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ORIGINAL PAPER

Comprehensive profiling of phytochemicals in the fruits of *Gardenia jasminoides* Ellis and its variety using liquid chromatography coupled with electrospray ionization quadrupole time-of-flight mass spectrometry

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Abstract

The fruits of *Gardenia jasminoides* Ellis are an important herb medicine in Traditional Chinese Medicine (TCM) and have been used for thousands of years for clearing away heat and toxic materials. It mainly contains iridoids, pigments, organic acids, and flavonoids. Although belonging to one species, it has two kinds of cultivars and one variety widely distributed and sold. This study aims to develop an integrated and efficient analytical strategy for comprehensive profiling of phytochemicals and clarify the differences in all three populations. Based on reversed-phase ultra-high performance liquid chromatography coupled with electrospray ionization quadrupole time-of-flight mass spectrometry (UHPLC/ESI-QTOFMS), an optimized analytical approach for comprehensive profiling of phytochemicals in the fruits of *G. jasminoides* was established in negative ionization mode. The holistic metabolites profiling was carried out on UHPLC/ESI-QTOFMS and data analysis program Progenesis QI, and a total of 80 metabolites were obtained and interpreted by chromatographic and tandem mass spectral data. The interpretation of metabolites comprises iridoids, pigments, organic acids, and flavonoids. Principal component analysis and partial least square-discriminant analysis were performed, and 19 main different components could be obtained to distinguish the three populations. Combined with non-targeted and targeted data analysis, the integrated strategy developed in this study was feasibly applied to discern differences in the profiles of the phytochemicals accumulating in the fruits of three populations of *G. jasminoides*.

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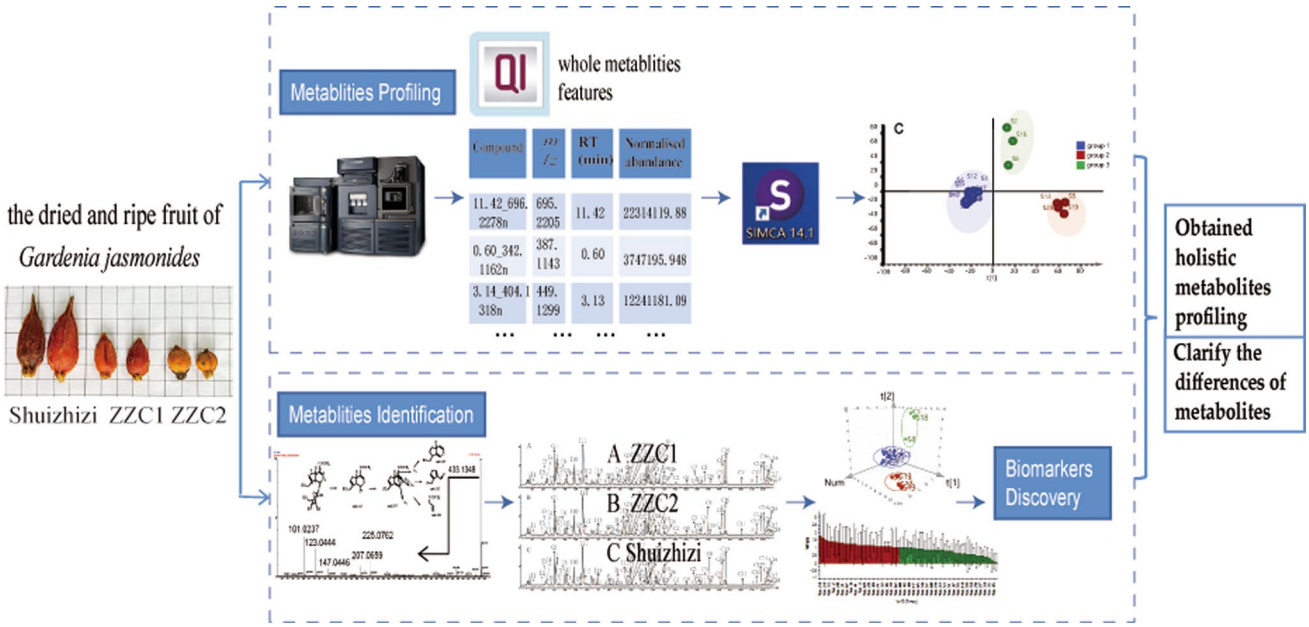
Graphical abstract



Keywords *Gardenia jasminoides* · Metabolomics · Tandem mass spectrometry · Iridoids · Crocins · Multivariate statistical analysis

Introduction

The genus Gardenia (Rubiaceae) comprises approximately 250 species in the world[1], most of which are used as ornamental plants, but *Gardenia jasminoides* Ellis, is not just for viewing, but also used as a kind of herbal medicine and edible food in China, Japan, and South Korea. Its dried and ripe fruit is firstly recorded in *Shen Nong's Herbal Classic* (A.D. 25-220) and has been used to clear away heat and toxic materials for thousands of years in Traditional Chinese Medicine (TCM) [2]. The fruit is traditionally called "Zhizi" or "Shanzhizi" in China and is recorded in a different version of *China Pharmacopoeia*, as well as *Japanese Pharmacopoeia* and *Korean Pharmacopoeia* [2–4]. Zhizi (the fruits of *G. jasminoides* Ellis) and Shuizhizi (the fruits of *G. jasminoides* var. radicans) are the two most cultivated species. However, by the theory of TCM, Zhizi is used for herb medicine, Shuizhizi is never for medicinal use and can only be used for dyeing. Until now, Shuizhizi is regarded as the counterfeit of Zhizhi [5–7]. Traditionally, Zhizi and Shuizhizi have distinct differences in appearance, and the former has a small and round appearance and is yellowish red but the latter is longer and redder [7, 8]. The *China Pharmacopoeia* (ChP) stipulates that the length of Zhizi is 1.5–3.5 cm [9], and the length of Shuizhizi is usually between 3.0 and 7.0 cm [10]. Due to the increasing demand for Zhizi, cultivars of *G. jasminoides* were selected by growers with large fruits and high productivity for higher economic benefits. In commercial Zhizi products, there are two mainstream cultivars in the markets (Fig. 1). One is small, round, and thin-skinned, more in line with the traditional description (ZZC1). The other is larger, redder as well as high-yield than the former (ZZC2) and it is intermediate in size and color between Zhizi and Shuizhizi [11, 12].

Previous phytochemical investigations of the fruit of *G. jasminoides* showed the presence of iridoid glycosides [13, 14], pigments [15], organic acids [16], and flavonoids [17], among which iridoids and pigments are considered as the main active and characteristic components. Geniposide is the representative iridoid component [18] and the percentage of geniposide in the fruits of *G. jasminoides* should be more than 1.8% by ChP. The current mandatory standard cannot distinguish Zhizi from Shuizhizi, while the literature reports that the content of geniposide in Zhizi was even higher than that in Shuizhizi [19, 20]. A multitude of classical analytical methods has been developed in the past to discriminate Zhizi and Shuizhizi [19–23]. The main analytical method was the combination of HPLC/UPLC fingerprint, multi-component determination, and multivariate statistical analysis. 22 common peaks of Zhizi and Shuizhizi were calibrated at most, crocin I,

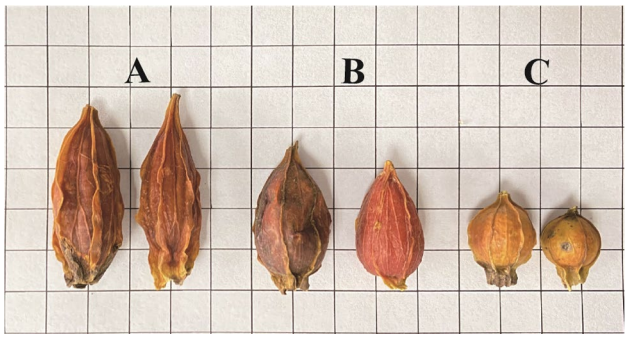


Fig. 1 **A** A variety of *G. jasminoides,* Shuizhizi (the fruit of *G. jasminoides* var.radians). **B** ZZC2, **C** ZZC1 Two kinds of cultivars of *G. jasminoides* in China.

genipin-1-β-D-gentiobioside, and other unknown compositions were identified as differential marker compositions. Such approaches, however, have failed to address the problem that the content of chemical components may be affected by post-harvest processing [24, 25]. Compounds calibrated in fingerprints were limited and the lack of reference cannot be identified. Comparative analysis of holistic phytochemicals profiling in traditional herbal medicine has a high potential for the determination of quality control of active ingredients as well as their different medicinal values. Thus, it is necessary here to comprehensively obtain the phytochemicals difference information, to distinguish and identify these three fruits, namely two kinds of cultivars of Zhizi widely distributed in China and Shuizhizi (the fruits of *G. jasminoides* var. radicans).

To fill this gap, samples of the fruits of *G. jasminoides* were collected from different districts in China with the same post-harvest processing at first. Secondly, the integrated strategy for comprehensive profiling of phytochemicals of these samples on basis of UHPLC/ESI-QTOFMS was developed. In addition, a comprehensive collection of chromatographic and mass spectral data for 80 metabolites was assembled in the course of this study. Finally, the strategy was feasibly applied to compare profiles of phytochemicals of two cultivars and one variety of *G. jasminoides* using non-targeted and targeted data analysis approaches.

Materials and methods

Samples used in this study

21 batches of different landraces of *G. jasminoides* were collected in different provinces of China from October to December 2020. 18 batches of the samples were identified as *Gardenia jasminoides* Ellis and three of them were identified as *G. jasminoides* var. radicans by Prof. Shilin Hu from Institute of Chinese Materia Medica, China Academy of Chinese Medical Sciences, where the voucher specimen was deposited. The detailed samples information are shown in Table 1.

Chemicals and reagents

MS grade acetonitrile and methanol were obtained from Fisher Scientific (Fair Lawn, NJ, USA); Formic acid (HPLC grade) and water were purchased from Tedia (Fairfield, OH, USA) and Watsons group (Guangzhou, China), respectively.

20 standards were purchased from different manufacturers. Crocin-I and crocin-II were purchased from Shanghai Yuanye Bio-Technology Co., Ltd. (Shanghai, China); crocin III, geniposide gentiobioside, gardenoside, deacetyl asperulosidic acid methyl ester, geniposidic acid, and scandoside methyl ester were purchased from Sichuan Weiqi Biotechnology Co., Ltd. (Chengdu, China); shanzhiside, gardoside, deacetyl asperulosidic acid, neochlorogenic acid, cryptochlorogenic acid, isochlorogenic acid A, isochlorogenic acid B, and cryptochlorogenic acid C were purchased from Chengdu Chroma-Biotech Co., Ltd. (Chengdu, China); rutin was purchased from Chengdu Must Biotechnology Co., Ltd. (Chengdu, China); crocin VI was purchased from Chengdu prifa Technology Development Co., Ltd. (Chengdu, China); geniposide and chlorogenic acid were purchased from Chengdu Herbpurty Co., Ltd. (Chengdu, China). The relative contents in the percentage of all the reference substances were over 98% calculated with area normalization method by HPLC.

Method for metabolite analyses of *G. jasminoides*

Preparation of sample solutions

The 21 batches of samples were pulverized into powder and sieved through a 50-mesh sieve before extraction. Then 200 mg of powder of each sample were weighed accurately and extracted with 20 mL of 70% methanol (v/v) for 30 min in an ultrasonic water bath (40 kHz, 250 W). After extraction, the solution was filtered through a 0.22 μm membrane filter and stored at 4 °C before use.

The quality control (QC) samples were obtained by mixing 21 batches of sample solutions and injected once before (after blank), in the middle, and at last to monitor the relative stability of the instrument.

Metabolite's profiling of *G. jasminoides* using UPLC-QTOF-MS/MS

Metabolite's profile was performed on an ACQUITY UPLC I-Class/Xevo G2-S QTOF system (Waters, Milford, MA, USA). A BEH C18 column (2.1 × 100 mm, 1.7 μm)

Table 1 Sample list of *G. jasminoides* collected in different provinces of China

Sample no.	Harvesting time	Location collected	Classification	Remarks
S1	2020.10.11	Yichun, Jiangxi	*G. jasminoides Ellis*	Cultivars (ZZC1)
S2	2020.10.13	Yichun, Jiangxi	*G. jasminoides* var. radicans	Shuizhizi
S3	2020.10.18	Nanyang, Henan	*G. jasminoides Ellis*	Cultivars (ZZC1)
S4	2020.10.20	Meizhou, Guangdong	*G. jasminoides Ellis*	Cultivars (ZZC1)
S5	2020.10.23	Wenzhou, Zhejiang	*G. jasminoides Ellis*	Cultivars (ZZC2)
S6	2020.10.25	Ganzhou, Jiangxi	*G. jasminoides Ellis*	Cultivars (ZZC1)
S7	2020.10.28	Fuzhou, Jiangxi	*G. jasminoides Ellis*	Cultivars (ZZC1)
S8	2020.10.29	Yibin, Sichuan	*G. jasminoides* var. radicans	Shuizhizi
S9	2020.10.30	Nanyang, Henan	*G. jasminoides Ellis*	Cultivars (ZZC1)
S10	2020.11.01	Yichun, Jiangxi	*G. jasminoides Ellis*	Cultivars (ZZC1)
S11	2020.11.01	Yichun, Jiangxi	*G. jasminoides Ellis*	Cultivars (ZZC1)
S12	2020.11.07	Chongqing	*G. jasminoides Ellis*	Cultivars (ZZC1)
S13	2020.11.08	Fuding, Fujian	*G. jasminoides Ellis*	Cultivars (ZZC2)
S14	2020.11.11	Zhuzhou, Hunan	*G. jasminoides Ellis*	Cultivars (ZZC1)
S15	2020.11.13	Yiwu, Zhejiang	*G. jasminoides Ellis*	Cultivars (ZZC1)
S16	2020.11.20	Jiujiang, Jiangxi	*G. jasminoides Ellis*	Cultivars (ZZC1)
S17	2020.11.22	Yichun, Jiangxi	*G. jasminoides Ellis*	Cultivars (ZZC1)
S18	2020.11.25	Jiujiang, Jiangxi	*G. jasminoides* var. radicans	Shuizhizi
S19	2020.11.25	Fuding, Fujian	*G. jasminoides Ellis*	Cultivars (ZZC2)
S20	2020.11.27	Jingdezhen, Jiangxi	*G. jasminoides Ellis*	Cultivars (ZZC2)
S21	2020.11.30	Yunfu, Guangdong	*G. jasminoides Ellis*	Cultivars (ZZC1)

equipped with an online filter at 25 °C was used to separate the compounds and eluted by a binary mobile phase of 0.1% formic acid in H_2O v/v (A) and acetonitrile (B) at a flow rate of 0.4 mL/min with a gradient elution: 0–4 min, 5%-12% (B); 4–10 min, 12%-21% (B); 10–14 min, 25%–33% (B); 17–19 min, 33% (B); 19–22 min, 33%–55% (B); 22–26 min, 90% (B). A 2–μL aliquot was injected for analysis.

