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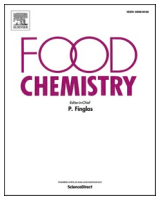

# Compositional diversity of iridoids, phenolic compounds, and crocins in *Gardenia jasminoides* fruits of different varieties

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ABSTRACT

By using UPLC-ESI-MS/MS$^2$ and HPLC-DAD, 62 phytochemicals were characterized from fruits of *Gardenia jasminoides* Ellis (GF) and *G. jasminoides* var. *radicans* Makino (GFV), mainly covering iridoids, crocins, hydroxycinnamic acids, and flavonols. Most identified compounds were found at higher levels in GF than in GFV. A clear compositional diversity was observed between hulls and dehulled fractions of fruits. The dehulled parts had higher levels of iridoids (71–75 *vs.* 61–66 mg/g dry weight, DW, 3 biological replicates applied) and crocins (14–21 *vs.* 10–17 mg/g DW), whereas minor phytochemicals such as hydroxycinnamic acids and flavonols were concentrated in the hulls. The dominant phytochemicals in the dehulled fruits were geniposide (44–46 mg/g DW) and crocin I (11–16 mg/g DW). In contrast, geniposide (20–28 mg/g dry weight, DW) and gardenoside (19–24 mg/g DW) represented half percentage of the total content of phytochemicals identified in the hulls.

## 1. Introduction

*Gardenia jasminoides* Ellis is a woody perennial shrub of *Rubiaceae* family with white jasmine-like flowers and characteristic fragrance (Tsanakas et al., 2013). As a native plant in Southern China (also named as "Zhizi" in China), *G. jasminoides* is first introduced to Britain in the middle of 18th century and has become a common garden ornamental in Europe nowadays (Jarvis et al., 2014).

In Asian countries like China, Korea, and Japan, the fruits of *G. jasminoides* have been used as natural food colorants for centuries (Chen et al., 2020). The phytochemicals in the fruits are the main pigment sources to produce gardenia yellow and gardenia blue and red. Crocins, as a major group of carotenoids in fruits of *G. jasminoides*, are the major components of gardenia yellow. Due to high water solubility of crocins, gardenia yellow is often used in beverages, jelly, and pastries (Yin et al., 2024). Gardenia blue and red are made from genipin glycosides, which are iridoid compounds isolated from *G. jasminoides* fruits (Li et al., 2023). This water-soluble bluish-violet pigment are now commercially applied in the United States and the European Union as colorants in concentrated juices (Neri-Numa et al., 2017). Besides conferring pleasant colors, *G. jasminoides* fruits have been often used to prepare tea in China (Jin et al., 2025). Recent studies have also investigated the potential of *G. jasminoides* fruits to produce novel vegetable oil. The oil made from *G. jasminoides* fruits are rich in geniposide,

*Abbreviations:* DaA, Deacetylasperulosidic acid; **Gdo**, Gardoside; **Sh**, Shanzhiside; **GpA**, Geniposidic acid; **Sc**, Scandoside; **Gde**, Gardenoside; **Ja**, Jasminoside B; **Ix**, Ixoroside; **Gl**, Galioside; **Gpi**, Genipin; **Gpo**, Geniposide; **CaQA**, Caffeoylquinic acid; **FA**, Ferulic acid; **SA**, Sinapic acid; **diCaQA**, Dicaffeoylquinic acid; **Qu**, Quercetin; **Cri**, Crocin; **Crt**, Crocetin; **Gen**, Gentiobioside; **Hex**, Hexoside; **diHex**, di-Hexoside; **Deox**, Deoxyhexoside; **Rut**, Rutinoside; **Glu**, Glucoside; **me-**, Methyl-; **co-**, Coumaroyl-; **si-**, Sinapoyl-; **fe-**, Feruloyl-; **ci-**, Cinnamoyl-; **ac-**, Acetyl-; **hmg-**, Hydroxy-methylglutaroyl-.

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vitamin E, carotenoids, polyphenols, and unsaturated fatty acids, and exhibits high levels of thermal stability and oxidative stability (Cai et al., 2015; Liu et al., 2022).

The bioactive components (iridoids, crocins, and flavonoids, in particular) in the fruits also exhibit protective effects on digestive, nervous, and cardiovascular systems (Chen et al., 2020; Jin et al., 2025). Previous research using *in vitro* assays or *in vivo* rat models has revealed the pharmacological activities of iridoid glycosides (*e.g.*, geniposide, gardenoside, and gardoside) protecting hepatocytes from acetaminophen hepatotoxicity, and attenuating diabetes-associated depression (Sun et al., 2021; Yang et al., 2019). Crocins are effective in treating diabetes by lowering blood glucose, increasing serum insulin levels, and improving diabetes-related symptoms (Zhang et al., 2021). Geniposide and crocins have potent anti-atherogenic activity due to clear inhibition against low density lipoprotein oxidation (Gan et al., 2023). Flavonoids in *G. jasminoides* are also reported extensively as their anti-oxidative, anti-inflammatory, hepatoprotective, and atherosclerosis capacities (Chen et al., 2020).

With a long history of food application and abundance of health-promoting components, the *G. jasminoides* fruits are ideal plant materials in the development of functional foods. Nevertheless, despite the increasing research interest, comprehensive studies on bioactive compounds in *G. jasminoides* fruits are still insufficient. Previous studies have mainly focused on determination of total content of iridoids or crocins using colorimetric assays, and identification of key compounds only (*e.g.*, geniposide, genipin gentiobioside, crocin I, crocin II, et al.) (Chen et al., 2010; Coran et al., 2014; Zhou et al., 2007). A detailed composition of iridoids or crocins is often missing from the studies. Apart from the major phytochemicals, other bioactive components in *G. jasminoides*, such as phenolic compounds, have received relatively little attention. For instance, some research suggests that the health benefits of *G. jasminoides* Ellis fruits are also ascribed to flavonoids (Chen et al., 2023; Debnath et al., 2011); however, the studies on phenolic profiling of *G. jasminoides* fruits are inadequate. A thorough understanding of phytochemical profiling in *G. jasminoides* fruit is critical to ensure its safety as a new food resource and to exploit its food application for different purposes. Furthermore, the efficiency of extraction solvents in recovering various phytochemicals has not been systematically assessed, which also limits the utilization of *G. jasminoides* fruits in the food industry.

To address these limitations, this study performed a structured phytochemical investigation of *G. jasminoides* fruits with particular emphasis on two varieties, which are interchangeably used as sources of pigments and bioactive constituents. Rather than broadly surveying multiple varieties, this work conducts a controlled comparison between *G. jasminoides* Ellis and *G. jasminoides* var. *radicans* Makino and their fruit tissues (*i.e.*, hulls *vs.* pulps), enabling targeted evaluation of tissue-associated compositional variation. Comprehensive metabolite profiling was achieved through integrated chromatographic quantification and cross-platform MS-based validation using both quadrupole time-of-flight and triple-quadrupole analyzers. Dual MS confirmation enhanced the accuracy and confidence of compound identification. In addition, three extraction solvents were systematically evaluated to optimize recovery of iridoids, crocins, and phenolic compounds. These findings will establish a detailed spectral reference dataset for future phytochemical studies of *G. jasminoides* fruits and provide a useful reference for the food industry to introduce this Asian therapeutic plant as sources of novel food products.

## 2. Materials and methods

### 2.1. Plant materials

*G. jasminoides* were cultivated in an experimental plantation in Jingdezhen, Jiangxi Province, China (latitude: 29° 17′ 40.92" N, longitude: 117° 12' 28.40" E). The fruits of *G. jasminoides* Ellis (GF) and *G. jasminoides* var. *radicans* Makino (GFV) were harvested at full maturity in late October 2021. All fruits were collected and thoroughly mixed. A representative 5 kg portion was randomly sampled. This portion was divided into three independent biological replicates, each consisting of an independent fruit pool. Steam blanching was applied to inactivate endogenous enzymes of the fruits and mitigate losses of key bioactive compounds such as geniposide and crocin I (Xiao et al., 2025). Accordingly, whole fruits were steam-blanched at 120 °C for 2–3 min and subsequently dried in a forced-air oven at 60 °C for 90–120 h until the moisture content was below 10%. After drying, hulls were separated from dried fruits. Both hulls and dehulled fruits were crushed into particles and stored at −20 °C till analysis.

### 2.2. Chemicals

Authentic standards of geniposidic acid, gardenoside, genipin gentiobioside, and geniposide were purchased from Shanghai Yuanye Bio-Technology Co., LTD (Shanghai, China). Crocin I and crocin II were purchased from Chengdu Biopurify Phytochemicals LTD (Chengdu, China). Caffeic acid, *p*-coumaric acid, ferulic acid, sinapic acid, and 3-*O*-caffeoylquinic acid were purchased from Sigma-Aldrich (St. Louis, United States). Standards of quercetin 3-*O*-rutinoside and quercetin 3-*O*-glucoside were purchased from Extrasynthese (Genay, France). The solvents of LC and MS grade (methanol, formic acid, and acetonitrile) were purchased from VWR International Oy (Espoo, Finland).

