, A.D. Yang, B. Tan, Emodin alleviated pulmonary inflammation in rats with LPS-induced acute lung injury through inhibiting the mTOR/HIF-1α/VEGF signaling pathway, Inflamm. Res. 69 (4) (2020) 365–373.
[37] Q. Chen, X.B. Shao, Y.Y. He, E.K. Lu, L.J. Zhu, W.D. Tang, Norisoboldine attenuates sepsis-induced acute lung injury by modulating macrophage polarization via PKM2/HIF-1α/PGC-1α pathway, Biol. Pharm. Bull. 44 (10) (2021) 1536–1547.
[38] X.B. Xin, D.H. Yao, K. Zhang, S. Han, D.N. Liu, H.Y. Wang, X.Y. Liu, G.Y. Li, J. Huang, J.H. Wang, Protective effects of Rosavin on bleomycin-induced pulmonary fibrosis via suppressing fibrotic and inflammatory signaling pathways in mice, Biomed. Pharmacother. 115 (2019) 108870.
[39] X.Y. He, L.J. Wu, W.X. Wang, P.J. Xie, Y.H. Chen, F. Wang, Amygdalin-A pharmacological and toxicological review, J. Ethnopharmacol. 254 (2020) 112717.