Mass spectral data acquisition was ESI source in negative ion mode and the parameters were set as follows: capillary voltage, 3.0 kV; sampling cone voltage, 20 V; source offset voltage, 80 V; source temperature, 100 °C; desolvation temperature, 400 °C; cone gas flow, 50 $L{\cdot}h^{-1}$; and desolvation gas flow, 700 $L{\cdot}h^{-1}$. The mass analyzer scanned over a mass range of *m/z* 100–1600 under low energy of 6 V, and a high energy ramp of 20–100 V was set to acquire the MS^2 data. Data calibration was performed using an external reference (LockSprayTM) by constant infusion of 1.0 μg/mL of leucine enkephalin at a flow rate of 10 μL/min and by reference to the ion *m/z* 554.2615. Data acquisition was controlled by MassLynx V4.1 software (Waters Corporation, Milford, USA).

Data pretreatment and multivariate statistical analysis

The MS raw data of samples and QC samples were collected by the UPLC-QTOF-MS/MS and imported into the Progenesis QI software (Waters, Milford, USA). Adduct ions with the different responses were selected by the patterns of $[M–H]^-$, $[M–H+HCOOH]^-$, $[M–H_2O\text{-}H]^-$, $[2\ M–H]^-$, and $[2\ M–H+HCOOH]^-$. After deconvolution and normalization, the Progenesis QI software can produce a data matrix composed of retention time, normalized peak area, and other information. The data including peak number, sample name, and normalized peak areas were exported to the SIMCA-P 14.0 software (Umetrics, Umea, Sweden) for multivariate analysis. Principle component analysis (PCA) and partial least-squares-discriminant analysis (PLS-DA) were carried out to obtain the tendency of different samples to group, after mean centering and unit variance scaling. According to the variable influence on the projection (VIP > 1) and the significance threshold of the two-tailed *t* test ($P < 0.05$), the difference of different metabolites was determined.

Results and discussion

Optimization of chromatographic and mass spectrometric conditions

To acquire phytochemicals information completely, chromatographic separation was optimized including chromatographic column, mobile phase ratio, and column temperature. By adjusting the proportion of the mobile phase, comparatively, the BEH C18 column showed a more desirable resolution than CSH C18 and HSS T3 column. The column temperature at 25 °C was more suitable than 30 °C,

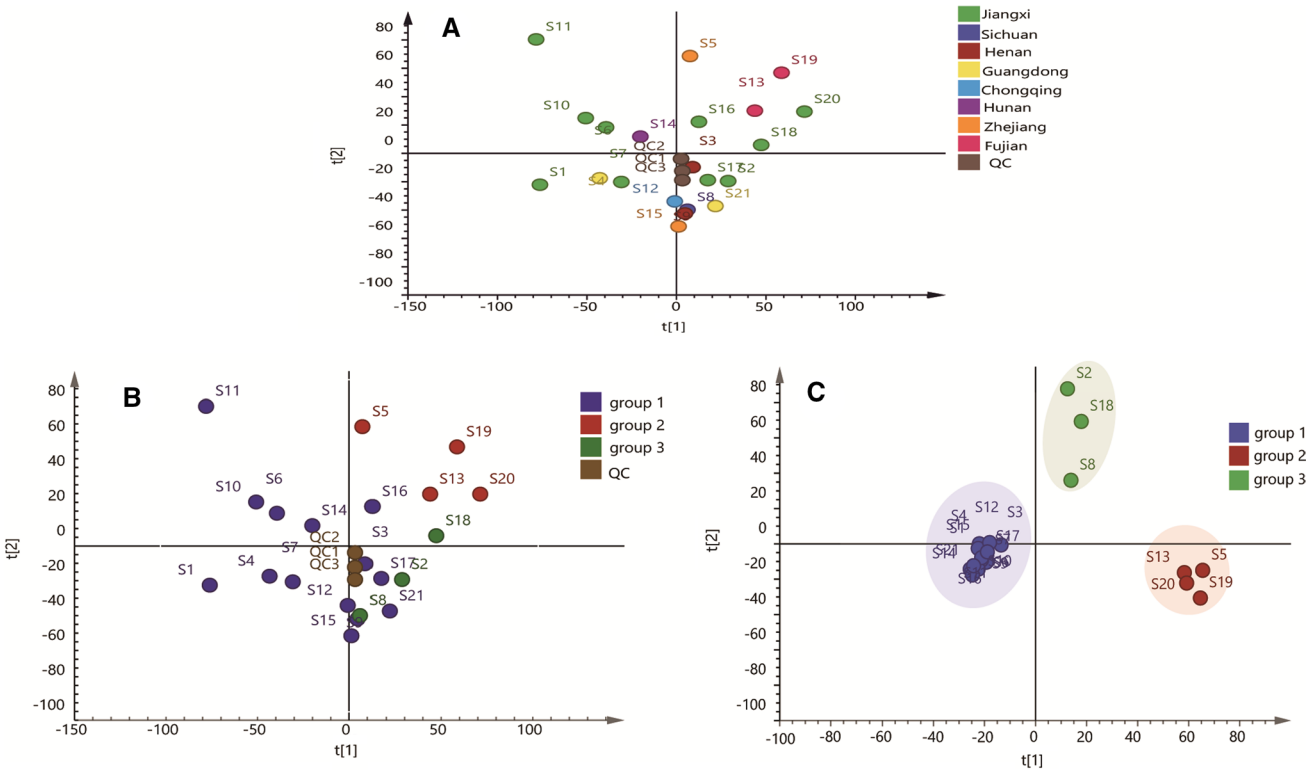


Fig. 2 Non-targeted analysis of metabolite profiles (8187 molecular features detected in negtive ion mode). **A** PCA score scatter plot of data from different geographical origins of *G. jasminoides* (PC1:18.2% PC2:15.5%). **B** PCA score scatter plot of data from different varieties or cultivars of *G. jasminoides* (PC:18.2% PC2:15.5%). **C** PLS-DA score scatter plot for 21 batches of *G. jasminoides* ($R^2X=0.534$ $R^2Y=0.988$ $Q^2(\text{cum})=0.79$). **B**, **C** group 1 representing ZZC1, group 2 representing ZZC2, group 3 representing Shuizhizi

35 °C and the flow rate at 0.4 ml/min were showed a better separation effect of iridoids and pigments.

Both positive and negative ionization modes were investigated. However, in the negative mode, mass spectrum peaks showed good response and the quasi-molecular and production ions were stable and reproducible. Therefore, the negative ionization mode was chosen for subsequent experiments.

Analysis of metabolomic profiling

After being processed by Progenesis QI software, as a result, a total of 8187 features were characterized from samples in negative ionization mode. The data matrix of the metabolite features was simply processed and exported into the SIMCA-P 14.0 software for chemometric analysis (principal component analysis, PCA and partial least square discriminant analysis, PLS-DA). As can be seen from Fig. 2A, different colors represented different geographical origins of 21 batches of the sample (taking origin as Class ID). The distribution of QC samples was concentrated, indicating the relative stability of the instrument during the test sample. The PCA analysis results suggested the distribution dispersion of samples in different producing areas was large. That is, the correlation between the sample and its origin was not significant. Then, the data of different varieties and cultivars of *G. jasminoides* were also analyzed by PCA and PLS-DA. As can be seen in Fig. 2B, three defined groups have a certain tendency of separation indicating there was some correlation between the chemical profile and its varieties or cultivars. Samples of two cultivars of Zhizi were divided into two groups segregated from each other, while there was a certain intersection between ZZC1 and Shuizhizi. However, when it comes to PLS-DA analysis, it can be seen in Fig. 2C that the three groups of *G. jasminoides* can be significantly separated.

Metabolites profiling by UPLC-QTOF-MS/MS

The base peak chromatogram of three groups of *G. jasminoides* was shown in Fig. 3. Data acquisition was controlled by Mass Lynx V4.1 software (Waters Corporation, Milford, USA). Compared with the accurate high-resolution mass measurements of adductions and characteristic fragmentation ions of the authentic substances or the literature data, the molecular structures were identified or tentatively deduced referring to MS splitting decomposition law. A total of 80 compounds were identified or tentatively

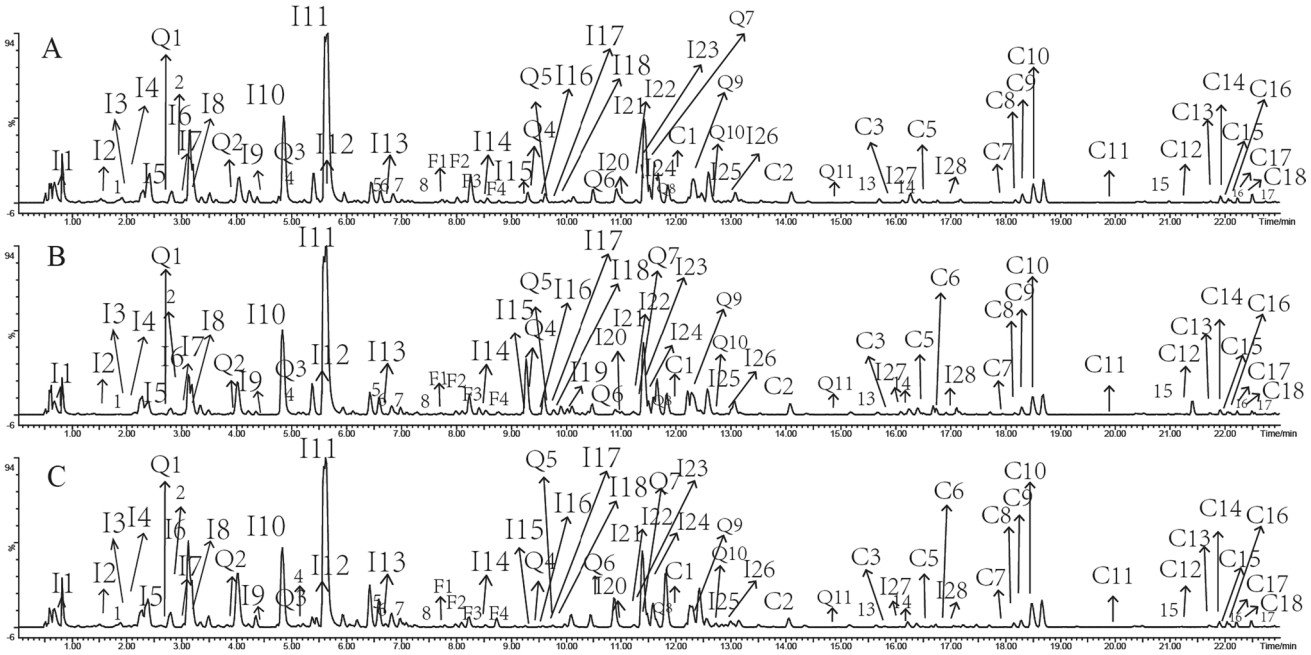


Fig. 3 The base peak chromatogram (BPC) in negative ion mode of three groups *G. jasminoides*. **A** ZZC1, **B** ZZC2, **C** Shuizhizi

characterized. Among them, 20 compounds were identified unambiguously using reference standards and the other 60 compounds were tentatively deduced by analyzing their MS/MS spectra.

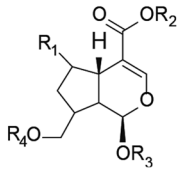
Iridoids

Iridoids were regarded as the main active constituent in *G. jasminoides*, with the skeleton of a kind of monoterpenoids based on a cyclopentane-[C]-pyran. A total of 28 iridoids were identified or tentatively deduced in this study (Fig. 4).

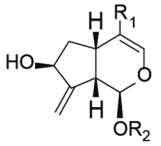
I11 was a representative iridoid in *G. jasminoides*, displayed an $[M–H+HCOOH]^-$ and $[M–H]^-$ ion at *m/z* 433.1348 ($C_{18}H_{25}O_{12}$) and *m/z* 387.1298 ($C_{17}H_{24}O_{10}$). The base peak at *m/z* 225.0762 and 207.0659 was generated by the cleavage of glycosidic bond and further losing H_2O (18 Da). Then, the fragment ions of *m/z* 147.0440, *m/z* 123.0445, and *m/z* 101.0238 were obtained by the losses of carboxymethyl moiety, Retro-Diels Alder (RDA) reaction, and the cleavage of $C_{4\text{-}5}$ and C_1-O_2 bond, respectively, coming from the A_1, A_2, and A_3 segments, as can be seen in Fig. 5A. By comparing with the reference standard, I11 was identified as geniposide. Besides, in contrast to the reference standard, I5 and I8 were identified as deacetyl asperulosidic acid methyl ester and scandoside methyl ester. The differences between the structures and geniposide were that the C_7 connected with α-OH, β-OH, respectively. Thus, I5 and I8 exhibited an $[M–H+HCOOH]^-$ and $[M–H]^-$ ion at *m/z* 449.1298 and *m/z* 403.1240 in the full mass spectrum. Similarly, as I11, the fragment ions at *m/z* 241.0712 and *m/z* 223.0602 were also due to the cleavage of glycosidic bond and further losing H_2O (18 Da). The fragment ions at *m/z* 165.0555, *m/z* 139.0413, and *m/z* 101.0239 were generated from the A_1, A_2, and A_3 segments. Different from I11, fragment ion displayed at *m/z* 193.0492 of I5 and I8 was triggered by the further loss of hydroxymethy after losing glucosyl residues and H_2O.