### 2.3. Extraction of iridoids, phenolic compounds, and crocins

Three solvents (including 50% aqueous methanol, 80% aqueous methanol, absolute methanol) were applied to evaluate the efficacy of extracting target compounds. The selection of solvents was based on previous research (Kyriakoudi et al., 2012; Tian, Kriisa, et al., 2022). For each solvent, the extraction was conducted in triplicates. Samples (~1.0100 g) were macerated in 5.0 mL extraction solvent for approximately 19–20 h at room temperature (20–25 °C). It allowed the solvent to penetrate into the solid particles, thereby to effectively extract phenolics, iridoids, and crocins. The maceration at 20–25 °C also avoided heat-induced degradation of the phytochemicals (Kocabey et al., 2016). The mixture was homogenized using T25 digital Ultra-Turrax high-performance disperser (IKAWerke GmbH & Co.KG, Staufen, Germany), followed by ultra-sonication (45 kHz, 20 min, at room temperature) and centrifugation (15 min, at 3000×*g*). The supernatants were collected after centrifugation and the precipitates were re-extracted with the same procedure for another 3 times. All supernatants from 4-time extraction were combined and diluted to 25 mL with the same extraction solvent. The diluted supernatant (1 mL) was filtered with 0.22 μm PTFE filters. All extracts were stored at −20 °C before following analyses.

### 2.4. Identification of iridoids, phenolic compounds, and crocins by UHPLC-PAD-ESI-MS

The characterization of chemicals in extracts was first carried out with a Shimazu ultra-performance liquid chromatography tandem mass spectrometry system (UHPLC-MS; Shimadzu Corp., Kyoto, Japan). The system is equipped with a triple-quadrupole (QqQ) mass spectrometer (LCMS-8045), an electrospray ionization interface (ESI), an SPD-M40 photo diode array detector (PDA), a CTO-40 AC column oven, two LC-40DXS pumps, and a SIL-40CXS auto sampler. The column oven temperature was maintained at 25 °C throughout the analysis. A binary elution method was applied by using aqueous formic acid (0.1: 99.9, formic acid: water, *v/v*, solvent A) and acetonitrile (solvent B) as mobile phases. The extracts of 10 μL were injected into a Phenomenex Aeris peptide XB-C18 column (150 × 4.60 mm, 3.6 μm, Torrance, CA, United States) at a total flow rate of 1 mL/min. Compared with conventional C18 phases, the stationary phase of this peptide-optimized C18 column has slightly increased surface polarity, which improves the retention and

peak shape of highly glycosylated and relatively polar compounds such as crocins. In the present study, the column provided adequate retention and resolution for crocins and other target phytochemicals. The LC gradient was set as: 0–15 min with 4–10% solvent B, 15–20 min with 10–13% B, 20–25 min with 13–16% B, 25–30 min with 16–18% B, 30–35 min. with 18–20% B, 35–40 min. with 20–22% B, 40–45 min with 22–25% B, 45–50 min with 25–35% B, 50–60 min with 3545% B, 60–63 min with 45–90% B, 63–65 min with 90–4% B, and 65–68 min with 4% B.

The eluents of 0.3–0.4 mL/min were flown into MS system. MS was operated with 2 L/min of nebulizing gas flow, 15 L/min of heating gas flow, and 5 L/min drying gas flow. The temperatures of interface, desolvation, DL, and heat block were set as 300, 526, 150, and 400 °C, respectively. Both MS full scan and $MS^2$ product ion scan were applied under both positive and negative ionization modes. The mass range scanned was 140–1500 *m/z* for MS and 50–1500 *m/z* for $MS^2$. Collision energies (CEs) were optimized by testing a range of 10–40 V with the external standards of geniposidic acid, gardenoside, genipin gentiobioside, geniposide, crocin I, crocin II, caffeic acid, *p*-coumaric acid, ferulic acid, sinapic acid, 3-*O*-caffeoylquinic acid, quercetin 3-*O*-rutinoside, and quercetin 3-*O*-glucoside. Most of standards showed sufficient fragmentation for confident identification when 20 V (under positive mode) and 23 V (negative mode) was set. No CE ramping was applied. MS data acquisition and processing, including peak detection and MS/MS interpretation, were performed using LabSolutions LCMS software (version 5.118, Shimadzu, Kyoto, Japan).

To improve tentative identification, a Bruker ultra-high performance liquid chromatography (UPLC) system, coupled with a diode-array detector (DAD), an Apollo II electrospray ion source (ESI), and a quadrupole time-of-flight tandem mass spectrometer (QTOF) was applied (Bruker Corp., Billerica, MA, United States). The LC separation condition was the same as that applied for the characterization using in QqQ mass spectrometer (LCMS-8045). The eluents of 0.3–0.4 mL/min were flown into MS system. Mass full-scan was operated under both positive and negative ionization modes, and $MS^2$ scan was performed using an auto MS/MS program in QTOF system. The key parameters are given in Supplemental Table 1. The external standard of sodium formate was used for MS calibration before each injection. The data was processed using Bruker Compass DataAnalysis software (version 5.3, Bruker, Billerica, United States).

The MS identification was based on comparison of MS/MS fragmentation patterns with authentic standards and literature-reported fragmentation data. Identification levels were assigned according to Metabolomics Standards Initiative (MSI) guidelines (Sumner et al., 2007).

### 2.5. Quantification of iridoids, phenolic compounds, and crocins by HPLC-DAD

Quantitative analysis of identified compounds was conducted by using a Shimadzu liquid chromatography (Shimadzu Corp., Kyoto, Japan), consisting of a SIL-30AC autosampler, a CTO-20AC column oven, LC-30AD pumps and an SPD-M20A diode array detector (DAD). The LC condition was set as same as that applied in the LC-MS identification. Chromatograms were recorded at 240 (for iridoids), 320 (hydroxycinnamic acids), 360 (flavonols), and 440 nm (crocins), respectively.

Quantification was performed by eleven authentic standards (including iridoids, crocins, and phenolic compounds) using external calibration. Approximately 0.3–1 mg of reference compounds were first dissolved in 10 mL methanol and diluted to 4–5 different concentrations. The calibration curves were constructed by plotting the peak areas at the recorded wavelengths of HPLC chromatogram as a function of concentrations. The compounds without corresponding standards were quantified by calibration curves of those standards which had similar chemical structures. Supplemental Table 2 shows the details of compound quantification. Briefly, iridoids were quantified as geniposidic acid, geniposide, gardenoside, and genipin gentiobioside equivalents; hydroxycinnamic acids as 3-*O*-caffeoylquinic acid, ferulic acid and sinapic acid equivalents; flavonols as quercetin 3-*O*-rutinoside and quercetin 3-*O*-glucoside equivalents; crocins as crocin I and crocin II equivalents.

The quantification method was validated through analytical performance tests (Supplemental Table 3). A representative compound was selected from each chemical class, including geniposide (as the class of iridoids), 3-*O*-caffeoylquinic acid (hydroxycinnamic acids), quercetin 3-*O*-rutinoside (flavonols), and crocin I (crocins). Intra-day ($n = 6$) and inter-day (three consecutive days) repeatability were evaluated using one representative *G. jasminoides* sample (GFV Hulls 2) to reflect matrix effects, focusing on four target compounds (geniposide, 3-*O*-caffeoylquinic acid, quercetin-3-*O*-rutinoside, and crocin I). Repeatability, Limit of Detection (LOD), Limit of Quantification (LOQ), and linearity ($R^2 > 0.99$) ($n = 3$) were determined using the corresponding authentic standards to ensure consistency of analytes (Al-Rimawi & Odeh, 2015). Relative standard deviation (RSD, %) of representative compounds both in the sample and the authentic standards were calculated.

### 2.6. Statistical analysis

Quantitative analysis was performed using three biologically independent samples. Each sample was extracted and analyzed separately, and results are presented as mean ± standard deviation (SD, n = 3). Statistical difference among the contents was carried out by one way-ANOVA and Tukey's *post hoc* test ($p < 0.05$) with IBM SPSS Statistics 26 for Windows (SPSS Inc., New York, Unite States). Heatmap and hierarchical clustering were generated using MetaboAnalyst (https://www.metaboanalyst.ca). All data was standardized prior to analysis. Hierarchical clustering was conducted using Ward's linkage method and Euclidean distance as the distance metric. The heatmap color scale represents relative concentration levels (z-scores). Principal Component Analysis (PCA) was performed using Unscrambler® 11 (Camo Process AS, Oslo, Norway) to visualize overall differences in phytochemical profiles among samples. Prior to analysis, data were normalized to dry weight and mean-centered with autoscaling. No log-transformation was applied. No missing values were present in the dataset. The percentage variance explained by each principal component was calculated based on the corresponding eigenvalues. Loading values for PC1 and PC2 are provided in Supplemental Table 7 and Supplemental Table 8.

## 3. Results and discussion

### 3.1. Method validation of the quantitative analysis

The validation results are presented in Supplemental Table 3. The intra-day and inter-day RSD values of the representative compounds (geniposide, 3-*O*-caffeoylquinic acid, quercetin 3-*O*-rutinoside, and crocin I) in the sample of GFV Hulls 2 were below 0.9% and 0.7%, respectively, demonstrating excellent method precision. The RSD of these authentic standards ranged from 2.3% to 6.7%, indicating acceptable analytical precision. The LOD concentration of geniposide, 3-*O*-caffeoylquinic acid, quercetin 3-*O*-rutinoside, and crocin I was 6, 0.35, 2, and 0.45 μg/mL, respectively, with mean S/N values of 2.7, 3.1, 4.1, and 2.4, and RSDs of 11.9%, 16.9%, 15.7%, and 4.4% ($n = 3$). The corresponding LOQ concentration was 23, 0.88, 5, and 1.4 μg/mL, with mean S/N values of 10.1, 8.1, 11.7, and 9.5, and RSDs of 8.9%, 8%, 5%, and 3.7% (n = 3), respectively. All results indicate reliable sensitivity and quantitative performance.