I4 was confirmed by matching with the reference substance and identified as geniposide acid. The difference between I4 and I11 (geniposide) was the carboxyl which was connected in the C_4 position. Therefore, I4 showed an $[M–H]^-$ ion at *m/z* 373.1135. In the MS^2 spectra, fragment ion *m/z* 211.0604 was owing to the cleavage of the glucosidic bond. And after breaking the glycoside bond, it did not continue to break C_1 hydroxyl groups as I11, but further lost the hydroxyl group and formed an ion at *m/z* 149.0599. Surely, it can also generate a fragment ion at *m/z* 123.0442 by the A_3 segment. By comparison with the reference substance, I10 was identified as genipin-1-β-gentiobioside whose structure is one more glucosyl residues than geniposide. Thus, there were ions at *m/z* 595.1882 and *m/z* 549.1824 attributed to $[M–H+HCOOH]^-$ and $[M–H]^-$, respectively. The fragment ion at *m/z* 225.0767 was caused by the losses of two molecules of glucose (324 Da). Other characteristic fragment ions *m/z* 123.0446 and *m/z* 101.0238 were got in the same way as I11.

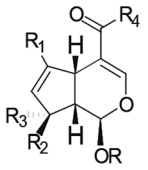
I25, I26, I28 showed the $[M–H]^-$ ions at *m/z* 593.1884 ($C_{28}H_{33}O_{14}$), *m/z* 533.1660 ($C_{26}H_{29}O_{12}$), and *m/z* 593.1859 ($C_{28}H_{33}O_{14}$) in the full mass spectra, respectively. I25 and I26 produced the diagnosed fragment ions at *m/z* 225.0756,



I1 R_1=α-OH R_2=H R_3=Glc R_4=H
I4 R_1=H R_2=H R_3=Glc R_4=H
I5 R_1=α-OH R_2=CH_3 R_3=Glc R_4=H
I8 R_1=β-OH R_2=CH_3 R_3=Glc R_4=H
I10 R_1=H R_2=CH_3 R_3=Glc-(1→6)-Glc R_4=H
I11 R_1=H R_2=CH_3 R_3=Glc R_4=H
I14 R_1=H R_2=CH_3 R_3=Glc R_4=Ac
I16 R_1=H R_2=H
R_3=6′-*O*-*trans*-*p*-courmaroyl-Glc R_4=H
I17 R_1=H R_2=CH_3 R_4=H
R_3=6″-*O*-*trans*-caffeoyl-Glc-(1→6)-Glc
I19 R_1=β-OH R_2=CH_3
R_3=6″-*O*-*tans*-caffeoyl-Glc R_4=H
I21 R_1=H R_2=CH_3 R_4=H
R_3=4″-*O*-*tans*-*p*-coumaroyl-Glc-(1→6)-Glc/
6″-*O*-*trans*-coumaroyl-Glc-(1→6)-Glc
I22 R_1=H R_2=CH_3 R_4=H
R_3=4″-*O*-*tans*-*p*-coumaroyl-Glc-(1→6)-Glc/
6″-*O*-*trans*-coumaroyl-Glc-(1→6)-Glc
I23 R_1=H R_2=CH_3 R_4=H
R_3=6″-*O*-*trans*-sinapoyl-Glc-(1→6)-Glc
I24 R_1=H R_2=CH_3 R_4=H
R_3=6″-*O*-*tans*-feruloyl-Glc-(1→6)-Glc
I25 R_1=H R_2=CH_3 R_3=6′-*O*-*trans*-sinapoyl-Glc R_4=H
I26 R_1=H R_2=CH_3 R_3=6′-*O*-*trans*-coumaroyl-Glc R_4=H
I27 R_1=H R_2=CH_3 R_4=H
R_3=4″-*O*-*tans*-*p*-cinnamoyl-Glc-(1→6)-Glc
I28 R_1=H R_2=CH_3 R_3=H R_4=10-*O*-*trans*-sinapoyl



I2 R_1=CHO R_2=Glc
I12 R_1=$COOCH_3$ R_2=Glc
I13 R_1=COOH R_2=2′-*O*-*trans*-coumaroyl-Glc
/2′-*O*-*cis*-p-coumaroyl-Glc
I15 R_1=COOH R_2=6′-*O*-*trans*-sinapoyl-Glc
I18 R_1=COOH R_2=2′-*O*-*trans*-feruloyl-Glc
I20 R_1=COOH R_2=2′-*O*-*trans*-caffeoyl-Glc



I3 R=Glc R_1=OH R_2=OH R_3=CH_3 R_4=OH
I6 R=Glc R_1=H R_2=OH R_3=CH_2OH R_4=OCH_3
I7 R=Glc R_1=H R_2=OH R_3=CH_3 R_4=H
I9 R=Glc R_1=H R_2=OH R_3=CH_3 R_4=OH

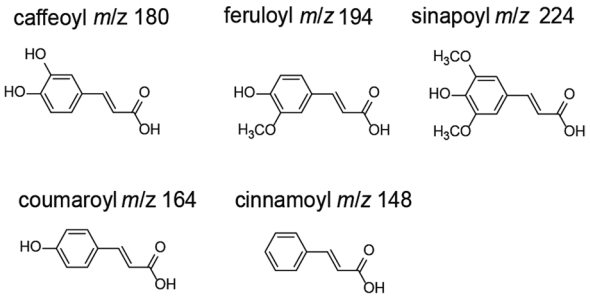


Fig. 4 The structure of iridoids has been identified or tentatively deduced

m/z 123.0443, and *m/z* 101.0237 which indicated the existence of the genipin moiety. In the MS^2 spectra, it has shown the fragment ions at *m/z* 223.0603 and *m/z* 205.0500 which were corresponded to characteristic ions of sinapoyl (224 Da) formed by [sinapoyl-H]$^-$ and [sinapoyl-H_2O-H]$^-$. The fragment ions at *m/z* 163.0390 and *m/z* 145.0283 were coumaroyl (164 Da) group and presented the patterns of [coumaroyl-H]$^-$ and [coumaroyl-H_2O-H]$^-$. Additionally, the fragment ions at *m/z* 367.1034 and *m/z* 307.0828 were caused by the cleavage of glycosidic bonds and generated the fragment ion formed by glycoside connected with sinapoyl or coumaroy. Thus, I25 and I26 were tentatively assigned as 6′-*O*-*trans*-sinapoylgeniposide [26] and 6′-*O*-*trans*-*p*-coumaroylgeniposide [27]. The characteristic fragment ions of I28 and I25 were almost the same but I28 showed another fragment ion at *m/z* 413.1238 which was generated by breaking the glycoside bond first. According to the literature reported, I28 was tentatively deduced to be 10-*O*-*trans*-sinapoylgeniposide [28].

The diagnostic ions of genipin at *m/z* 225.0756, *m/z* 123.0445, and *m/z* 101.0241 were also found in the MS/MS data of I17, I21, I22, I23, I24, and I27. Besides, the characteristic fragment ions of caffeoyl (180 Da), coumaroyl (164 Da), feruloyl (194 Da), sinapoyl (224 Da), cinnamoyl (148 Da) groups (expressed in X) generated in the patterns of [X–H]$^-$ and [X-H_2O-H]$^-$ were found in the MS/MS analysis, respectively. Moreover, I17, I21, I22, I23, I24, and I27 have all produced a diagnostic ion [X + gentiobiosyl-H_2O-H]$^-$ which was caused by the cleavage of the glycosidic bonds. Bearing in mind of all the iridoids isolated from *G. jasminoides*, I17, I23, I24, and I27 were tentatively deduced as 6″-*O*-*trans*-caffeoylgenipin gentiobioside [29], 6″-*O*-*trans*-sinapoylgenipin gentiobioside [30], 6″-*O*-*trans*-feruloylgenipin gentiobioside [21], and 6″-*O*-*trans*-cinnamoylgenipin gentiobioside [30]. Because of the same neutral loss to result in the same fragment ions, I21 and I22 were tentatively deduced as 6″-*O*-*trans*-*p*-coumaroylgenpin

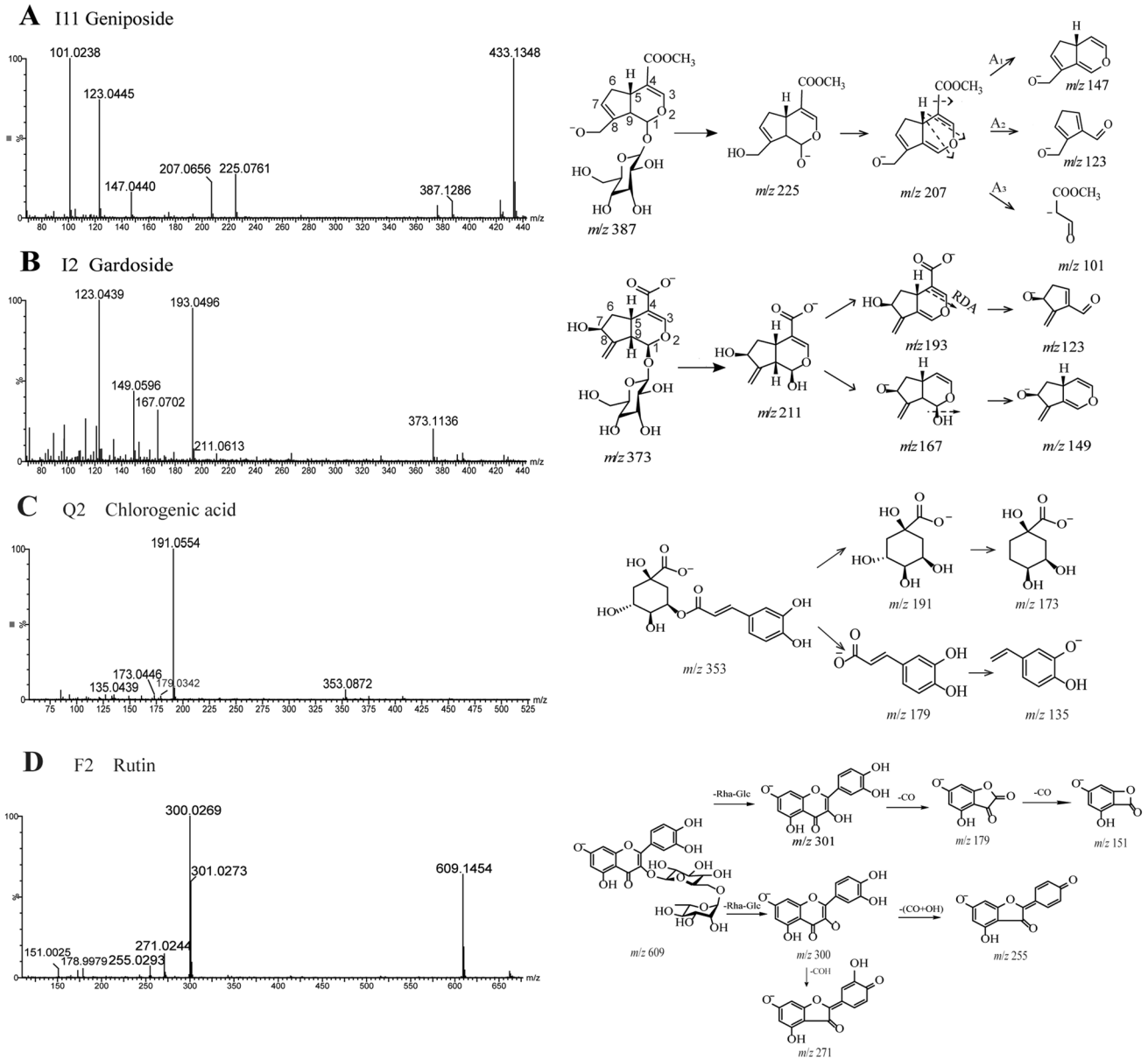


Fig. 5 **A** The MS^2 spectra and plausible fragmentation pathway of geniposide (I11). **B** The MS^2 spectra and plausible fragmentation pathways of gardoside (I2). **C** The MS^2 spectra and plausible fragmentation pathway of chlorogenic acid (Q2). **D** The MS^2 spectra and plausible fragmentation pathways of rutin (F2)

gentiobioside or 4″-*O*-*trans*-*p*-coumaroyl gentiobiosylgenipin [27, 30].

I2 was identified as gardoside by comparing with the reference standard, which was illustrated briefly in Fig. 5B. Different from the geninpside, the C8 position of I2 was linked with a double bond. The fragment ion at *m*/*z* 211.0613, *m*/*z* 193.0496, *m*/*z* 123.0439, *m*/*z* 167.0702, and *m*/*z* 149.0596 were found on the MS^2 spectra of gardoside and they were the characteristic fragment ion of gardoside derivatives. The MS^2 spectra of compounds I13, I15, I15, and I20 contain all the above-mentioned fragment ions, so they share the same skeleton of gardoside. Besides, the characteristic fragment ions of *m*/*z* 179.0350, *m*/*z* 161.0244, *m*/*z* 163.0401, *m*/*z* 145.0290, *m*/*z* 193.0506, *m*/*z* 175.0406, *m*/*z* 223.0612, and *m*/*z* 205.0506 produced in the patterns of $[X–H]^-$ and $[X\text{-}H_2O\text{-}H]^-$ of caffeoyl (180 Da), coumaroyl (164 Da), feruloyl (194 Da), sinapoyl (224 Da) groups appeared in the spectra of I13, I15, I18, and I20, respectively. Furthermore, a specific fragment ion at *m*/*z* 307.0809 occurred in I13, indicating the presence of a glucose-bearing coumaroyl. Thus, I13 was tentatively assigned as 2′-*O*-*trans*-*p*-coumaroyl gardoside or 2′-*O*-*cis*-*p*-coumaroyl gardoside [31], and I15,

I18, and I20 were deduced as 6′-*O*-*trans*-sinapoyl gardoside [27], 2′-*O*-*trans*-feruloyl gardoside, and 2′-*O*-*trans*-caffeoyl gardoside [31], respectively. Finally, the MS fragmentation of other iridoid compounds can be seen in Table 2.

Pigments

G. jasminoides are an excellent source of natural pigments. These pigments are another important active ingredient both in saffron (*Crocus sativus* L.) and *G. jasminoides* and the structures of the pigments are in all-*trans*- and 13-*cis*-crocetin esterified with one or two glucose, gentibiose, or neapolitanose sugar moieties et al. Owing to the existence of cis and trans isomers, there were semblable MS data. By combining the literature data and the splitting rules of four reference standards, the structures of 19 pigments in *G. jasminoides* were identified or tentatively deduced (Fig. 6).