**Table 1**
Identification of iridoids, hydroxycinnamic acids, flavonols, and crocins by UHPLC-PAD-ESI-QqQ-MS.

| Compounds | UV $\lambda_{max}$ (nm) | LC retention time (min) | MS adducts ($m/z$) | Key fragments ($MS^2$, $m/z$) | Level of identification* |
|---|---|---|---|---|---|
| **Cyclopentane iridoids** | | | | | |
| 1. Deacetylasperulosidic acid | 236 | 4.382 | 389.2 ([**M-H**]$^-$), 435.2 ([**M + HCOOH-H**]$^-$), 779.2 ([**2 M-H**]$^-$), 391.2 ([**M + H**]$^+$), 413.2 ([**M + Na**]$^+$) | 389.2 → **227.1**, 208.9, 190.9, 183.2, 165.1, 147.3, 143.2, 139.1, 137.2, 129.3, 121.2, 119.0, 113.1, 109.2, 101.1 | Level 2 Literature [1,2] |
| 2. Gardoside | 236 | 5.210 | 373.2 ([**M-H**]$^-$), 419.1 ([**M + HCOOH-H**]$^-$), 747.2 ([**2 M-H**]$^-$), 392.1 (**M + NH$_4$**]$^+$), 397.1 ([**M + Na**]$^+$) | 373.2 → **210.8**, 193.4, 174.8, 167.0, 149.1, 123.2, 101.0 | Level 2 Literature [1,2] |
| 3. Shanzhiside | 235 | 6.263 | 391.2 ([**M-H**]$^-$), 437.2 ([**M + HCOOH-H**]$^-$), 783.3 ([**2 M-H**]$^-$), 415.2 ([**M + Na**]$^+$) | 391.2 → 373.0, **228.9**, 210.9, 185.2, 167.1, 149.1, 141.2, 119.1, 113.2, 109.3, 107.2, 101.1 | Level 2 Literature [1,2,9] |
| 4. Geniposidic acid | 238 | 6.861 | 373.2 ([**M-H**]$^-$), 419.2 ([**M + HCOOH-H**]$^-$), 747.1 ([**2 M-H**]$^-$), 375.3 ([**M + H**]$^+$), 392.2 (**M + NH$_4$**]$^+$), 397.2 ([**M + Na**]$^+$) | 373.2 → 193.0, 166.8, 149.1, 134.3, 130.8, 122.9, 101.0 | Level 1 Literature [1,2,9] |
| 5. Scandoside methyl ester | 237 | 7.317 | 449.2 ([**M + HCOOH-H**]$^-$), 422.2 (**M + NH$_4$**]$^+$), 427.2 ([**M + Na**]$^+$) | 449.2 → **241.1**, 223.0, 179.3, 139.1, 119.3, 101.2 | Level 2 Literature [1,3] |
| 6. Gardenoside | 238 | 8.168 | 403.2 ([**M-H**]$^-$), 449.1 ([**M + HCOOH-H**]$^-$), 422.2 (**M + NH$_4$**]$^+$), 427.2 ([**M + Na**]$^+$) | 449.1 → **403.2**, **241.1**, 223.1, 193.2, 191.0, 127.2, 119.2, 101.1 | Level 1 Literature [1,2,3] |
| 8. Ixoroside | 249 | 9.243 | 405.2 ([**M + HCOOH-H**]$^-$), 383.1 ([**M + Na**]$^+$) | 405.2 → **359.3**, 239.4, **197.1**, 151.2 | Level 2 Literature [1] |
| 9. Galioside | 239 | 9.988 | 449.2 ([**M + HCOOH-H**]$^-$), 427.2 ([**M + Na**]$^+$) | 449.2 → **241.1**, 139.2, 101.1 | Level 2 Literature [1] |
| 11. Genipin gentiobioside | 240 | 15.250 | 549.2 ([**M-H**]$^-$), 595.2 ([**M + HCOOH-H**]$^-$), 551.2 ([**M + H**]$^+$), 573.2 ([**M + Na**]$^+$) | 595.2 → **549.2**, **225.1**, 207.0, 123.1, 117.1, 101.2 | Level 1 Literature [1,2,3] |
| 12. Geniposide | 240 | 17.678 | 387.3 ([**M-H**]$^-$), 433.2 ([**M + HCOOH-H**]$^-$), 389.2 ([**M + H**]$^+$), 406.2 (**M + NH$_4$**]$^+$), 411.2 ([**M + Na**]$^+$) | 433.2 → **225.0**, 207.2, 123.2, 101.1 | Level 1 Literature [1, 3] |
| 16. Coumaroyl-geniposidic acid | 235, 312 | 24.670 | 519.1 ([**M-H**]$^-$), 543.2 ([**M + Na**]$^+$) | 519.1 → 354.8, 307.1, 265.2, 167.0, **163.0**, 149.3, 145.0, 123.3, 113.3 | Level 2 Literature [1,4] |

| Compounds | UV λmax (nm) | LC retention time (min) | MS adducts ($m/z$) | Key fragments ($MS^2$, $m/z$) | Level of identification* |
|---|---|---|---|---|---|
| 61. Acetyl-genipin-hexoside | 251 | 28.087 | 429.3 ([**M-H**]$^-$), 475.3 ([**M + HCOOH-H**]$^-$), 431.3 ([**M + H**]$^+$), 453.3 ([**M + Na**]$^+$) | 475.3 → 429.3, 279.2, 209.3, 191.3, 179.3, 161.2, 149.3, 146.3, 119.1<br>431.3 → **269.4**, 251.3, 233.1, 207.2, 205.2, 181.1, 179.2, 163.2, 161.2 | Level 2 Literature [3,4] |
| 18. Sinapoyl-shanzhiside | 238, 328 | 30.523 | 597.2 ([**M-H**]$^-$), 599.2 ([**M + H**]$^+$), 616.3 (**M + NH$_4$**]$^+$), 621.3 ([**M + Na**]$^+$) | 597.2 → **391.1**, 295.1, 265.1, **223.1**, **205.2**, 191.2, 167.1 | Level 3 |
| 19. Sinapoyl-gardoside | 239, 328 | 31.670 | 579.2 ([**M-H**]$^-$), 625.2 ([**M + HCOOH-H**]$^-$), 581.3 ([**M + H**]$^+$), 603.2 ([**M + Na**]$^+$) | 579.2 → 535.3, 385.2, **367.1**, 325.1, 295.1, 265.3, **223.1**, **205.1**, 193.3, 166.7, 149.2, 123.1, 113.2 | Level 2 Literature [4] |
| 20. Sinapoyl-genipin-hexoside | 238, 328 | 33.338 | 593.2 ([**M-H**]$^-$), 595.3 ([**M + H**]$^+$), 612.2 (**M + NH$_4$**]$^+$), 617.3 ([**M + Na**]$^+$) | 593.2 → 549.3, **385.2**, 366.8, 343.2, 325.1, 294.9, 265.2, **223.1**, 220.6, 207.0, **205.3**, 191.2, 181.2, 162.9, 136.7, 120.8 | Level 2 Literature [4] |
| 21. Coumaroyl-genipin gentiobioside | 231, 312 | 37.466 | 695.3 ([**M-H**]$^-$), 741.3 ([**M + HCOOH-H**]$^-$), 1391.5 ([**2 M-H**]$^-$), 697.4 ([**M + H**]$^+$), 714.4 (**M + NH$_4$**]$^+$), 719.4 ([**M + Na**]$^+$) | 695.3 → **469.3**, 265.0, **225.2**, **163.3**, 145.2, 123.1, 101.3 | Level 2 Literature [1,4] |
| 22. Sinapoyl-genipin gentiobioside | 236, 328 | 38.074 | 755.4 ([**M-H**]$^-$), 757.5 ([**M + H**]$^+$), 774.4 (**M + NH$_4$**]$^+$), 779.4 ([**M + Na**]$^+$) | 755.4 → 723.3, **529.2**, **225.2**, **204.8**, 123.1, 101.3 | Level 2 Literature [1,4] |
| 24. Feruloyl-genipin-dihexoside | 241, 328 | 38.776 | 725.4 ([**M-H**]$^-$), 771.4 ([**M + HCOOH-H**]$^-$), 727.4 ([**M + H**]$^+$), 744.4 (**M + NH$_4$**]$^+$), 749.4 ([**M + Na**]$^+$) | 725.4 → **499.3**, **225.3**, **193.3**, 175.1, 123.1, 101.3 | Level 2 Literature [4] |

(*continued on next page*)