C1 was identified as crocetin-digentiobioside ester (crocin-1) by matching with the reference substance. Its parental molecular ions [M–H-HCOOH]$^-$ and [M–H]$^-$ were displayed at *m/z* 1021.3787 ($C_{45}H_{65}O_{26}$) and *m/z* 975.3720 ($C_{44}H_{63}O_{24}$). Due to the structure being composed of crocin and two molecules of gentiobioside, in the MS/MS spectrum, the characteristic fragment ions at *m/z* 651.2665 and *m/z* 327.1604 were produced by the losses of gentiobiose via cleavage by each side of the glycosidic bond. Then, ions at *m/z* 283.1704 and *m/z* 239.1802 were also obtained by the losses of CO_2 (44 Da) on each side. Since another compound C10 which displayed semblable MS data with C1, it was tentatively assigned as 13-*Z*-Crocetin-digentiobioside esters [32]. Apart from the same molecular ions at *m/z* 1021.3793 and *m/z* 975.3726 and the characteristic fragment ions at *m/z* 651.2653, *m/z* 327.1597, and *m/z* 283.1694, compounds C4 and C6 showed another diagnostic ion at *m/z* 813.3183, which suggested the loss of a glucose moiety (162 Da) from *m/z* 975.3716 [M–H]$^-$. Therefore, in combination with the chromatographic behavior [32], C4 and C6 have tentatively been deduced as *trans*-crocetin (*β*-D-neapolitanosyl)-(*β*-D-glucosyl) ester and *cis*-crocetin (*β*-D-neapolitanosyl)-(*β*-D-glucosyl) ester.

C2 generated [M–H-HCOOH]$^-$ and [M–H]$^-$ ions at *m/z* 859.3254 ($C_{39}H_{55}O_{21}$) and *m/z* 813.3189 ($C_{38}H_{39}O_{20}$) in the full mass spectrum. The fragment ions of C2 at *m/z* 651.2665, *m/z* 489.2111, and *m/z* 327.1594 were generated by the cleavage of the glycosidic bond on both sides resulting in the loss of the glucose (162 Da) and gentiobiose (324 Da), respectively. The diagnosed ions at *m/z* 283.1700 and *m/z* 239.1799 were similar to the C1 which were the characteristic fragment ions of crocin derivatives. Consequently, C2 was identified as crocin-2 (Crocetin gentiobioside monoglucoside ester), which was confirmed by comparing it with the reference substance. C17 and C18 exhibited the same MS data with C2, according to the literature data and the chromatographic behaviors [32] they were annotated to be 13-*cis*-crocetin-8-*O*-*β*-D-gentiobiosyl-8′-*O*-*β*-D-glucopyranoside (C17) and 13-*cis*-crocetin-8-*O*-*β*-D-glucopyranosyl-8′-*O*-*β*-D-gentiobioside (C18). C9, C14, C15, and C16 were showed the same parental molecular ions [M–H]$^-$ at *m/z* 651.2669 under negative ionization mode. C14 to be crocin-3 (Crocetin-monogentiobiosdie ester) was confirmed by matching retention time and MS^2 spectral data with an authentic standard of crocin-3 (Crocetin-monogentiobioside ester). Its characteristic fragment ions at *m/z* 327.1589, *m/z* 283.1693, and *m/z* 239.1794 were generated by the loss of gentibiose (324 Da) and further losses of CO_2 (44 Da) on each side. With the same MS^2 spectral data of C14, C15 and C16 were the isomers of C14 and they were tentatively assigned to be 13-*cis*-crocetin-8-*O*-*β*-D-gentiobioside and 13′-*cis*-crocetin-8-*O*-*β*-D-gentiobioside based on the chromatographic behavior [15]. Besides, the MS^2 spectral data of C9 were similar to that of C15 and C16, except for a fragment ion at *m/z* 489.2111[M–H-162]$^-$, as suggested that there was the cleavage of a glycosidic bond to lose glucose (162 Da) in the structure of C9. Thus, C9 [33] were deduced as crocetin-diglucoside ester.

C7, C8, and C13 exhibited the same molecular ion at *m/z* 987.3515 [M–H]$^-$. According to the literature, three crocin compounds isolated from *G. jasminoides* named neocrocin B–D all showed the molecular ion at *m/z* 987.3498. The structures of these compounds were characterized by the gentibiose and caffeoyl + $C_7H_{11}O_5$ (Fig. 6B) substituent on each side of the parent nucleus crocetin as shown in Fig. 6. Therefore, the fragment ions at *m/z* 825.3206 and *m/z* 651.2662 were caused by the loss of glucose or the loss of B moiety from the molecular ion. The fragment ion at *m/z* 501.2128 was caused by the loss of gentiobiose and caffeoyl at the same time. Other fragment ions at *m/z* 327.1595, *m/z* 283.1701, and *m/z* 239.1805 were the diagnostic ions of crocetin. Among these three compounds, the MS^2 spectral data of C8 and C13 were the same. Therefore, C8 and C13 were deduced as *cis*- and *trans*-isomers. Simultaneously, considering the appearance time at the C18 column in the literature [15], C7, C8, and C13 were tentatively deduced as neocrocin C, neocrocin B, and neocrocin D, respectively.

C5 exhibited an [M–H]$^-$ ion at *m/z* 1181.4347 in the full mass spectrum. In the MS/MS analysis, there were characteristic fragment ions at *m/z* 223.0603 and *m/z* 205.0499 which suggested the substituent group of sinapoyl. Besides, the fragment ions at *m/z* 857.3232 and *m/z* 529.1556 were shown by the loss of gentiobiose and the gentiobiose with sinapoyl [gentiobiosyl + sinapoyl-H]$^-$. Fragment ions at *m/z* 651.2656 and *m/z* 327.1593 were the common fragment ions of crocin compounds. Referring to the crocin compounds isolated from *G. jasminoides*

Table 2 MS data for characterization of compounds by UPLC-Q-TOF/MS in the *G. jasminoides*

Peak	t_R (min)	Measured (*m/z*)	formula	Thoretical	Error (ppm)	Fragmentation ions (*m/z*)	Compound identification
I1*	1.52	389.1085 $[M–H]^-$	$C_{16}H_{21}O_{11}$	389.1084	0.3	227.0559 [M-Glc-H]$^-$, 209.0444 [M-Glc-H_2O-H]$^-$, 165.0547 [M-Glc-H_2O-CO_2-H]$^-$, 147.0441 [M-Glc-$2H_2O$-CO_2-H]$^-$, 139.0391 $[C_7H_7O_3]^-$, 101.0237 $[C_4H_5O_3]^-$	Deacetyl asperulosidic acid [45]
I2*	1.92	373.1129 $[M–H]^-$	$C_{16}H_{21}O_{10}$	373.1135	− 1.6	211.0613 [M-Glc-H]$^-$, 193.0496 [M-Glc-H_2O-H]$^-$, 167.0702 [M-Glc-CO_2-H]$^-$, 149.0596 [M-Glc-H_2O-CO_2-H]$^-$, 123.0439 $[C_7H_7O_2]^-$	Gardoside [46]
I3*	2.41	391.1238 $[M–H]^-$	$C_{16}H_{23}O_{11}$	391.1240	0	229.0711 [M-Glc-H]$^-$, 211.0599 [M-Glc-H_2O-H]$^-$, 185.0813 [M-Glc-CO_2-H]$^-$, 167.0704 [M-Glc-H_2O-CO_2-H]$^-$, 149.0596 [M-Glc-$2H_2O$-CO_2-H]$^-$, 123.0442 $[C_7H_7O_2]^-$	Shanzhiside [46]
I4*	2.51	373.1135 $[M–H]^-$	$C_{16}H_{21}O_{10}$	373.1135	0	211.0605 [M-Glc-H]$^-$, 167.0705 [M-Glc-CO_2-H]$^-$, 149.0607 [M-Glc-H_2O-CO_2-H]$^-$, 123.0448 $[C_7H_7O_2]^-$	Geniposidic acid [46]
I5*	2.82	449.1298 $[M–H+HCOOH]^-$	$C_{18}H_{25}O_{13}$	449.1295	0.3	403.1240 [M–H]$^-$, 241.0712 [M-Glc-H]$^-$, 223.0602 [M-Glc-H_2O-H]$^-$, 193.0492 [M-Glc-H_2O-CH_2OH-H]$^-$, 165.139.0392 $[C_9H_9O_3]^-$, 139.0392 $[C_7H_7O_3]^-$, 101.0235 $[C_4H_5O_3]^-$	Deacetyl asperulosidic acid methyl ester [45]
I6*	3.16	449.1301 $[M–H+HCOOH]^-$	$C_{18}H_{25}O_{13}$	449.1295	1.3	403.1246 [M–H]$^-$, 241.0713 [M-Glc-H]$^-$, 223.0605 [M-Glc-H_2O-H]$^-$, 165.0553[M-Glc-H_2O-CH_3COOH-H]$^-$, 127.0393 $[C_7H_{11}O_2]^-$, 101.0236 $[C_4H_5O_3]^-$	Gardenoside [47]
I7	3.37	405.1392 $[M–H+HCOOH]^-$	$C_{17}H_{25}O_{11}$	405.1397	− 1.2	359.1342 [M–H]$^-$, 197.0807 [M-Glc-H]$^-$, 179.0716 [M-Glc-H_2O-H]$^-$, 125.0236 $[C_7O_9O_2]^-$	Ixoroside [47]
I8	3.51	449.1295 $[M–H-HCOOH]^-$	$C_{18}H_{25}O_{13}$	449.1295	0	403.1236 [M–H]$^-$, 241.0710 [M-Glc-H]$^-$, 223.0602 [M-Glc-H_2O-H]$^-$, 139.0397 $[C_7H_7O_3]^-$, 101.0235 $[C_4H_5O_3]^-$,	Scandoside methyl ester [48]
I9*	4.76	375.1290[M–H]$^-$	$C_{16}H_{23}O_{10}$	375.1291	− 0.3	213.0764 [M-Glc-H]$^-$, 195.0556 [M-Glc-H_2O-H]$^-$, 169.0861 [M-Glc-CO_2-H]$^-$, 151.0756 [M-Glc-$2H_2O$-H]$^-$, 125.0596 $[C_7H_9O_2]^-$	Mussaenosidic acid [49]
I10*	4.86	595.1882 $[M–H+HCOOH]^-$	$C_{24}H_{35}O_{17}$	595.1850	1.3	549.1824 [M–H]$^-$, 225.0767 [M-2Glc-H]$^-$, 207.0656 [M-2Glc-H_2O -H]$^-$, 123.0446 $[C_7H_7O_2]^-$, 101.0238 $[C_4H_5O_3]^-$	Genipin geniobioside [50]
I11	5.60	433.1348 $[M–H+HCOOH]^-$	$C_{18}H_{25}O_{12}$	433.1346	0.5	387.1298 [M–H] $^-$, 225.0762 [M-Glc-H]$^-$, 207.0659 [M-Glc-H_2O-H]$^-$, 147.0440 [M-Glc-H_2O-$COOCH_3$-H]$^-$, 123.0445 $[C_7H_7O_2]^-$, 101.0238 $[C_4H_5O_3]^-$	Geniposide [50]
I12	5.77	433.1357 $[M–H+HCOOH]^-$	$C_{18}H_{25}O_{12}$	433.1346	2.5	387.1294 [M -H]$^-$, 225.0766 [M-Glc -H]$^-$, 207.0645 [M-Glc –H_2O-H]$^-$, 105.3401 $[C_7H_5O]^-$, 101.0340 $[C_4H_5O_3]^-$	7-deoxygardoside [51]

Table 2 (continued)

Peak	t_R (min)	Measured (*m/z*)	formula	Thoretical	Error (ppm)	Fragmentation ions (*m/z*)	Compound identification
I13	7.02	519.1497[M–H]$^-$	$C_{25}H_{27}O_{12}$	519.1503	− 1.2	307.0809 [coumaroyl + Glc-H_2O-H]$^-$, 211.0616 [M-coumaroyl-Glc + H_2O-H]$^-$, 193.0506 [M-coumaroyl-Glc-H]$^-$, 163.0393 [coumaroyl-H]$^-$, 149.0605 [M-coumaroyl-Glc-CO_2-H]$^-$, 145.0283 [coumaroyl-H_2O-H]$^-$, 123.0437 [$C_7H_7O_2$]$^-$, 101.0237 [$C_4H_5O_3$]$^-$	2′-*O*-*trans*-*p*-coumaroyl gardoside/2′-*O*-*cis*-*p*-coumaroyl gardoside [31]
I14	8.77	475.2181 [M–H + HCOOH] $^-$	$C_{16}H_{23}O_{10}$	475.2179	0.2	429.2132 [M–H]$^-$, 265.0714 [M-Glc-H]$^-$, 249.1498 [M-Glc-H_2O-H]$^-$, 191.1068 [M-Glc-H_2O-Ac-H]$^-$, 109.0568 [C_7H_9O]$^-$, 101.0238 [$C_4H_5O_3$]$^-$	10-*O*-acetylgeniposide [52]
I15	9.61	579.1720[M–H]$^-$	$C_{27}H_{31}O_{14}$	579.1690	1.0	367.1035 [sinapoyl + Glc-H_2O-H]$^-$, 211.0602 [M-sinapoyl-Glc + H_2O-H]$^-$, 223.0605 [sinapoyl-H]$^-$, 205.0499 [sinapoyl-H_2O-H]$^-$, 193.0496 [M-sinapoyl-H_2O-Glc-H]$^-$, 167.0716 [M-sinapoyl-Glc-CO_2-H]$^-$ 149.0595 [M-sinapoyl-Glc-CO_2-H]$^-$, 123.0442 [$C_7H_7O_2$]$^-$	6′-*O*-*trans*-sinapoyl gardoside [27]
I16	9.77	519.1500[M–H]$^-$	$C_{25}H_{27}O_{12}$	519.1503	− 0.6	307.0827 [coumaroyl + Glc-H_2O-H]$^-$, 211.0606 [M-coumaroyl-Glc + H_2O-H]$^-$, 193.0501 [M-coumaroyl-Glc-H_2O-H]$^-$, 163.0396 [coumaroyl-H]$^-$, 145.0287 [coumaroyl-H_2O-H]$^-$, 123.0438 [$C_7H_7O_2$]$^-$	6′-*O*-*trans*-*p*-coumaroyl geniposidic acid [30]
I17	10.10	711.2145[M–H]$^-$	$C_{32}H_{39}O_{18}$	711.2136	1.3	485.1294 [caffeoyl + gentiobiosyl-H_2O-H]$^-$, 325.0898 [caffeoy + Glc-H]$^-$, 225.0756 [M-caffeoyl-gentiobiosy + H_2O-H]$^-$, 179.0338 [caffeoy-H]$^-$, 161.0231 [caffeoy-H_2O-H]$^-$, 123.0445 [$C_7H_7O_2$]$^-$, 101.0241 [$C_4H_5O_3$]$^-$	6″-*O*-*trans*-caffeoylgenipin gentiobioside [29]
I18	10.20	549.1613[M–H]$^-$	$C_{26}H_{29}O_{13}$	549.1608	0.9	337.0925 [feruloyl + Glc-H_2O-H]$^-$, 211.0609 [M-feruloyl-Glc + H_2O-H]$^-$, 193.0493 [feruloyl-H]$^-$, 175.0389 [feruloyl-H_2O-H]$^-$, 167.0345 [M-feruloyl + H_2O-Glc-CO_2-H]$^-$, 149.0598 [M-feruloyl-Glc-CO_2-H]$^-$, 123.0442 [$C_7H_7O_2$]$^-$	2′-*O*-*trans*-feruloyl gardoside [31]
I19	10.34	565.1573[M–H]$^-$	$C_{26}H_{29}O_{14}$	565.1557	2.8	325.0911 [caffeoyl + Glc-H_2O-H]$^-$, 223.0604 [M-caffeoyl-Glc-H]$^-$, 205.0499 [M-caffeoy-Glc-H_2O-H]$^-$, 179.0338 [caffeoyl-H]$^-$, 165.0559 [M-caffeoy-Glc-H_2O-CO_2-H]$^-$, 161.0232 [caffeoyl-H_2O-H]$^-$, 139.0389 [$C_7H_7O_3$]$^-$, 101.0236 [$C_4H_5O_3$]$^-$	6′-*O*-*trans*-caffeoyl deacetyl asperulosidic acid methyl ester [27]
I20	11.25	535.1441[M–H]$^-$	$C_{25}H_{27}O_{13}$	535.1452	− 2.1	325.0920 [caffeoyl + Glc-H_2O-H]$^-$, 193.0501 [M-caffeoyl-Glc -H]$^-$, 179.0551 [caffeoyl-H]$^-$, 163.0392 [caffeoyl-H_2O-H]$^-$, 167.0335 [M-caffeoyl + H_2O-Glc-CO_2-H]$^-$, 123.0443 [$C_7H_7O_2$]$^-$	2-*O*-*trans*-caffeoylgardoside [31]
I21	11.29	695.2198[M–H]$^-$	$C_{32}H_{39}O_{17}$	695.2187	1.6	469.1344 [coumaroyl + gentiobiosyl-H_2O-H]$^-$, 225.0756 [M-coumaroyl-gentiobiosyl + H_2O-H]$^-$, 163.0392 [coumaroy-H]$^-$, 145.0285 [coumaroy-H_2O-H]$^-$, 123.0442 [$C_7H_7O_2$]$^-$, 101.0235 [$C_4H_5O_3$]$^-$	6″-*O*-*trans*-*p*coumaroylgenpin gentiobiosdie/4″-*O*-*trans*-*p*-coumaroylgentiobiosylgenipin [27, 30]

Table 2 (continued)

Peak	t_R (min)	Measured (*m/z*)	formula	Thoretical	Error (ppm)	Fragmentation ions (*m/z*)	Compound identification
I22	11.42	695.2192[M–H]$^-$	$C_{32}H_{39}O_{17}$	695.2187	0.7	469.1371 [coumaroyl + gentiobiosyl-H_2O-H]$^-$, 225.0757 [M-coumaroyl-gentiobiosyl + H_2O-H]$^-$, 163.0395 [coumaroy-H]$^-$, 145.0290 [coumaroy-H_2O-H]$^-$, 123.0442 [$C_7H_7O_2$]$^-$, 101.0241 [$C_4H_5O_3$]$^-$	6″-*O*-*trans*-*p*coumaroylgenpin gentiobioside/4″-*O*-*trans*-*p*-coumaroylgentiobiosylgenipin [27, 30]
I23	11.66	755.2421[M–H]$^-$	$C_{34}H_{43}O_{19}$	755.2399	2.9	529.1555 [sinapoyl + gentiobiosyl-H_2O-H]$^-$, 367.1012 [sinapoyl + Glc-H_2O-H]$^-$, 225.0496 [M-sinapoyl-gentiobiosyl + H_2O-H]$^-$, 223.0603 [sinapoyl-H]$^-$, 205.0496 [sinapoyl-H_2O-H]$^-$, 123.0443 [$C_7H_7O_2$]$^-$, 101.0237 [$C_4H_5O_3$]$^-$	6″-*O*-*trans*-sinapoylgenipin gentiobioside [30]
I24	11.88	725.2295 [M–H]$^-$	$C_{33}H_{41}O_{18}$	725.2293	0.3	499.1448 [feruloyl + gentiobiosyl-H_2O-H]$^-$, 225.0758 [M-feruloyl-gentiobiosyl + H_2O-H]$^-$, 193.0499 [feruloyl-H]$^-$, 175.0391 [feruloyl-H_2O-H]$^-$, 123.0441 [$C_7H_7O_2$]$^-$, 101.0234 [$C_4H_5O_3$]$^-$	6″-*O*-*trans*-feruloylgenpin gentiobioside [31]
I25	13.08	593.1884 [M–H]$^-$	$C_{28}H_{33}O_{14}$	593.1870	2.4	367.1034 [sinapoyl + Glc-H_2O-H]$^-$, 225.0756 [M-sinapoyl-Glc + H_2O-H]$^-$, 223.0603 [sinapoyl-H]$^-$, 205.0500 [sinapoyl-H_2O-H]$^-$, 190.0265 [M-sinapoyl-Glc-2H_2O-H]$^-$, 123.0443 [$C_7H_7O_2$]$^-$, 101.0237 [$C_4H_5O_3$]$^-$	6′-*O*-*trans*-sinapoylgeniposide [26]
I26	13.20	533.1660 [M–H]$^-$	$C_{26}H_{29}O_{12}$	533.1659	0.2	307.0828 [coumaroyl + Glc-H_2O-H]$^-$, 225.0751 [M-coumaroyl-Glc + H_2O-H]$^-$, 190.0265 [M-coumaroyl-Glc-2H_2O-H]$^-$, 163.0390 [coumaroyl-H]$^-$, 145.0283 [coumaroyl-H_2O-H]$^-$, 123.0440 [$C_7H_7O_2$]$^-$, 101.0231 [$C_4H_5O_3$]$^-$	6′-*O*-*trans*-*p*-coumaroylgeniposide [30]
I27	16.28	725.2306 [M–H + HCOOH]$^-$	$C_{33}H_{41}O_{18}$	725.2293	1.8	679.2242 [M–H]$^-$, 531.1759 [M-cinnamoyl -H]$^-$, 225.0763 [M-cinnamoy-gentiobiosyl + H_2O-H]$^-$, 147.0442 [cinnamoyl-H]$^-$, 123.0443 [$C_7H_7O_2$]$^-$, 101.0236 [$C_4H_5O_3$]$^-$	6″-*O*-*trans*-*p*-cinnamoylgenpin gentiobioside [30]
I28	17.18	593.1859 [M–H]$^-$	$C_{28}H_{33}O_{14}$	593.1870	− 1.9	413.1238 [M-Glc-H_2O-H] $^-$, 207.0653 [M-sinapoy-Glc + H_2O-H]$^-$, 223.0606 [sinapoyl-H] $^-$, 205.0496 [sinapoyl-H_2O-H]$^-$, 123.0445 [$C_7H_7O_2$]$^-$, 101.0234 [$C_4H_5O_3$]$^-$	10-*O*-*trans*-sinapoylgeniposide [28]
C1*	12.30	1021.3787 [M–H + HCOOH] $^-$	$C_{45}H_{65}O_{26}$	1021.3764	2.3	975.3720 [M–H]$^-$, 651.2664 [M-gentiobiosyl-H]$^-$, 327.1602 [M-2gentiobiosyl-H]$^-$, 283.1700 [M-2gentiobiosyl-CO_2-H]$^-$, 239.1799 [M-2gentiobiosyl-2CO_2-H]$^-$	Crocetin-digentiobioside ester (Crocin-1) [33]
C2*	14.10	859.3254 [M–H + HCOOH] $^-$	$C_{39}H_{55}O_{21}$	859.3236	1.8	813.3189 [M–H]$^-$, 651.2653 [M-Glc-H]$^-$, 489.2111 [M-gentiobiosyl-H]$^-$, 327.1594 [M-Glc-gentiobiosyl-H]$^-$, 283.1792 [M-Glc-gentiobiosyl-CO_2-H]$^-$, 239.1790 [M-Glc-gentiobiosyl-2CO_2-H]$^-$	Crocetin gentiobioside monoglucoside ester (Crocin-2) [33]
C3*	16.07	489.2127 [M–H] $^-$	$C_{26}H_{33}O_9$	489.2125	0.4	327.1594 [M-Glc-H]$^-$, 283.1700 [M-Glc-CO_2-H] $^-$, 239.1799 [M-Glc-2CO_2-H]$^-$	Crocetin-monoglucoside ester (Crocin-4) [33]

Table 2 (continued)

Peak	t_R (min)	Measured (*m/z*)	formula	Thoretical	Error (ppm)	Fragmentation ions (*m/z*)	Compound identification
C4	16.67	1021.3793 $[M–H+HCOOH]^-$	$C_{45}H_{65}O_{26}$	1021.3764	2.8	975.3716 $[M–H]^-$, 813.3183 [M-Glc-H] $^-$, 651.2650 [M-2Glc-H]$^-$, 327.1596 [M-Glc-neapolitanosyl-H] $^-$, 283.1694 [M-Glc-neapolitanosyl-CO_2-H] $^-$, 239.1799 [M-Glc-neapolitanosyl-2CO_2-H] $^-$,	*Trans*-crocetin (*β*-D-neapolitanosyl)-(*β*-D-glucosyl) ester [32]
C5	16.76	1181.4347 $[M–H]^-$	$C_{55}H_{73}O_{28}$	1181.4288	1.3	857.3232 [M-gentiobiosyl-H]$^-$, 651.2656 [M-gentiobiosyl-sinapoyl-H]$^-$, 529.1556 [gentiobiosyl + sinapoyl-H]$^-$, 327.1593 [M-2gentiobiosyl-sinapoyl-H]$^-$, 223.0603 [sinapoyl + H_2O-H]$^-$, 205.0499 [sinapoyl-H]$^-$	Neocrocin G [15]
C6	17.01	1021.3784 $[M–H+HCOOH]^-$	$C_{45}H_{65}O_{26}$	1021.3764	2.0	975.3726 [M–H]$^-$, 813.3113 [M-Glc-H]$^-$, 651.2659 [M-2Glc-H]$^-$, 327.1595 [M-Glc-neapolitanosyl-H]$^-$, 283.1692 [M-Glc-neapolitanosyl-CO_2-H]$^-$, 239.1802 [M-Glc-neapolitanosyl-2CO_2-H]$^-$	*Cis*-crocetin (*β*-D-neapolitanosyl)-(*β*-D-glucosyl) ester [32]
C7	18.09	987.3511 $[M–H]^-$	$C_{48}H_{59}O_{22}$	987.3498	1.3	825.3189 [M-Glc-H]$^-$, 651.2668 [M-caffeoyl-$C_7H_9O_5$-H]$^-$, 501.2115 [M-gentiobiosyl-caffeoyl-H]$^-$, 327.1601 [M-gentiobiosyl-caffeoyl-$C_7H_9O_5$-H]$^-$, 283.1702 [M-gentiobiosyl-caffeoyl-$C_7H_9O_5$-CO_2-H]$^-$, 239.1801 [M-gentiobiosyl-caffeoyl-$C_7H_{11}O_5$-2CO_2-H]$^-$	Neocrocin C [15]
C8	18.28	987.3515 $[M–H]^-$	$C_{48}H_{59}O_{22}$	987.3498	1.7	825.3206 [M-Glc-H]$^-$, 651.2662 [M-caffeoyl-$C_7H_{11}O_5$-H]$^-$, 501.2128 [M-gentiobiosyl-caffeoyl-H]$^-$, 327.1595 [M-gentiobiosyl-caffeoyl-$C_7H_{11}O_5$ + H_2O-H]$^-$, 283.1701 [M-gentiobiosyl-caffeoyl-$C_7H_{11}O_5$-CO_2 + H_2O-H]$^-$, 239.1805 [M-gentiobiosyl-caffeoyl-$C_7H_{11}O_5$-2CO_2 + H_2O-H]$^-$	Neocrocin B [15]
C9	18.46	697.2731 $[M–H+HCOOH]^-$	$C_{33}H_{45}O_{16}$	697.2708	3.3	651.2669 [M–H]$^-$, 489.2111 [M-Glc-H]$^-$, 327.1602 [M-2Glc -H]$^-$, 283.1701 [M-2Glc-CO_2-H]$^-$, 239.1799 [M-2Glc-2CO_2-H]$^-$	Crocetin-diglucoside ester [33]
C10	18.68	1021.3790 $[M–H+HCOOH]^-$	$C_{45}H_{65}O_{26}$	1021.3764	2.5	975.3737 [M–H]$^-$, 651.2653 [M-gentiobiosyl-H]$^-$, 327.1596 [M-2gentiobiosyl-H]$^-$, 283.1696 [M-2gentiobiosyl-CO_2-H]$^-$, 239.1796 [M-2gentiobiosyl-2CO_2-H]$^-$	*Cis*-crocin 1 (13*Z*-Crocetin-digentiobioside ester) [32]
C11	20.98	987.3533 $[M–H]^-$	$C_{48}H_{59}O_{22}$	987.3498	3.5	825.3221 [M-Glc-H]$^-$, 651.2711 [M-caffeoyl-$C_7H_9O_5$-H]$^-$, 501.2136 [M-gentiobiosyl-caffeoyl-H]$^-$, 327.1591 [M-gentiobiosyl-caffeoyl-$C_7H_9O_5$-H]$^-$, 283.1685 [M-gentiobiosyl-caffeoyl-$C_7H_9O_5$-CO_2-H]$^-$, 239.1770 [M-gentiobiosyl-caffeoyl-$C_7H_9O_5$ -2CO_2-H]$^-$	Neocrocin E [15]
C12	21.43	857.3237 $[M–H]^-$	$C_{43}H_{53}O_{18}$	857.3232	0.6	651.2654 [M-sinapoyl-H]$^-$, 327.1595 [M-gentiobiosyl-sinapoyl-H]$^-$, 529.1566 [gentiobiosyl + sinapoyl-H]$^-$, 223.0605 [sinapoyl + H_2O-H]$^-$, 205.0496 [sinapoyl-H]$^-$	Neocrocin F [15]