**Table 1** (*continued*)

| Compounds | UV λmax (nm) | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|---|
| 27. Sinapoyl-geniposide | 241, 328 | 42.128 | 593.3 ([**M-H**] $^-$), 639.3 ([**M + HCOOH-H**] $^-$), 595.3 ([**M + H**] $^+$), 617.3 ([**M + Na**] $^+$) | 593.3 → 561.1, **367.4**, 294.4, 265.1, **222.9**, **205.3**, 175.0, 161.9, 131.2, 123.2, 101.0 | Level 2 Literature [1,4] |
| 28. Cinnamoyl-genipin-dihexoside | 240, 329 | 48.146 | 725.3 ([**M + HCOOH-H**] $^-$), 681.4 ([**M + H**] $^+$), 698.4 (**M + $NH_4$**] $^+$), 703.3 ([**M + Na**] $^+$) | 725.3 → **679.4**, 531.4, 355.2, 249.3, **225.1**, **147.3**, 123.3, 101.1 | Level 2 Literature [1,4] |

| Compounds | UV $\lambda_{max}$ (nm) | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|---|
| **Seco-iridoids** | | | | | |
| 7. Jasminoside B/D/G 1 | 242 | 8.378 | 345.2 ([**M-H**] $^-$), 391.2 ([**M + HCOOH-H**] $^-$), 691.4 ([**2 M-H**] $^-$), 347.2 ([**M + H**] $^+$), 364.3 (**M + $NH_4$**] $^+$), 369.2 ([**M + Na**] $^+$) | 345.2 → 165.1, 149.1, 121.2, 118.9, 113.0, 107.3, 101.1<br>391.2 → 179.0, 165.2, 161.2, 158.9, 153.3, 149.1, 143.2, 131.3, 119.1, 113.1, 101.2 | Level 2 Literature [4] |
| 10. Jasminoside B/D/G 2 | 241 | 11.157 | 391.2 ([**M + HCOOH-H**] $^-$), 347.2 ([**M + H**] $^+$), 369.2 ([**M + Na**] $^+$) | 391.2 → 315.2, 179.0, 165.3, 161.2, 158.8, 119.1, 113.0, 107.0, 101.1<br>347.2 → 311.5, **185.2**, 167.2, 149.3, 145.4, 137.2, 127.2, 123.3, 109.2 | Level 2 Literature [4] |
| 14. Jasminoside A/E/K 1 | 242 | 20.203 | 375.2 ([**M + HCOOH-H**] $^-$), 331.2 ([**M + H**] $^+$), 353.2 ([**M + Na**] $^+$) | 375.2 → 179.3, 160.8, 143.2, 119.1, 112.9, 101.0<br>331.2 → **169.2**, 109.2 | Level 2 Literature [4] |
| 15. Jasminoside A/E/K 2 | 242 | 20.764 | 375.2 ([**M + HCOOH-H**] $^-$), 331.2 ([**M + H**] $^+$), 353.2 ([**M + Na**] $^+$) | 375.2 → 179.3, 160.8, 143.2, 119.1, 112.9, 101.0<br>331.2 → **169.2**, 109.2 | Level 2 Literature [4] |
| 25. Sinapoyl-jasminoside B/D/G/L 1 | 241, 328 | 39.990 | 551.3 ([**M-H**] $^-$), 597.3 ([**M + HCOOH-H**] $^-$), 553.4 ([**M + H**] $^+$), 575.4 ([**M + Na**] $^+$) | 551.3 → 533.3, 521.3, **367.2**, 325.3, 295.3, 265.2, **223.1**, **205.0**, 165.3<br>553.4 → 369.2, **207.2**, 167.2 | Level 2 Literature [4] |
| 26. Sinapoyl-jasminoside B/D/G/L 2 | 241, 328 | 40.347 | 551.3 ([**M-H**] $^-$), 597.3 ([**M + HCOOH-H**] $^-$), 553.4 ([**M + H**] $^+$), 575.4 ([**M + Na**] $^+$) | 551.3 → 533.3, 521.3, **367.2**, 325.3, 295.3, 265.2, **223.1**, **205.0**, 165.3 | Level 2 Literature [4] |
| 29. Sinapoyl-jasminoside A/E/K | 241, 327 | 48.909 | 535.3 ([**M-H**] $^-$), 581.3 ([**M + HCOOH-H**] $^-$), 537.3 ([**M + H**] $^+$), 559.3 ([**M + Na**] $^+$) | 535.3 → 325.2, 294.9, 265.3, 247.2, 223.4, 205.3, 179.1<br>537.3 → 207.2, 175.2, 169.2 | Level 2 Literature [4] |

| Compounds | UV λmax (nm) | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|---|
| **other iridoids** | | | | | |
| 13. unknown iridoid | 232 | 19.536 | 385.2 ([**M-H**] $^-$), 431.2 ([**M + HCOOH-H**] $^-$), 404.2 (**M + $NH_4$**] $^+$), 409.2 ([**M + Na**] $^+$) | 431.2 → 290.0, **223.0**, 205.4, 178.8, 149.3, 119.2, 113.1, 101.5<br>409.2 → **247.1**, 212.6 | Level 3 |
| 17. unknown coumaroyl iridoid | 236, 313 | 28.856 | 521.2 ([**M-H**] $^-$), 545.3 ([**M + Na**] $^+$) | 521.2 → 357.3, 212.9, 186.8, 169.3, **163.3**, 151.3, 145.1, 142.7, 125.3 | Level 3 |
| 23. unknown sinapoyl iridoid 1 | 236, 328 | 38.074 | 563.3 ([**M-H**] $^-$), 583.4 (**M + $NH_4$**] $^+$), 587.3 ([**M + Na**] $^+$) | 563.3 → 545.3, 367.2, 357.0, 247.0, **223.2**, **205.2**, 195.2, 180.1 | Level 3 |
| 62. unknown sinapoyl iridoid 2 | 240, 329 | 47.895 | 787.2 ([**M-H**] $^-$), 833.2 ([**M + HCOOH-H**] $^-$), 789.3 ([**M + H**] $^+$), 806.4 (**M + $NH_4$**] $^+$), 811.2 ([**M + Na**] $^+$) | 787.2 → 371.0, 264.2, 239.3, **205.0** | Level 3 |
| **Hydroxycinnamic acids** | | | | | |
| 30. 5-*O*-Caffeoylquinic acid | 298(sh), 324 | 9.070 | 353.1 ([**M-H**] $^-$), 355.1 ([**M + H**] $^+$), | | Level 2 Literature [6,9] |
| 31. 3-*O*-Caffeoylquinic acid | 298(sh), 326 | 14.622 | 353.2 ([**M-H**] $^-$), 707.2 ([**2 M-H**] $^-$), 355.2 ([**M + H**] $^+$), 377.1 ([**M + Na**] $^+$) | 353.2 → 191.1<br>355.2 → 163.2, 145.1 | Level 1 Literature [5,6,9] |

(*continued on next page*)

**Table 1** (*continued*)

| Compounds | UV λmax (nm) | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|---|
| 32. 4-*O*-Caffeoylquinic acid | 298(sh), 326 | 15.927 | 353.2 ([**M-H**]$^-$), 355.2 ([**M + H**]$^+$) | 353.2 → 191.1, 179.1, 173.1, 135.2 | Level 2<br>Literature [6,9] |
| 33. Ferulic acid-hexoside | 298(sh), 329 | 17.027 | 355.2 ([**M-H**]$^-$), 379.2 ([**M + Na**]$^+$) | 355.2 → **193.1**, 175.1, 160.1, 133.8, 119.0, 101.1 | Level 2<br>Literature [6] |
| 34. Sinapic acid-hexoside 1 | 298(sh), 331 | 18.334 | 385.2 ([**M-H**]$^-$), 409.2 ([**M + Na**]$^+$) | 385.2 → **223.1**, **205.1**, 190.1, 175.1 | Level 2<br>Literature [7] |
| 35. Sinapic acid-hexoside 2 | 298(sh), 326 | 20.540 | 385.2 ([**M-H**]$^-$), 387.2 ([**M + H**]$^+$), 409.2 ([**M + Na**]$^+$) | 385.2 → 325.2, 265.2, 247.5, **223.1**, **205.0**, 190.3, 174.9 | Level 2<br>Literature [7] |
| 36. Sinapic acid-hexoside 3 | 298(sh), 326 | 22.233 | 385.2 ([**M-H**]$^-$), 387.2 ([**M + H**]$^+$), 409.2 ([**M + Na**]$^+$) | 385.2 → 325.1, 295.2, 265.0, 247.1, **223.2**, **205.2**, 190.0, 164.2, 119.2<br>387.2 → **207.2**, 175.1 | Level 2<br>Literature [7] |

| Compounds | UV λmax (nm) | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|---|
| 37. Sinapic acid | 298(sh), 323 | 26.050 | 223.2 ([**M-H**]$^-$), 225.1 ([**M + H**]$^+$) | 225.1 → **207.2**, 192.1, 175.1, 146.9, 119.0 | Level 1<br>Literature [7] |
| 38. Dicaffeoylquinic acid 1 | 298(sh), 326 | 34.054 | 515.2 ([**M-H**]$^-$), 517.3 ([**M + H**]$^+$), 539.2 ([**M + Na**]$^+$) | | Level 2<br>Literature [5,6,9] |
| 39. Dicaffeoylquinic acid 2 | 298(sh), 327 | 37.209 | 515.2 ([**M-H**]$^-$), 517.3 ([**M + H**]$^+$), 539.2 ([**M + Na**]$^+$) | 515.2 → **353.1**, **191.1**, 179.2, 173.2, 135.0 | Level 2<br>Literature [5,6,9] |
| 40. Dicaffeoyl-hydroxy-methylglutaroyl-quinic acid | 298(sh), 328 | 40.350 | 659.3 ([**M-H**]$^-$), 661.4 ([**M + H**]$^+$), 683.3 ([**M + Na**]$^+$) | 659.3 → **497.2**, **353.3**, 335.0, **191.1**, 173.2, 161.1 | Level 2<br>Literature [3,5] |
| **Flavonols** | | | | | |
| 41. Quercetin-hexoside-deoxyhexoside | 254, 265(sh), 352 | 28.397 | 609.1 ([**M-H**]$^-$), 611.3 ([**M + H**]$^+$), 633.2 ([**M + Na**]$^+$) | 609.1 → **300.1**<br>611.3 → **303.1** | Level 2<br>Literature [5,6] |
| 42. Quercetin 3-*O*-rutinoside | 254, 265(sh), 353 | 28.905 | 609.2 ([**M-H**]$^-$), 1219.4 ([**2 M-H**]$^-$), 611.2 ([**M + H**]$^+$), 633.2 ([**M + Na**]$^+$) | 609.2 → **300.1**<br>611.2 → **303.1** | Level 1<br>Literature [5,6] |
| 43. Quercetin 3-*O*-glucoside | 255, 265(sh), 352 | 29.893 | 463.1 ([**M-H**]$^-$), 465.1 ([**M + H**]$^+$), 487.2 ([**M + Na**]$^+$) | 463.1 → 301.0, **300.1**, 271.0, 255.2<br>465.1 → **303.0** | Level 1<br>Literature [5,6] |
| **Crocins** | | | | | |
| 44. Crocin I | 440 | 42.900 | 975.4 ([**M-H**]$^-$), 1021.5 ([**M + HCOOH-H**]$^-$), 999.4 ([**M + Na**]$^+$) | | Level 1<br>Literature [3,8,9] |
| 45. Crocetin-dihexoside-dihexoside 1 | 439 | 43.225 | 999.5 ([**M + Na**]$^+$) | | Level 2<br>Literature [8] |
| 46. unknown crocin 1 | 439 | 45.651 | 991.5 ([**M + HCOOH-H**]$^-$), 969.5 ([**M + Na**]$^+$) | | Level 3 |
| 47. Crocin II | 440 | 47.398 | 859.5 ([**M + HCOOH-H**]$^-$), 837.5 ([**M + Na**]$^+$) | | Level 1<br>Literature [3,8,9] |
| 48. Crocetin-dihexoside-dihexoside 2 | 439 | 49.151 | 975.4 ([**M-H**]$^-$), 1021.4 ([**M + HCOOH-H**]$^-$), 999.5 ([**M + Na**]$^+$) | | Level 2<br>Literature [8] |

| Compounds | UV λmax (nm) | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|---|
| 49. Crocetin-dihexoside 1 | 440 | 49.669 | 697.4 ([**M + HCOOH-H**]$^-$), 675.5 ([**M + Na**]$^+$) | | Level 2<br>Literature [8] |
| 50. Crocetin-dihexoside-sinapoyl-dihexoside | 440 | 49.850 | 1181.6 ([**M-H**]$^-$), 1205.7 ([**M + Na**]$^+$) | | Level 2<br>Literature [8] |
| 51. unknown crocin 2 | 438 | 50.361 | 1007.5 ([**M-H**]$^-$), 1031.5 ([**M + Na**]$^+$) | | Level 3 |
| 52. Crocetin-dihexoside-dihexoside 3 | 440 | 51.216 | 975.4 ([**M-H**]$^-$), 1021.4 ([**M + HCOOH-H**]$^-$), 999.4 ([**M + Na**]$^+$) | | Level 2<br>Literature [8] |
| 53. unknown crocin 3 | 440 | 51.958 | 1067.5 ([**M + HCOOH-H**]$^-$), 1045.6 ([**M + Na**]$^+$) | | Level 3 |

(*continued on next page*)

**Table 1** (*continued*)

| Compounds | UV λmax (nm) | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|---|
| 54. Crocetin-dihexoside-caffeoylquinic acid | 440 | 52.175 | 987.6 ([**M-H**] $^-$), 989.6 ([**M + H**] $^+$), 1011.6 ([**M + Na**] $^+$) | | Level 2<br>Literature [8] |
| 55. Crocetin-dihexoside 2 | 440 | 52.301 | 651.4 ([**M-H**] $^-$), 697.4 ([**M + HCOOH-H**] $^-$), 675.4 ([**M + Na**] $^+$) | | Level 2<br>Literature [8] |
| 56. Crocetin-dihexoside-hexoside 1 | 440 | 52.821 | 813.2 ([**M-H**] $^-$), 859.4 ([**M + HCOOH-H**] $^-$), 837.5 ([**M + Na**] $^+$) | | Level 2<br>Literature [8] |
| 57. Crocetin-dihexoside-hexoside 2 | 440 | 52.988 | 813.4 ([**M-H**] $^-$), 859.3 ([**M + HCOOH-H**] $^-$), 837.5 ([**M + Na**] $^+$) | | Level 2<br>Literature [8] |
| 58. Crocetin-hexoside | 440 | 55.244 | 489.3 ([**M-H**] $^-$), 535.3 ([**M + HCOOH-H**] $^-$), 513.3 ([**M + Na**] $^+$) | | Level 2<br>Literature [3,8] |
| 59. Crocetin-dihexoside 3 | 440 | 56.814 | 651.3 ([**M-H**] $^-$), 675.4 ([**M + Na**] $^+$) | | Level 2<br>Literature [8] |
| 60. Crocetin-dihexoside 4 | 440 | 57.294 | 651.3 ([**M-H**] $^-$), 675.4 ([**M + Na**] $^+$) | | Level 2<br>Literature [8] |

* Identification levels are assigned according to Metabolomics Standards Initiative (MSI) guidelines: Identified compounds confirmed with authentic standards (Level 1), identified compounds based on previous research (Level 2), and putatively characterized compounds (Level 3).
Reference literature includes: 1. Fu et al., 2014; 2. Zhou et al., 2010; 3. Bergonzi et al., 2012; 4. Tian, Kriisa, et al., 2022; 5. Liu et al., 2021; 6. Tian et al., 2017; 7. Tian, Qin, et al., 2022; 8. Ni et al., 2017; 9. Shan et al., 2019

### 3.2. Characterization of iridoids, phenolic compounds, and crocins in the extracts

Altogether 62 compounds were identified from the fruits and hulls of *G. jasminoides*, including 31 iridoids, 11 hydroxycinnamic acids, 3 flavonols, and 17 crocins (Supplemental Fig. 1). Compounds lacking authentic standards but showing characteristic fragmentation patterns were tentatively classified according to their structural class (*e.g.,* iridoids, crocins, phenolics) and labeled as "unknown" compounds with numbering based on elution order of LC. Both ESI-MS full scan and ESI-$MS^2$ product scan were performed to unveil the structural characteristics of compounds in details. The characterization was conducted by comparing their MS fragmentation with authentic standards and the data from previous research (Bergonzi et al., 2012; Cai et al., 2015; Fu et al., 2014; Liu et al., 2021; Ni et al., 2017; Shan et al., 2019; Tian, Kriisa, et al., 2022; Tian et al., 2017, Tian, Qin, et al., 2022; Ye et al., 2022; Zhou et al., 2010). All MS and $MS^2$ data are given in Table 1 and Table 2. The MS and $MS^2$ spectra of tentatively-identified compounds are provided in Supplemental Fig. 2.

#### 3.2.1. Iridoids

The iridoids found in the *G. jasminoides* samples had a maximum UV absorption around 240 nm (Tables 1 & 2). MS data suggested that the iridoids mainly belonged to cyclopentane iridoids and seco-iridoids, presenting as glycosides conjugated mostly with glucose or gentiobioside (two units of D-glucose bonding with a $\beta$ (1 → 6) linkage) as sugar moieties (Xiao et al., 2017).

Most of the cyclopentane iridoids were identified by high-intensity adduct ions $[M + HCOOH\text{-}H]^-$ in the $ESI^-$-MS spectra and their product ions in the $MS^2$ spectra (Tables 1 & 2). For example, compound 11 with $[M + HCOOH\text{-}H]^-$ at *m/z* 595 were defined as genipin gentiobioside. Under $MS^2$ product ion scan, the $[M + HCOOH\text{-}H]^-$ first lost adduct group (-HCOOH) to produce $[M\text{-}H]^-$ at *m/z* 549 and subsequently formed [M-H-162-162]$^-$ at *m/z* 225 due to gentiobioside cleavage. Similarly, geniposide (*i.e.*, genipin glucoside, compound 12) displayed $[M + HCOOH\text{-}H]^-$ at *m/z* 433, $[M\text{-}H]^-$ at *m/z* 387, and [M-H-162]$^-$ at *m/z* 225.

The characterization of seco-iridoids were based mainly on protonated molecule ions $[M + H]^+$ and corresponding fragmentation ions (Tables 1 & 2). Two types of jasminosides were detected in both GF and GFV extracts. Compounds 7 and 10 were preliminarily identified as isomers of Jasminoside B, D, or G all with the molecular formula $C_{16}H_{26}O_8$ ($[M + H]^+$ at *m/z* 347). Compounds 14 and 15 were assigned as isomers of Jasminoside A, E, or K, all with molecular formula $C_{16}H_{26}O_7$ ($[M + H]^+$ at *m/z* 331). In both cases, the resulting positive product ions at *m/z* 167 and *m/z* 169 suggested the presence of different cyclohexenone-type aglycone units. Nevertheless, our MS method was not successful in revealing the detained structures of the seco-iridoids for the lack of authentic standards.