Table 2 (continued)

Peak	t_R (min)	Measured (*m/z*)	formula	Thoretical	Error (ppm)	Fragmentation ions (*m/z*)	Compound identification
C13	21.94	987.3524 $[M–H]^-$	$C_{48}H_{59}O_{22}$	987.3498	2.6	825.3194 $[M\text{-}Glc\text{-}H]^-$, 651.2641 $[M\text{-}caffeoyl\text{-}C_7H_9O_5\text{-}H]^-$, 501.2136 [M-gentiobiosyl-caffeoyl-H]$^-$, 327.1584[M-gentiobiosyl-caffeoyl-$C_7H_9O_5$-H]$^-$, 283.1688 [M-gentiobiosyl-caffeoyl-$C_7H_9O_5$-CO_2-H]$^-$, 239.1791 [M-gentiobiosyl-caffeoyl-$C_7H_9O_5$-2CO_2-H]$^-$	Neocrocin D [15]
C14*	22.06	651.2647 $[M–H]^-$	$C_{32}H_{43}O_{14}$	651.2653	− 0.9	327.1589 [M-gentiobiosyl-H]$^-$, 283.1693 [M-gentiobiosyl-CO_2-H]$^-$, 239.1794 [M-gentiobiosyl-2CO_2-H]$^-$	Crocetin-monogentiobioside ester (Crocin-3) [33]
C15	22.09	651.2659 $[M–H]^-$	$C_{32}H_{43}O_{14}$	651.2653	0.9	327.1589 [M-gentiobiosyl -H$^-$, 283.1693 [M-gentiobiosyl-CO_2-H]$^-$, 239.1794 [M-gentiobiosyl-2CO_2-H]$^-$	13-*Cis*-crocetin-8-*O*-*β*-D-gentiobioside [15]
C16	22.23	651.2653 $[M–H]^-$	$C_{32}H_{43}O_{14}$	651.2653	0	327.1593 [M-gentiobiosyl-H]$^-$, 283.1691 [M-gentiobiosyl-CO_2-H]$^-$, 239.1790 [M-gentiobiosyl-2CO_2-H]$^-$	13′-*Cis*-crocetin-8-*O*-*β*-D-gentiobioside [15]
C17	22.45	859.3272 $[M–H+HCOOH]^-$	$C_{39}H_{55}O_{21}$	859.3236	4.2	813.3204 [M–H]$^-$, 651.2649 [M-Glc-H]$^-$, 489.2155 [M-gentiobiosyl-H]$^-$, 327.1598 [M-Glc-gentiobiosyl-H] $^-$, 283.1691 [M-Glc-gentiobiosyl-CO_2-H] $^-$, 239.1794 [M-Glc-gentiobiosyl-2CO_2-H] $^-$	13-*Cis*-crocetin-8-*O*-*β*-D-gentiobiosyl-8’-*O*-*β*-D-glucopyranoside [32]
C18	22.54	859.3248 $[M–H+HCOOH]^-$	$C_{39}H_{55}O_{21}$	859.3236	1.4	813.3206 [M–H]$^-$, 651.2656 [M-Glc-H]$^-$, 489.2137 [M-gentiobiosyl-H] $^-$, 327.1591 [M-Glc-gentiobiosyl-H] $^-$, 283.1692 [M-Glc-gentiobiosyl-CO_2-H]$^-$, 239.1789 [M-Glc-gentiobiosyl-2CO_2-H]$^-$,	13-*Cis*-crocetin-8-*O*-*β*-D-glucopyranosyl-8’-*O*-*β*-D-gentiobioside [15]
C19	24.02	833.3961 $[M–H+HCOOH]^-$	$C_{43}H_{61}O_{16}$	833.3960	0.1	787.3958 [M–H]$^-$, 463.2833 [M-gentiobiosyl-H]$^-$, 419.2945 [M-gentiobiosyl-CO_2-H]$^-$,	Gardecin [53]
Q1*	3.01	353.0870 $[M–H]^-$	$C_{16}H_{17}O_9$	353.0873	− 0.8	191.0554 [M-caffeoyl + H_2O-H]$^-$, 179.0342 [caffeoyl-H]$^-$, 173.0446 [M-caffeoyl-H]$^-$, 135.0449 [caffeoyl-CO_2-H]$^-$	Neochlorogenic acid [37]
Q2*	4.25	353.0878 $[M–H]^-$	$C_{16}H_{17}O_{91}$	353.0873	1.4	191.0555 [M-caffeoyl + H_2O-H]$^-$, 179.0340 [caffeoyl-H]$^-$, 173.0446 [M-caffeoyl-H]$^-$, 135.0446 [caffeoyl-CO_2-H]$^-$	Chlorogenic acid [37]
Q3*	4.65	353.0876 $[M–H]^-$	$C_{16}H_{17}O_9$	353.0873	2.7	191.0556 [M-caffeoyl + H_2O-H]$^-$, 179.0344 [caffeoyl + H_2O-H]$^-$, 173.0452 [M-caffeoyl-H]$^-$, 135.0444 [caffeoyl-CO_2-H]$^-$	Cryptochlorogenic acid [37]
Q4*	9.69	515.1186 $[M–H]^-$	$C_{25}H_{23}O_{12}$	515.1190	-0.8	353.0880 [M-caffeoyl + H_2O-H]$^-$, 191.0554 [M-2caffeoyl + 2H_2O-H]$^-$, 179.0347 [caffeoyl-H]$^-$, 173.0450 [M-2caffeoyl-H]$^-$, 135.0448 [caffeoyl-CO_2-H]$^-$	Isochlorogenic acid B (3,4-Dicaffeoylquinic acid) [37]
Q5*	9.90	515.1187 $[M–H]^-$	$C_{25}H_{23}O_{12}$	515.1190	− 0.6	353.0879 [M-caffeoyl + H_2O-H]$^-$, 191.0553 [M-2caffeoyl + 2H_2O-H]$^-$, 179.0344 [caffeoyl-H]$^-$, 173.0450 [M-2caffeoyl-H]$^-$, 135.0442 [caffeoyl-CO_2-H]$^-$	Isochlorogenic acid A (3,5-Dicaffeoylquinic acid) [54]
Q6*	10.99	515.1193 $[M–H]^-$	$C_{25}H_{23}O_{12}$	515.1190	0.6	353.0894 [M-caffeoyl + H_2O-H]$^-$, 191.0550 [M-2caffeoyl + 2H_2O-H]$^-$, 179.0341 [caffeoyl-H]$^-$, 173.0446 [M-2caffeoyl-H]$^-$, 135.0442 [caffeoyl-CO_2-H]$^-$	Isochlorogenic acid C (4,5-Dicaffeoylquinic acid) [54]

Table 2 (continued)

Peak	t_R (min)	Measured (*m/z*)	formula	Thoretical	Error (ppm)	Fragmentation ions (*m/z*)	Compound identification
Q7	11.62	659.1613 $[M–H]^-$	$C_{31}H_{31}O_{16}$	659.1612	0.2	497.1302 [M-caffeoyl + H_2O-H]$^-$, 353.0869 [M-2caffeoyl + H_2O-H]$^-$ 335.0800 [M-2caffeoyl + $2H_2O$-H]$^-$, 191.0560 [M-2caffeoyl + H_2O-$C_6H_9O_4$-H]$^-$, 179.0345 [caffeoyl-H]$^-$, 173.0453 [M-2caffeoyl-$C_6H_9O_4$-H]$^-$, 161.0437 $[C_6H_9O_5]^-$	3,4-Dicaffeoyl-5-(3-hydroxy-3-methylglutaroyl)quinic acid /3,5-Di-*O*-caffeoyl-4-*O*-(3-hydroxy-3-methyl) glutaroyl-quinic acid [36]
Q8	11.93	559.1450 $[M–H]^-$	$C_{27}H_{27}O_{13}$	559.1452	− 0.4	397.1126 [M-caffeoyl + H_2O-H]$^-$, 367.1043 [caffeoyl-sinapoyl-2H_2O-H]$^-$, 335.0776 [M-sinapoyl-H]$^-$, 223.0605 [sinapoyl-H]$^-$, 205.0497 [sinapoyl-H_2O-H]$^-$, 179.0344 [caffeoyl-H]$^-$, 173.0441 [M-caffeoyl-sinapoyl + H_2O-H]$^-$	4-*O*-sinapoyl-5-*O*-caffeoylquinic acid [28]
Q9	12.59	559.1451 $[M–H]^-$	$C_{27}H_{27}O_{13}$	559.1451	− 0.2	397.1123 [M-caffeoyl + H_2O -H] $^-$, 223.0600 [sinapoyl-H]$^-$, 205.0497 [sinapoyl-H_2O-H]$^-$, 179.0335 [caffeoyl-H]$^-$, 173.0447 [M-caffeoyl-sinapoyl + H_2O-H]$^-$	3-*O*-caffeoyl-4-sinapoylquinic acid [35]
Q10	12.94	529.1351 $[M–H]^-$	$C_{26}H_{25}O_{12}$	529.1346	0.9	367.1023 [M-caffeoyl + H_2O-H]$^-$, 205.0712 [M-2caffeoyl + $2H_2O$-H]$^-$, 179.0348 [caffeoyl-H]$^-$, 173.0445 [M-2caffeoyl + H_2O-CO_2-H] $^-$	3,4-Di-*O*-caffeoylquinic methyl ester/4,5-Di-*O*-caffeoylquinic methyl ester[28]
Q11	15.07	573.1603 $[M–H]^-$	$C_{28}H_{29}O_{13}$	573.1608	− 0.9	367.1042 [M-sinapoyl + H_2O-H] $^-$, 223.0602 [sinapoyl-H]$^-$, 205.0712 [M-sinapoyl-caffeoyl + $2H_2O$-H]$^-$, 179.0335 [caffeoyl-H]$^-$, 173.0447 [M-sinapoyl-caffeoyl + H_2O-H]$^-$	Methyl 5-*O*-caffeoyl-sinapoylquinate/Methyl 5-*O*-caffeoyl-4-*O*-sinapoylquinate [54]
F1	8.01	609.1458 $[M–H]^-$	$C_{27}H_{31}O_{16}$	611.1612	− 1.5	300.0266 [M-Rha-Glc-H]$^{-\cdot}$, 271.0241[M-Rha-Glc-HCO-H]$^-$, 255.0286 [M-Rha-Glc-CO–OH- H]$^-$, 178.9973 $[C_8H_3O_5]^-$, 151.0031 $[C_7H_3O_4]^-$	Isorutin [38]
F2*	8.25	609.1463 $[M–H]^-$	$C_{27}H_{29}O_{16}$	609.1456	1.1	301.0273 [M-Rha-Glc-H]$^-$, 271.0244 [M-Rha-Glc-HCO-H]$^-$, 255.0293 [M-Rha-Glc-CO–OH-H]$^-$, 178.9979 $[C_8H_3O_5]^-$, 151.0025 $[C_7H_3O_4]^-$	Rutin [40]
F3	8.53	463.0887 $[M–H]^-$	$C_{21}H_{19}O_{12}$	463.0877	− 0.6	300.0276 [M-Glc-H]$^{-\cdot}$, 271.0247 [M-Glc-CO + H]$^-$, 255.0305 [M-Glc-CO_2-H]$^-$, 151.0024 $[C_7H_3O_4]^-$	Isoquercetin (Quercetin3-*O*-*β*-D-glucopyranoside) [26, 39]
F4	8.90	593.1508 $[M–H]^-$	$C_{27}H_{29}O_{15}$	593.1506	0.3	285.0392 [M-Rha-Glc-H]$^-$, 284.0316 [M-Rha-Glc-H]$^{-\cdot}$ 255.0300 [M-Rha-Glc-CO–H]$^-$	Nicotiflorin (Kaempferol-3-*O*-rutinoside) [40]
F5	9.57	593.1515 $[M–H]^-$	$C_{27}H_{29}O_{15}$	593.1506	1.5	285.0387 [M-Rha-Glc-H]$^-$, 284.0325 [M-Rha-Glc-H]$^{-\cdot}$ 255.0290 [M-Rha-Glc-CO–H]$^-$	Kaempferol-3-*O*-[2-*O*-(*β*-D- glucosyl)-*α*-L-rhamnoside [39]
1	2.17	407.1546 $[M–H+HCOOH]^-$	$C_{17}H_{27}O_{11}$	407.1553	− 1.7	361.1496 [M–H]$^-$, 181.0859 [M-Glc-H_2O-H]$^-$, 137.0964 [M-Glc-H_2O-CO_2-H]$^-$	Jasminoside F [55]
2	3.21	391.1609 $[M–H+HCOOH]^-$	$C_{17}H_{27}O_{10}$	391.1604	1.3	345.1552 [M–H]$^-$, 179.0554 [Glc-H]$^-$, 165.0915 [M-Glc-H_2O-H]$^-$, 151.0759 [M-Glc-H_2O-CH_2-H]$^-$	Jasminoside B [55]
3	5.41	385.1134 $[M–H]^-$	$C_{17}H_{21}O_{10}$	358.1135	− 0.3	223.0602 [sinapoyl-H] $^-$, 205.0499 [sinapoyl-H_2O-H]$^-$, 193.0503 [M-Glc-OCH_3-H]$^-$, 163.0396 [M-Glc-2OCH_3-H]$^-$	1-Sinapoyl-*β*-D-glucopyranoside [40]
4	5.47	537.2191 $[M–H+HCOOH]^-$	$C_{23}H_{37}O_{14}$	537.2183	2.0	491.2129 [M–H]$^-$, 323.0974 [2Glc-H]$^-$, 167.1071 [M-2Glc-H]$^-$	Jasminoside P [56]