Moreover, the esters of iridoids and phenolic acids were also found in the samples. Typical deprotonated ions of sinapic acid (*m/z* at 223), coumaric acid (*m/z* at 163), ferulic acid (*m/z* at 193), and cinnamic acid (*m/z* at 147) were detected in the $ESI^-$-$MS^2$ spectra of both acylated cyclopentane iridoids and seco-iridoids (Tables 1 & 2). The acylation of iridoids with hydroxycinnamic acids caused a variation in UV absorption. In addition to showing absorption around 240 nm like common iridoids, the hydroxycinnamic acid-iridoid esters had high absorbance around 320 nm, which was also typical maximum absorption band of hydroxycinnamic acids (Tables 1 & 2, Supplemental Fig. 1a & 1b).

#### 3.2.2. Hydroxycinnamic acids

Compounds 30, 31, and 32 with $[M\text{-}H]^-$ ions at *m/z* 353 were characterized as mono-caffeoylquinic acids ($C_{16}H_{18}O_9$, Tables 1 & 2). All these compounds produced [M-H-162]$^-$ at *m/z* 191 for losing one caffeoyl unit. Compounds 38 and 39 ($C_{25}H_{24}O_{12}$) were evidently di-caffeoylquinic acid isomers due to $[M\text{-}H]^-$ at *m/z* 515, [M-H-162]$^-$ at

**Table 2**
Identification of iridoids, hydroxycinnamic acids, flavonols, and crocins by UPLC-DAD-ESI-QTOF-MS.

| Compounds | LC retention time (min) | MS adducts ($m/z$) | Key fragments ($MS^2$, $m/z$) | Level of identification* |
|---|---|---|---|---|
| **Cyclopentane iridoids** | | | | |
| 1. Deacetylasperulosidic acid | 4.32 | 389.1109 ( **[M-H]** $^-$) | 389.1109 → **227.0565**, 209.0469, 183.0680, 165.0577, 147.0474, 139.0412 | Level 2 |
| | | 779.2310 ( **[2 M-H]** $^-$) | 413.1055 → 395.0945, 361.0490, 303.0433, **251.0527**, 233.0424, 215.0312, | Literature [1,2] |
| | | 413.1055 ( **[M + Na]** $^+$) | 203.0525, 185.0423 | |
| 2. Gardoside | 5.05 | 373.1157 ( **[M-H]** $^-$) | 373.1157 → **211.0632**, 193.0518, 167.0723, 149.0627, 123.0467 | Level 2 |
| | | 747.2374 ( **[2 M-H]** $^-$) | 397.1110 → 379.1016, 305.0598, **235.0582**, 217.0476, 203.0528, 185.0426 | Literature [1,2] |
| | | 397.1110 ( **[M + Na]** $^+$) | | |
| 3. Shanzhiside | 6.20 | 391.1262 ( **[M-H]** $^-$), | 391.1262 → **229.0728**, 211.0627, 185.0831, 167.0728, 149.0616, 149.0616, | Level 2 |
| | | 783.2582 ( **[2 M-H]** $^-$) | 141.0574, 127.0413, 119.0365 | Literature [1,2,9] |
| | | 415.1215 ( **[M + Na]** $^+$) | 415.1215 → 397.1102, **253.0687**, 235.0581, 217.0479, 203.0530, 185.0426 | |
| 4. Geniposidic acid | 6.89 | 373.1152 ( **[M-H]** $^-$) | 373.1152 → **211.0658**, 193.0491, 167.0709, 149.0622, 123.0466 | Level 1 |
| | | 397.1112 ( **[M + Na]** $^+$) | 397.1112 → 381.0767, **235.0575**, 217.0478, 203.0525 | Literature [1,2,9] |
| 5. Scandoside methyl ester | 7.22 | 403.1256 ( **[M-H]** $^-$) | 403.1256 → **241.0723**, 223.0622, 191.0351, 179.0368, 165.0564, 147.0456, | Level 2 |
| | | 449.1315 ( **[M + HCOOH-H]** $^-$) | 139.0425 | Literature [1,3] |
| | | 422.1659 ( **[M + $NH_4$]** $^+$) | 449.1315 → **403.1251**, **241.0723**, 223.0618, 191.0351, 179.0571, 165.0567, | |
| | | 427.1212 ( **[M + Na]** $^+$) | 139.0409, 119.0361 | |
| | | | 427.1212 → **265.0687**, 247.0583, 233.0426, 203.0532 | |
| 6. Gardenoside | 8.08 | 403.1250 ( **[M-H]** $^-$) | 403.1250 → **241.0714**, 223.0590, 193.0500, 191.0344, 177.0561, 165.0564, | Level 1 |
| | | 449.1306 ( **[M + HCOOH-H]** $^-$) | 161.0258, 127.0416 | Literature [1,2,3] |
| | | 422.1660 ( **[M + $NH_4$]** $^+$) | 449.1306 → **403.1251**, **241.0721**, 223.0617, 193.0501, 191.0350, 127.0410 | |
| | | 427.1215 ( **[M + Na]** $^+$) | 427.1215 → 409.1110, 395.0958, **265.0688**, 247.0582, 233.0426, 203.0532, | |
| | | | 185.0426 | |
| 8. Ixoroside | 9.14 | 359.1359 ( **[M-H]** $^-$) | 359.1359 → 326.0656, 309.6800, 290.3516, 280.8629, 278.2243, 263.9041, | Level 2 |
| | | 405.1416 ( **[M + HCOOH-H]** $^-$) | 245.8552, 221.0791, **197.0858**, 193.0879, 185.8849, 179.0714, | Literature [1] |
| | | 383.1319 ( **[M + Na]** $^+$) | 129.7248, 123.0501, 121.6171 | |
| | | | 405.1416 → **359.1365**, 239.0941, **197.0828**, 383.1319, 221.0788, 203.0671, | |
| | | | 185.0429 | |

| Compounds | LC retention time (min) | MS adducts ($m/z$) | Key fragments ($MS^2$, $m/z$) | Level of identification* |
|---|---|---|---|---|
| 9. Galioside | 9.88 | 403.1259 ( **[M-H]** $^-$) | 403.1259 → 371.1024, **241.0728**, 209.0488, 139.0417 | Level 2 |
| | | 449.1314 ( **[M + HCOOH-H]** $^-$) | 449.1314 → **403.1256**, 371.1003, **241.0730**, 139.0415 | Literature [1] |
| | | 427.1209 ( **[M + Na]** $^+$) | 427.1209 → **265.0684**, 247.0578, 233.0421, 203.0529 | |
| 11. Genipin gentiobioside | 15.30 | 549.1848 ( **[M-H]** $^-$) | 549.1848 → 517.1558, **225.0775**, 207.0671, 179.0574, 123.0463 | Level 1 |
| | | 595.1909 ( **[M + HCOOH-H]** $^-$) | 595.1909 → **549.1828**, **225.0780**, 207.0670, 179.0570, 123.0464 | Literature [1,2,3] |
| | | 1099.3709 ( **[2 M-H]** $^-$) | 573.1785 → 365.1055 | |
| | | 573.1785 ( **[M + Na]** $^+$) | | |
| 12. Geniposide | 17.71 | 387.1317 ( **[M-H]** $^-$) | 387.1317 → 355.1079, **225.0781**, 207.0679, 193.0516, 175.0449, 147.0459, | Level 1 |
| | | 433.1382 ( **[M + HCOOH-H]** $^-$) | 143.0377, 123.0469 | Literature [1, 3] |
| | | 775.2686 ( **[M-H]** $^-$) | 433.1382 → **387.1306**, 355.1051, **225.0780**, 207.0675, 123.0467 | |
| | | 411.1267 ( **[M + Na]** $^+$) | 411.1267 → **249.0739**, 231.0634, 217.0477, 203.0531 | |
| 16. Coumaroyl-geniposidic acid | 24.66 | 519.1528 ( **[M-H]** $^-$) | 519.1528 → **373.1175**, **355.1044**, 345.1552, 325.0942, 307.0839, 211.0619, | Level 2 |
| | | 538.1662 ( **[M + $NH_4$]** $^+$) | 205.0525, 193.0521, 187.0416, 167.0730, 163.0420, 149.0618, | Literature [1,4] |
| | | 543.1480 ( **[M + Na]** $^+$) | 145.0310, 123.0464 | |
| | | | 543.1480 → 525.1374, 429.1148, 349.0897, 331.0797, 309.0975, 147.0448 | |
| 61. Acetyl-genipin-hexoside | 28.30 | 429.2134 ( **[M-H]** $^-$) | 429.2134 → 339.1816, 279.1105, 266.1548, 251.1283, 231.1349, 209.1181, | Level 2 |
| | | 475.2189 ( **[M + HCOOH-H]** $^-$) | 191.1082, 161.0463 | Literature [3,4] |
| | | 431.2281 ( **[M + H]** $^+$) | 475.2189 → **429.2133**, 411.2025, 339.1813, 309.1715, 279.1091, **267.1603**, | |
| | | 453.2100 ( **[M + Na]** $^+$) | 249.1504, 209.1187, 191.1082, 179.0569, 161.0465 | |
| | | | 431.2281 → **269.1752**, 251.1647, 233.1541, 215.1436, 207.1385, 205.1591, | |
| | | | 193.1127, 179.1072, 163.1125, 145.0505, 137.0966 | |
| 18. Sinapoyl-shanzhiside | 30.99 | 597.1836 ( **[M-H]** $^-$) | 597.1836 → **391.1263**, 325.0944, 295.0829, 265.0728, **229.0722**, **223.0622**, | Level 3 |
| | | 599.1959 ( **[M + H]** $^+$) | 205.0516, 185.0829, 167.0728 | |
| | | 621.1786 ( **[M + Na]** $^+$) | 599.1959 → 386.1118, 369.1196, **207.0655**, 195.0678, 177.0544 | |
| 19. Sinapoyl-gardoside | 32.20 | 579.1737 ( **[M-H]** $^-$) | 579.1737 → 535.1837, 385.1156, **367.1048**, 325.0936, 295.0832, 265.0726, | Level 2 |
| | | 581.1859 ( **[M + H]** $^+$) | **223.0618**, 205.0516, 193.0516, 167.0724, 149.0617, 123.0463 | Literature [4] |
| | | 603.1680 ( **[M + Na]** $^+$) | 581.1859 → **369.1180**, 352.1167, 226.0845, **207.0654**, 195.0657, 175.0397 | |