Table 2 (continued)

Peak	t_R (min)	Measured (*m/z*)	formula	Thoretical	Error (ppm)	Fragmentation ions (*m/z*)	Compound identification
5	6.84	183.1021 $[M–H]^-$	$C_{10}H_{15}O_3$	183.1021	0	165.0924 $[M–H_2O-H]^-$, 151.0765 $[M\text{-}OH\text{-}CH_3]^-$, 139.1121 $[M\text{-}CO_2\text{-}H]^-$	Rehmapicrogenin [57]
6	6.90	503.1725 $[M–H]^-$	$C_{22}H_{31}O_{13}$	503.1765	− 3.0	385.1135 [sinapoyl + Glc-H_2O-H]$^-$, 223.0600 [sinapoyl-H]$^-$, 205.0490 [sinapoyl-H_2O-H]$^-$, 193.0500 [sinapoyl-OCH_3-H]$^-$, 161.0447 [M-sinapoyl-$C_5H_{10}O_4$-H_2O-H]$^-$, 135.0659 $[C_5H_{10}O_4]^-$	2-Methyl-L-erythritol-4-*O*-(6-*O*-trans-sinapoyl)-*β*-D-glucopyranoside/2-Methyl-L-erythritol-1-*O*-(6-*O*-*trans*-sinapoyl)-*β*-D-glucopyranoside[57]
7	7.28	503.1761 $[M–H]^-$	$C_{22}H_{31}O_{13}$	503.1765	− 0.4	385.1137 [sinapoyl + Glc-H_2O-H]$^-$, 223.0612 [sinapoyl-H]$^-$, 205.0492 [sinapoyl-H_2O-H]$^-$, 193.0500 [sinapoyl-OCH_3-H]$^-$, 161.0453 [M-sinapoyl-$C_5H_{10}O_4$-H_2O-H]$^-$, 135.0652 $[C_5H_{10}O_4]^-$	2-Methyl-L-erythritol-4-*O*-(6-*O*-*trans*-sinapoyl)-*β*-D-glucopyranoside/2-Methyl-L-erythritol-1-*O*-(6-*O*-*trans*-sinapoyl)-*β*-D-glucopyranoside [57]
8	7.62	627.2292 $[M–H\text{-}HCOOH]^-$	$C_{29}H_{39}O_{15}$	627.2289	0.5	581.2231 $[M–H]^-$, 419.1689 [M-Glc-H]$^-$, 373.1285 [M-Glc-CH_3-CH_2OH-H]$^-$ 179.0543 $[C_6H_{11}O_6]^-$, 153.0543 $[C_8H_9O_3]^-$	Lyoniresinol-9-*O*-*β*-D-glucopyranoside [58]
9	10.12	535.2027 $[M–H+HCOOH]^-$	$C_{23}H_{35}O_{14}$	535.2027	0	489.1971 $[M–H]^-$, 323.0986 [2Glc-H]$^-$, 165.0911 [M-2Glc-H]$^-$, 121.1021 [M-2Glc-CO_2-H]$^-$	Jasminoside R [29]
10	12.21	551.2126 $[M–H]^-$	$C_{27}H_{35}O_{12}$	551.2129	− 0.5	385.1123 [sinapoyl + Glc-H_2O-H]$^-$, 223.0603 [sinapoyl -H]$^-$, 205.0499 [sinapoyl-H_2O-H]$^-$	6′-*O*-*trans* sinapoy-l jasminoside B/6′-*O*-*trans*-sinapoyljasminoside L
11	12.48	507.2072 $[M–H\text{-}HCOOH]^-$	$C_{22}H_{35}O_{13}$	507.2078	− 1.2	461.2036 $[M–H]^-$, 167.1069 [M-Glc-Xyl-H]$^-$, 125.0605 $[C_7H_9O_2]^-$	Jasminoside T [56]
12	12.98	551.2145$[M–H]^-$	$C_{27}H_{35}O_{12}$	551.2129	2.9	385.1134 [sinapoyl + Glc-H_2O-H]$^-$, 223.0609 [sinapoyl-H]$^-$, 205.0502 [sinapoyl-H_2O-H]$^-$ 161.0443 [M-sinapoyl-$C_{10}H_{15}O_2$-H]$^-$	6′-*O*-*trans*-sinapoyl-jasminoside B/6′-*O*-*trans*-sinapoyljasminoside L [56]
13	15.21	591.1719 $[M–H]^-$	$C_{28}H_{31}O_{14}$	591.1714	0.7	385.1134 [M-$C_{10}H_{14}$O-H]$^-$, 223.0595 [sinapoyl-H]$^-$, 205.0495 [sinapoyl-H_2O-H]$^-$	6-Di-*O*-*E*-sinapoyl-glucopyranose [40]
14	16.38	535.2181$[M–H]^-$	$C_{27}H_{35}O_{11}$	535.2179	0.4	367.1019 [sinapoyl + Glc-H_2O-H]$^-$, 325.0916 [sinapoyl + Glc-2OCH_3-H_2O-H]$^-$, 223.0604 [sinapoyl-H]$^-$, 205.0498 [sinapoyl-H_2O-H]$^-$	6′-*O*-*trans*-sinapoyl-jasminoside A [59]
15	20.99	503.3382 $[M–H]^-$	$C_{30}H_{48}O_6$	503.3373	1.8	485.3288 $[M–H_2O-H]^-$, 455.3201[M-CH_2OH-H_2O-2H]$^-$, 263.1660 $[C_{15}H_{20}O_3]^-$	Myrianthic acid [60]
16	22.74	533.3482 $[M–H+HCOOH]^-$	$C_{31}H_{49}O_7$	533.3478	0.7	487.3427 $[M–H]^-$, 455.3201 [M-CH_2OH-H_2O-H]$^-$, 239.2033$[C_{14}H_{23}O_3]^-$,	Rotundic acid/Barbinervic acid [60]
17	23.74	503.3372$[M–H]^-$	$C_{30}H_{48}O_6$	503.3373	− 0.2	485.3253 $[M–H_2O-H]^-$, 473.2826 [M-CH_2OH-H]$^-$, 263.1676 $[C_{15}H_{20}O_3]^-$	Clethric acid [60]

*Identified using the reference standards

previously, C5 was deduced as Neocrocin G. The fragment ion at *m/z* 651.2656 was supposed to be caused by the substituent group of D in Fig. 6. C12 produced an $[M–H]^-$ ion at *m/z* 857.3237 and generated the same characteristic fragment ions *m/z* 651.2654, *m/z* 327.1595, *m/z* 529.1556, and *m/z* 223.0603 with C5 in the MS/MS spectrum. Going through the pigments isolated from *G. jasminoides* previously [15], C12 was annotated as Neocrocin F.

C19 found an $[M–H+HCOOH]^-$ and $[M–H]^-$ ions at *m/z* 833.3961 and *m/z* 787.3958 in the full mass spectrum. The fragment ions at *m/z* 463.2833 and *m/z* 419.2945 were suggested by the loss of one gentiobiose and one CO_2 (44 Da) successively. In the MS/MS analysis, there

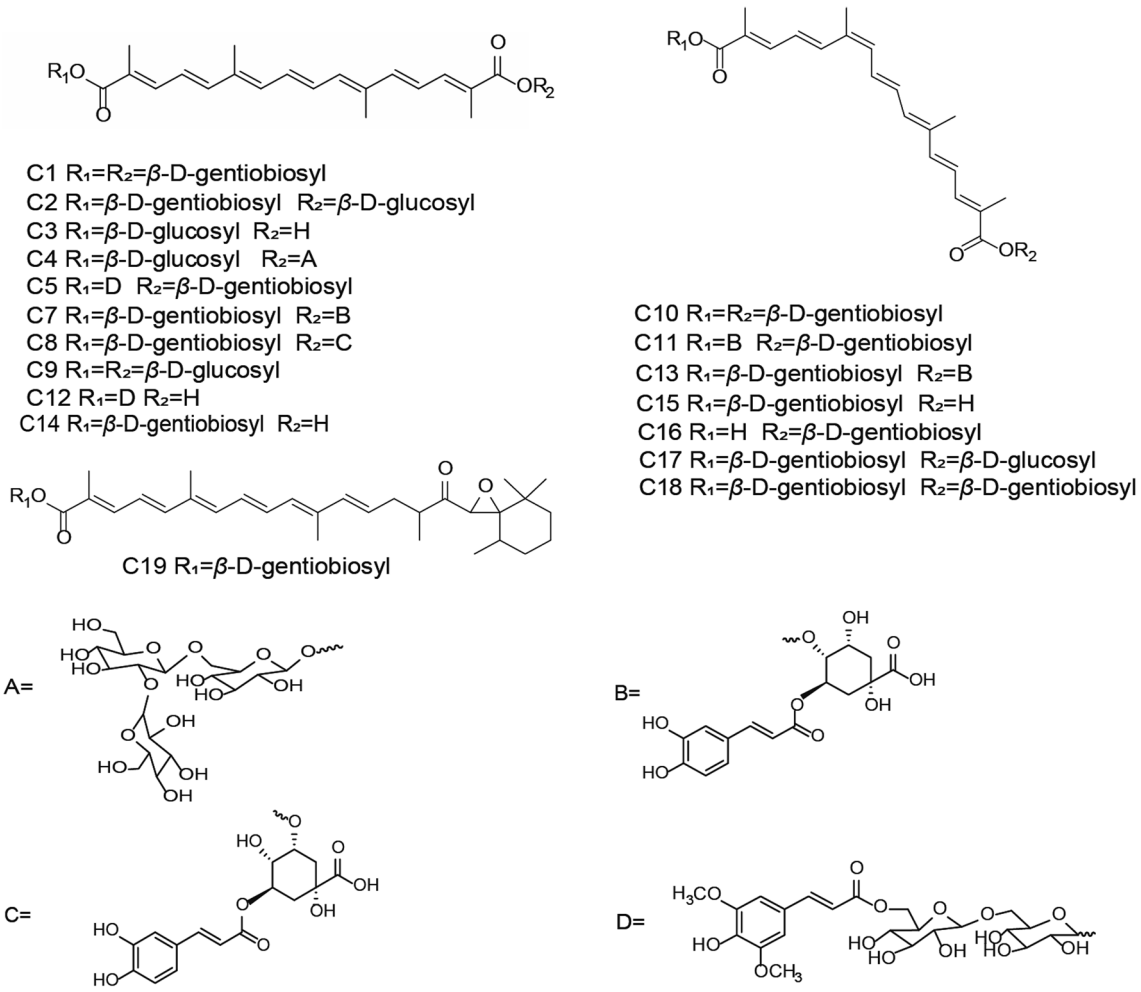


Fig. 6 The structure of crocins has been identified or tentatively deduced

have not characteristic ions similar to other pigments compounds. So, referring to the literature reported previously [34], C19 was tentatively assigned as gardecin.

Organic acids

The organic acids mostly characterized in *G. jasminoides* were quinic acids. Quinic acids are commonly characteristic with 1-hydroxy-hexahydro-gallic acid as the basic parent nucleus, and its C3, C4, C5 positions are often connected with caffeoyl, sinapoyl, and so on. A total of 13 organic acids were identified or tentatively characterized from *G. jasminoides*, 6 of them were identified by comparing with the reference standards.

Compounds Q1 and Q2 were the isomeric neochlorogenic acid and chlorogenic acid, whereas Q3 was assigned as cryptochlorogenic acid. All of these compounds showed the expected spectral data and matched those obtained for reference standards. The structures of these compounds belong to the same type of mono-caffeoylquinic (MCQA) with the only difference of the connected position of caffeoyl connected with quinic acid. Q1, Q2, and Q3 showed the same parental molecular ion $[M–H]^-$ at *m/z* 353.0870 ($C_{16}H_{17}O_9$). The characteristic fragment ions at *m/z* 191.0554 and *m/z* 173.0446 were generated by the losses of the caffeoyl residue and H_2O continually. Simultaneously, fragment ions at the *m/z* 179.0342 and *m/z* 135.0439 were caused by the caffeoyl residue ionized by the patterns of [caffeic acid-H]$^-$ and [caffeic acid-H-CO_2]$^-$, represented in Fig. 5C below.

Compound Q4, Q5, and Q6 showed the same $[M–H]^-$ ion at *m/z* 515.1186 ($C_{25}H_{23}O_{12}$). By comparing with the reference standards, these compounds were identified as isochlorogenic acid B (3,4-dicaffeoylquinic acid), isochlorogenic acid A (3,5-dicaffeoyl-quinic acid), and isochlorogenic acid C (4,5-dicaffeoylquinic acid). Due to the two molecules of caffeoyl attached to two positions of quinic acid, Q4, Q5, and Q6 belonged to dicaffeoylquinic acids (DCQA). Thus, there was a diagnostic fragment ion at *m/z* 353 which was produced by the loss of a caffeoyl residue, and other

characteristic ions at *m/z* 191.0554, *m/z* 179.0343, *m/z* 173.0446, and *m/z* 135.0448 were produced in the same way as that in Q1.

Compound Q8 and Q9 were tentatively deduced as isomers which gave the same [M–H]- ion at *m/z* 559.1450 ($C_{27}H_{27}O_{13}$). In their MS^2 spectra, there were characteristic fragment ions for caffeoyl residue and sinapoyl residue at *m/z* 179.0343, *m/z* 161.0232, *m/z* 223.0612, and *m/z* 205.0506. Besides, there was a fragment ion at *m/z* 173.0447 so that Q8 and Q9 can be assigned to quinic acid derivatives. Referring to the reported quinic acid derivatives [28, 35] isolated from *G. jasminoides*, Q8 and Q9 were tentatively deduced as 4-*O*-sinapoyl-5-*O*-caffeoylquinic acid or 3-*O*-caffeoyl-4-sinapoylquinic acid. Consequently, the fragment ion at *m/z* 397.1126 was caused by the loss of caffeoyl residue from the molecule. Besides, there was a strong diagnostic fragment ion at *m/z* 335.0776 only can found in Q8 which suggested the base peak was produced by losing sinapoyl residue directly from the molecule. Finally, Q8 and Q9 were deduced as 4-*O*-sinapoyl-5-*O*-caffeoylquinic acid and 3-*O*-caffeoyl-4-sinapoylquinic acid, respectively.

Q7 exhibited an $[M–H]^-$ ion at *m/z* 659.1613 ($C_{31}H_{31}O_{16}$) in the full mass spectrum. In the MS/MS spectrum, there were characteristic fragment ions at *m/z* 191.0560, *m/z* 179.0345, *m/z* 173.0453, and *m/z* 135.0442 which indicated the structure of quinic acid derivatives. The fragment ions at *m/z* 497.1302 and *m/z* 335.0800 were created by the losses of two molecules of caffeoyl residue successively from the molecule. According to the reported quinic acid derivatives which isolated from *G. jasminoides*, Q7 was tentatively assigned as 3,4-dicaffeoyl-5-(3-hydroxy-3-methylglutaroyl) quinic acid [36] or 3,5-di-*O*-caffeoyl-4-*O*-(3-hydroxy-3-methyl) glutaroylquinic acid [37].

Flavonoids

Flavonoids were mostly reported from the flowers and leaves of *G. jasminoides*. In this paper, combined with literature data and the mass spectrometric data of reference standards, a total of five flavonoids were identified or tentatively deduced. Among them, one structure was confirmed by the comparison to the MS data of the reference substance.

F2 was identified as rutin by comparison with the retention time and MS data of reference standard. In negative ion mode, there was a parental molecular ion at *m/z* 609.1463 ($[M–H]^-$). A series of fragment ions appeared in the MS/MS spectrum and were illustrated briefly in Fig. 5D. F1 and F2 were isomers displaying the same parental ion. Based on the same characteristic fragment ions with F2, combining with the literature, compound F1 was deduced as neoisorutin [38], which has not been reported in *G. jasminoides*.

F4 and F5 both showed an $[M–H]^-$ ion at *m/z* 593.1508 in the full mass spectrum. There were diagnostic fragment ions at *m/z* 285.0392 (*m/z* 284.0316) and *m/z* 255.0397 in their MS^2 spectra which suggested the compounds were kaempferol derivatives. Additionally, referring to the molecular weight, these compounds were supposed to be flavonoid *O*-diglycosides. However, F4 displayed a fragment ion at *m/z* 284.0316 with a higher abundance than *m/z* 285.0392, and F5 exhibited a strong signal at *m/z* 285.0387. According to the literature previously [39], for flavonoid *O*-diglycosides, the relative intensity and specific fragmentation patterns were determined by the sequence of saccharidic parts and the type of sugar residue. In these compounds, compared with the 1 → 6 linkage of saccharidic parts, 1 → 2 linkages of saccharidic parts are beneficial to the formation of radical aglycone ion $[Y_0\text{-}H]^{-\cdot}$ (aglycone expressed in Y_0). Thus, F4 and F5 were tentatively deduced as nicotiflorin [40] and kaempferol 3-*O*-[2-*O*-(*β*-D-glucosyl)-*α*-L-rhamnoside, respectively, by comparing the reported flavonoids isolated from *G. jasminoides*.

F3 displayed an $[M–H]^-$ ion at *m/z* 463.0887. The signals at *m/z* 300.0276, *m/z* 271.0247, *m/z* 255.0305, and *m/z* 151.0024 in the MS^2 spectra were attributable to the quercetin aglycone. The characteristic fragment ion at *m/z* 300.0276 was suggested to the patterns of $[M\text{-}Glc\text{-}H]^{-\cdot}$. With the literature reported previously [39], for flavonoid mono-*O*-glycosides, the glycosylation position of flavanol 3-*O*-glycosides was more likely to generate the radical aglycone ion (300.0276 $[M\text{-}Glc\text{-}H]^{-\cdot}$) than flavanol 7-*O*-glycosides. Therefore, F3 was tentatively annotated as isoquercetin (quercetin3-*O*-*β*-D-glucopyranoside) [26].

Others

In addition to the above-mentioned compounds, there reported monoterpenes, triterpenes, glycosides, and lignans in *G. jasminoides*. By similar approaches, miscellaneous compounds were tentatively deduced by the fragment ions shown in Table 2.

Analysis of metabolomic profiling based on the identified or tentatively deduced compounds

To further understand the material differences between the three groups of *G. jasminoides*, 80 compounds were identified or tentatively to avoid the repeatable identities from the software mechanically and can ensure the structure of the biomarkers. The data of corresponding compounds were imported into the SIMCA14.0 from the Progenesis QI software for partial least square discriminant analysis (PLS-DA). As shown in Fig. 7A, different color spots were represented different varieties and cultivars of *G. jasminoides*. When the PLS-DA analysis was carried out, it can be seen that the three groups have a certain degree of dispersion and can be

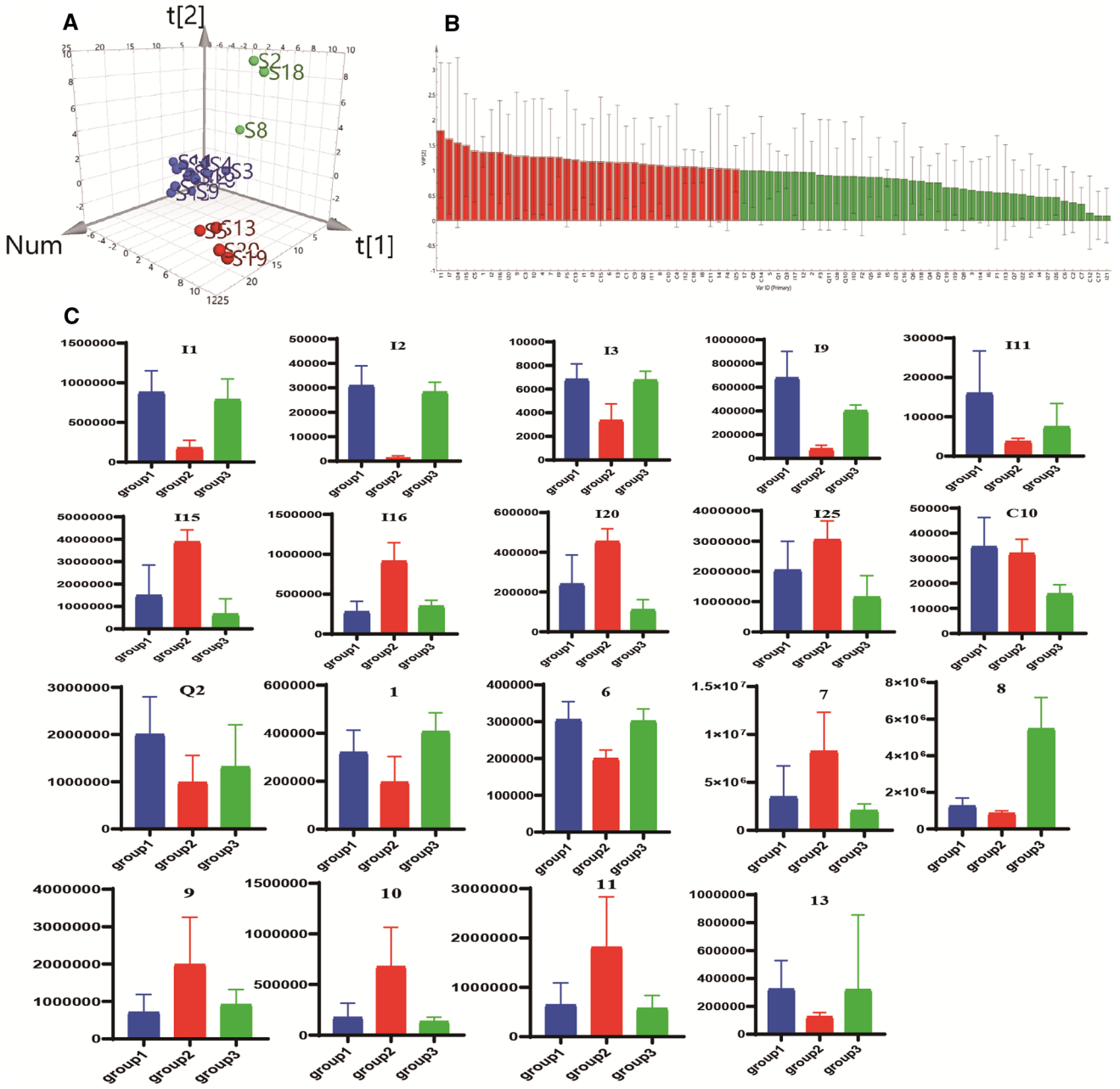


Fig. 7 Targeted analysis of metabolite profiles (metabolite profiles were obtained from 80 compounds in negative ion modes). **A** PLS-DA score scatter plot for *G. jasminoides* samples ($R^2X=0.461$ $R^2Y=0.773$ $Q^2(\text{cum})=0.626$). **B** VIP plot. **C** The relative content of 19 different components. Group 1 represents ZZC1, group 2 represents ZZC2, group 3 represents Shuizhizi. I1: Deacetyl asperulosidic acid, I2: Gardoside, I3: Shanzhiside, I9: Mussaenosidic acid, I11: 7-Deoxygardoside, I15: 6′-*O*-*trans*-sinapoyl gardoside, I16: 6′-*O*-*trans*-*p*-coumaroylgeniposidic acid, I20: 2-*O*-*trans*-3-caffeoylgardoside, I25: 6′-*O*-*trans*-sinapoylgeniposide;C10: Crocetin-diglucoside ester, Q2: Chlorogenic acid, 1: Jasminoside F, 6: Jasminoside R, 7: 6′-*O*-*trans*-sinapoyljasminoside B/L, 8: Jasminoside T, 9: 3-Methyl-L-erythritol-4-*O*-(6-*O*-*trans*-sinapoyl)-*β*-D-glucopyranoside, 10: 2-Methyl-L-erythritol-1-*O*-(6-*O*-*trans*-sinapoyl)-*β*-D-glucopyranoside, 11: 2,6-Di-*O*-*E*-sinapoyl-glucopyranose, 13: Lyoniresinol-9-*O*-*β*-D-glucopyranoside

significantly separated, which was consistent with the results of variable analysis of 8227 metabolite features characterized by QI software. Therefore, it can be explained that the metabolites in grouping *G. jasminoides* were different, and the differences showed a tight relation with the botanical classification and morphological characters.

For the purpose of finding the most contributing variables of the three groups *G. jasminoides*, PLS-DA, and the VIP plot were served. Based on the VIP value graph (Fig. 7B)

obtained by PLS-DA analysis, those variables with VIP > 1.0 are considered as relevant to group discrimination and found 36 metabolites in this range. Additionally, aiming at avoiding false-positive results, parameters were set with max fold change > 1.5 and Anova $P < 0.05$.

As a result, 19 potential biomarkers were discovered suitable for simultaneous differentiation of the 3 groups of *G. jasminoides*, including 9 iridoids compounds, 1 pigment, 1 organic acid, 4 monoterpenoids, 3 glycosides and,1 lignan component. The contents of these 19 metabolites were expressed by the normalized peak area and can be seen in Fig. 7C, displaying the specific differences between 3 groups.

Conclusions

No matter as an edible food providing numerous nutrients or as a medical plant exerting special function, it is inseparable from the plant's metabolites. Moreover, as an herbal medicine, phytochemical composition was also found to be significantly associated with the post-harvest processing. According to the Chinese Pharmacopoeia, the post-harvest processing of Gardenia Frutucs is dry after boiling, dry after steaming and direct dry in the sun. However, the time of specific methods are not clear. Literature have shown that the active constituents in Gardenia Frutucs can be better retained after boiling or steaming and then drying due to the mechanism of killing enzyme and protecting glycoside [41–44]. It has been reported the content of geniposide in Gardenia Frutucs was 2.38% and 5.82%, respectively, after direct drying in the sun and dry after boiling for 15 min [42]. As the time of different post-harvest processing changes, the composition was generally increased and then decreased. Researchers reported changes in the content of geniposide and crocin-I by drying after boiled within 15 min. The content of geniposide was increased from 2.69% at 1 min to 3.86% at 13 min and finally decreased to 3.80% at 15 min. The content of crocin I was increased from 0.52% at 1 min to 0.87% at 8 min and then decreased to 0.70% at 13 min [43]. Studies also found that the low temperature drying has little effect on the content of active the constituents [41]. Thus, to avoid the influence of post-harvest processing on chemical composition, it is necessary to use the same post-harvest processing to compare their profiling of phytochemicals in the fruits of *G. jasminoides*.

Based on reversed-phase UHPLC/ESI-QTOFMS, an integrated analytical strategy for comprehensive profiling of phytochemicals from fruits of *G. jasminoides* was proposed. An accurate data pretreatment was provided by Progenesis QI, so that the metabolites features was thoroughly obtained conveniently. In addition, based on literature searches and analyses of reference compounds, the main secondary metabolites such as iridoids, pigments, organic acids and flavonoids were analyzed as primary target of secondary metabolites. A total of 80 metabolites were identified or tentatively deduced in this study, including 28 iridoids, 19 pigments, 11 organic acids, 5 flavonoids and 17 other compounds. The 3 kinds of fruits all contained these 80 compounds, but their contents and proportional relation were different in different populations. PCA and PLS-DA analysis of the holistic metabolites features and the 80 components showed that there was no close relationship between these components and the producing place, but they grouped according to their cultivar or variety. Further analysis results in 19 components were discovered suitable for simultaneous differentiation of the 3 populations of fruits of *G. jasminoides.*

Combined with non-targeted and targeted data analysis strategies, the proposed analytical strategy was effectively applied to discern differences in the profiles of secondary metabolites in the fruits of two cultivars and one variety of *G. jasminoides*. Unlike the common analytical methods which focus only on limited components, this attempt offers a thoroughly comprehensive view on the complex metabolic profile of *G. jasminoides* fruits and describes a straightforward protocol to catalogue their metabolic diversity contingent on genetic and environmental factors.

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Author contributions XY, X-QL, DZ and W-HF did the LC–MS/MS experiments and MS data analysis, as well as statistical analysis of MS data. Y-HL and CL collected the plant material. XY and CL prepared the manuscript together. CL and Z-MW planned, designed and organized the whole research of this study. All the authors have read and approved the final submitted manuscript.

Declarations

Conflict of interest The authors declare no conflict of interest.

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