| Compounds | LC retention time (min) | MS adducts ($m/z$) | Key fragments ($MS^2$, $m/z$) | Level of identification* |
|---|---|---|---|---|
| 20. Sinapoyl-genipin-hexoside | 33.96 | 593.1537 ( **[M-H]** $^-$) | 593.1537 → 549.1612, **385.1164**, 367.1078, 343.1049, 325.0957, 295.0835, 265.0726, **223.0626**, 207.0309, 205.0518, 181.0520, 163.0424, 137.0263 | Level 2 Literature [4] |
| 21. Coumaroyl-genipin gentiobioside | 37.28 | 695.2232 ( **[M-H]** $^-$) 697.2331 ( **[M + H]** $^+$) 719.2145 ( **[M + Na]** $^+$) | 695.2232 → **469.1364**, **225.0782**, **163.0418**, 145.0313, 123.0466 697.2331 → 309.0969, 291.0860, 209.0808, 165.0542, 147.0440 | Level 2 Literature [1,4] |
| 22. Sinapoyl-genipin gentiobioside | 37.89 | 755.2423 ( **[M-H]** $^-$) 774.2807 ( **[M + $NH_4$]** $^+$) 779.2356 ( **[M + Na]** $^+$) | 755.2423 → **529.1548**, **225.0778**, **205.0505**, 123.0463 774.2807 → **369.1172**, **207.0652** | Level 2 Literature [1,4] |

(*continued on next page*)

**Table 2** (*continued*)

| Compounds | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|
| 24. Feruloyl-genipin-dihexoside | 38.25 | 725.2323 ( **[M-H]** $^-$) | 725.2323 → **499.1470**, **225.0779**, **193.0518**, 175.0414, 123.0466 | Level 2 |
| | | 727.2443 ( **[M + H]** $^+$) | 727.2443 → 339.1080, 321.0931, 299.0705, 209.0830, **195.0658**, 177.0545 | Literature [4] |
| | | 744.2705 ( **[M + $NH_4$]** $^+$) | 744.2705 → 339.1072, 177.0547 | |
| | | 749.2255 ( **[M + Na]** $^+$) | | |
| 27. Sinapoyl-geniposide | 42.10 | 593.1878 ( **[M-H]** $^-$) | 593.1878 → **367.1030**, 265.0723, **225.0772**, **223.0614**, **205.0506**, 123.0459 | Level 2 |
| | | 595.2023 ( **[M + H]** $^+$) | 595.2023 → **369.1189**, 351.1072, **207.0654** | Literature [1,4] |
| | | 617.1840 ( **[M + Na]** $^+$) | 617.1840 → 409.1103 | |
| 28. Cinnamoyl-genipin-dihexoside | 47.93 | 679.2269 ( **[M-H]** $^-$) | 679.2269 → **531.1691**, **355.1160**, **225.0791**, **207.0688**, **147.0461**, 123.0469 | Level 2 |
| | | 725.2321 ( **[M + HCOOH-H]** $^-$) | 725.2321 → **679.2272**, 531.1734, 355.1192, **225.0782**, **147.0465**, 123.0468 | Literature [1,4] |
| | | 681.2402 ( **[M + H]** $^+$) | 681.2402 → 429.0905, 293.1020, 207.0634, 177.0566, 131.0497 | |
| | | 698.2654 ( **[M + $NH_4$]** $^+$) | 698.2654 → 703.2218, 681.1732, 456.1604, 360.0996, 293.1028, 275.0931, | |
| | | 703.2209 ( **[M + Na]** $^+$) | 207.0660, 149.0604, 131.0495 | |
| **Seco-iridoids** | | | | |
| 7. Jasminoside B/D/G 1 | 8.37 | 345.1559 ( **[M-H]** $^-$) | 345.1559 → **165.0929**, 119.0359, 127.0410 | Level 2 |
| | | 691.3190 ( **[2 M-H]** $^-$) | 364.1969 → **167.1072**, 149.0967, 145.0501, 139.1124, 123.1175, 121.1019 | Literature [4] |
| | | 347.1705 ( **[M + H]** $^+$) | 369.1523 → **167.1072** | |
| | | 364.1969 ( **[M + $NH_4$]** $^+$) | | |
| | | 369.1523 ( **[M + Na]** $^+$) | | |

| Compounds | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|
| 10. Jasminoside B/D/G 2 | 10.97 | 345.1572 ( **[M-H]** $^-$) | 345.1572 → 282.3301, 213.8836, 152.9035, 149.0488 | Level 2 |
| | | 391.1625 ( **[M + HCOOH-H]** $^-$) | 391.1625 → 345.1530, 179.0570, **165.0935**, 161.0469, 153.0937 | Literature [4] |
| | | 347.1697 ( **[M + H]** $^+$) | 347.1697 → 185.1171, **167.1064**, 149.0960, 137.0963, 121.1014 | |
| | | 369.1515 ( **[M + Na]** $^+$) | | |
| 14. Jasminoside A/E/K 1 | 20.13 | 375.1663 ( **[M + HCOOH-H]** $^-$) | 375.1663 → 324.3134, 318.2457, 309.8141, 281.8340, 179.0541, 161.0507, | Level 2 |
| | | 331.1755 ( **[M + H]** $^+$) | 149.0483, 145.2928, 136.5749, 131.0348, 120.0405 | Literature [4] |
| | | 353.1573 ( **[M + Na]** $^+$) | 331.1755 → **169.1227**, 151.1121, 139.1120, 123.1173 | |
| 15. Jasminoside A/E/K 2 | 20.72 | 375.1681 ( **[M + HCOOH-H]** $^-$) | 375.1681 → 371.7825, 360.8173, 347.8468, 342.8137, 314.5730, 311.9027, | Level 2 |
| | | 331.1756 ( **[M + H]** $^+$) | 297.8619, 280.8647, 179.0547, 160.1994, 149.0459, 120.7901 | Literature [4] |
| | | 353.1575 ( **[M + Na]** $^+$) | 331.1756 → **169.1228**, 151.1122, 139.1124, 123.1172 | |
| 25. Sinapoyl-jasminoside B/D/G/L 1 | 39.87 | 551.2147 ( **[M-H]** $^-$) | 551.2147 → 533.2039, 521.2035, 367.1043, **223.0621**, **205.0512**, 190.0276, | Level 2 |
| | | 553.2281 ( **[M + H]** $^+$) | **165.0932** | Literature [4] |
| | | 575.2101 ( **[M + Na]** $^+$) | 553.2281 → 369.1181, 351.1077, **207.0654**, 175.0394, **167.1070** | |
| 26. Sinapoyl-jasminoside B/D/G/L 2 | 40.38 | 551.2143 ( **[M-H]** $^-$) | 551.2143 → 385.1148, 325.0934, 295.0826, 265.0722, **223.0617**, **205.0511**, | Level 2 |
| | | 553.2284 ( **[M + H]** $^+$) | **165.0930** | Literature [4] |
| | | 575.2102 ( **[M + Na]** $^+$) | 553.2284 → 369.1180, 351.1085, **207.0655**, 175.0396, **167.1073** | |
| 29. Sinapoyl-jasminoside A/E/K | 49.09 | 535.2201 ( **[M-H]** $^-$) | 535.2201 → 385.1165, 325.0942, 295.0835, 265.0729, **223.0622**, **205.0515** | Level 2 |
| | | 537.2340 ( **[M + H]** $^+$) | 537.2340 → 369.1195, **207.0660**, 175.0398, **169.1234** | Literature [4] |
| | | 559.2162 ( **[M + Na]** $^+$) | | |
| **other iridoids** | | | | |
| 13. unknown iridoid | 19.51 | 385.1162 ( **[M-H]** $^-$) | 385.1162 → 223.0630, 208.0391, 205.0513, 179.0705, 164.0486 | Level 3 |
| | | 404.1548 ( **[M + $NH_4$]** $^+$) | 409.1099 → 247.0570, 215.0315, 211.0949, 185.0416 | |
| | | 409.1099 ( **[M + Na]** $^+$) | | |
| 17. unknown coumaroyl iridoid | 27.71 | 521.1683 ( **[M-H]** $^-$) | 521.1683 → 477.1747, 375.1312, 357.1202, 329.1406, 307.0811, 213.0775, | Level 3 |
| | | 545.1994 ( **[M + Na]** $^+$) | 169.0878, **163.0411**, 151.0776, 145.0306, 125.0619 | |

| Compounds | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|
| 23. unknown sinapoyl iridoid 1 | 38.13 | 563.1793 ( **[M-H]** $^-$) | 563.1793 → 545.1674, 367.1046, **223.0622**, **205.0516**, 195.0672, 180.0439 | Level 3 |
| | | 587.1727 ( **[M + Na]** $^+$) | 587.1727 → 391.0997 | |
| 62. unknown sinapoyl iridoid 2 | 48.09 | 787.2836 ( **[M-H]** $^-$) | 787.2836 → 385.1159, 325.0940, 295.0845, 265.0732, **223.0625**, **205.0516**, | Level 3 |
| | | 789.2965 ( **[M + H]** $^+$) | 146.9683 | |
| | | 811.2787 ( **[M + Na]** $^+$) | 789.2965 → 455.1709, 420.1776, 401.1604, 385.1668, 369.1181, 267.1228, | |
| | | | 249.1133, 233.0831, **207.0657** | |
| **Hydroxycinnamic acids** | | | | |
| 30. 5-*O*-Caffeoylquinic acid | 8.95 | 353.0892 ( **[M-H]** $^-$) | 353.0892 → **191.0566**, 179.0363, 135.0455 | Level 2 |
| | | 707.1793 ( **[2 M-H]** $^-$) | | Literature [6,9] |
| 31. 3-*O*-Caffeoylquinic acid | 14.84 | 353.0898 ( **[M-H]** $^-$) | 353.0898 → **191.0576** | Level 1 |
| | | 707.1857 ( **[2 M-H]** $^-$) | 355.1019 → **163.0389**, 145.0285, 135.0441 | Literature [5,6,9] |
| | | 355.1019 ( **[M + H]** $^+$) | | |
| | | 377.0839 ( **[M + Na]** $^+$) | | |
| 32. 4-*O*-Caffeoylquinic acid | 15.87 | 353.0896 ( **[M-H]** $^-$) | 353.0896 → **191.0574**, 179.0369, 173.0469, 135.0464 | Level 2 |
| | | 707.1841 ( **[2 M-H]** $^-$) | 355.1025 → **163.0389**, 145.0283, 135.0453 | Literature [6,9] |
| | | 355.1025 ( **[M + H]** $^+$) | | |
| | | 377.0846 ( **[M + Na]** $^+$) | | |
| 33. Ferulic acid-hexoside | 17.05 | 355.1048 ( **[M-H]** $^-$) | 355.1048 → **193.0517**, 175.0416, 160.0183, 134.0391 | Level 2 |
| | | 379.1000 ( **[M + Na]** $^+$) | 379.1000 → 235.0575, 217.0474, 203.0527, 185.0423, 177.0556 | Literature [6] |

(*continued on next page*)

**Table 2** (*continued*)

| Compounds | LC retention time (min) | MS adducts (*m/z*) | Key fragments ($MS^2$, *m/z*) | Level of identification* |
|---|---|---|---|---|
| 34. Sinapic acid-hexoside 1 | 18.50 | 385.1150 ( **[M-H]** $^-$) 409.1108 ( **[M + Na]** $^+$) | 385.1150 → **223.0618**, **205.0513**, 190.0278, 175.0051, 164.0488 409.1108 → 381.0760, 353.0814, 327.0657, 265.0684, 247.0579, **207.0655**, 185.0424 | Level 2 Literature [7] |
| 35. Sinapic acid-hexoside 2 | 20.68 | 385.1142 ( **[M-H]** $^-$) 409.1109 ( **[M + Na]** $^+$) | 385.1142 → 325.0934, 265.0722, **223.0613**, **205.0508**, 190.0272, 179.0720, 164.0487, 149.0251 409.1109 → **207.0652** | Level 2 Literature [7] |
| 36. Sinapic acid-hexoside 3 | 22.39 | 385.1145 ( **[M-H]** $^-$) 387.1292 ( **[M + H]** $^+$) 409.1109 ( **[M + Na]** $^+$) | 385.1145 → 325.0930, 295.0830, 265.0721, 247.0605, **223.0615**, **205.0510**, 190.0272, 179.0718, 164.0491, 149.0256 387.1292 → 351.1078, 224.0690, **207.0657**, 175.0396, 147.0449 409.1109 → **207.0662** | Level 2 Literature [7] |
| 38. Dicaffeoylquinic acid 1 | 34.36 | 515.1207 ( **[M-H]** $^-$) | 515.1207 → **353.0888**, **191.0567**, 179.0356, 135.0462 | Level 2 Literature [5,6,9] |
| 39. Dicaffeoylquinic acid 2 | 37.55 | 515.1216 ( **[M-H]** $^-$) | 515.1216 → **353.0894**, **191.0577**, 179.0366, 173.0476, 135.0463 | Level 2 Literature [5,6,9] |
| 40. Dicaffeoyl-hydroxy-methylglutaroyl-quinic acid | 40.33 | 659.1646 ( **[M-H]** $^-$) 661.1765 ( **[M + H]** $^+$) 683.1582 ( **[M + Na]** $^+$) | 659.1646 → **497.1312**, **353.0890**, 335.0858, **191.0570**, 161.0466 661.1765 → 517.1360, 499.1231, 463.1240, 355.1031, 343.0808, 337.0930, 325.0707, 319.1029, 301.0917, 283.0808, 193.0712, 163.0396 | Level 2 Literature [3,5] |
| **Flavonols** | | | | |
| 41. Quercetin-hexoside-deoxyhexoside | 28.69 | 609.1484 ( **[M-H]** $^-$) 611.1611 ( **[M + H]** $^+$) 633.1429 ( **[M + Na]** $^+$) | 609.1484 → **300.0288** 611.1611 → **465.1035**, **303.0505** | Level 2 Literature [5,6] |
| 42. Quercetin 3-*O*-rutinoside | 29.25 | 609.1492 ( **[M-H]** $^-$) 611.1605 ( **[M + H]** $^+$) 633.1424 ( **[M + Na]** $^+$) | 609.1492 → **301.0365** 611.1605 → **465.1033**, **303.0505** | Level 1 Literature [5,6] |
| 43. Quercetin 3-*O*-glucoside | 30.20 | 463.0902 ( **[M-H]** $^-$) 927.1847 ( **[2 M-H]** $^-$) 465.1030 ( **[M + H]** $^+$) 487.0849 ( **[M + Na]** $^+$) | 463.0902 → **300.0290** 465.1030 → **303.0501** | Level 1 Literature [5,6] |
| **Crocins** | | | | |
| 44. Crocin I | 43.18 | 975.3715 ( **[M-H]** $^-$) 1021.3766 ( **[M + HCOOH-H]** $^-$) 994.4120 ( **[M + $NH_4$]** $^+$) 999.3671 ( **[M + Na]** $^+$) | 975.3715 → 651.2659, 341.1097, **323.0988**, 179.0565 994.4120 → 999.3668, 649.2195, 487.1665, **329.1753**, **325.1136**, 311.1648, 289.0927, 163.0607 999.3671 → 675.2630, 487.1663, **329.1753**, **325.1136**, 311.1649 | Level 1 Literature [3,8,9] |
| 45. Crocetin-dihexoside-dihexoside 1 | 44.30 | 975.3701 ( **[M-H]** $^-$) 999.3677 ( **[M + Na]** $^+$) | 975.3701 → 915.3520, 693.2816, 651.2671, 591.2401, **323.0988**, 305.0863, 251.0775, 179.0570, 146.9673 999.3677 → 649.3022 | Level 2 Literature [8] |
| 46. unknown crocin 1 | 45.90 | 945.3593 ( **[M-H]** $^-$) 964.4005 ( **[M + $NH_4$]** $^+$) 969.3570 ( **[M + Na]** $^+$) | 945.3593 → 651.2659, 621.2556, **323.0979**, 179.0578, 146.9670 964.4005 → 969.3541, 930.0114, 896.5432, 501.2039, 458.1648, **329.1742**, **325.1124**, 311.1646, 295.1035, 259.0847, 249.1152, 225.0756, 151.0755 969.3570 → 675.2650, **329.1756** | Level 3 |
| 47. Crocin II | 47.28 | 813.3203 ( **[M-H]** $^-$) 859.3256 ( **[M + HCOOH-H]** $^-$) 832.3600 ( **[M + $NH_4$]** $^+$) 837.3147 ( **[M + Na]** $^+$) | 813.3203 → 651.2672, 489.2154, **327.1619**, **323.1004**, 283.1731, 221.0681, 179.0579 859.3256 → 813.3183, 651.2676, 489.2153, **327.1615**, **323.1002**, 221.0679, 179.0579 832.3600 → 837.3139, 675.2647, 513.2096, **329.1752**, 311.1648, 293.1545, 163.0615, 145.0502 837.3147 → 675.2623, 513.2107, **329.1753** | Level 1 Literature [3,8,9] |
| 48. Crocetin-dihexoside-dihexoside 2 | 49.06 | 975.3708 ( **[M-H]** $^-$) 994.4129 ( **[M + $NH_4$]** $^+$) 999.3660 ( **[M + Na]** $^+$) | 975.3708 → 651.2670, **327.1605** 994.4129 → 999.3590, 635.2677, 487.1684, **329.1755**, **325.1139**, 311.1652, 293.1533, 289.0933, 163.0621 999.3660 → 488.1685, **329.1741**, 326.1164, 312.1686, 163.0569 | Level 2 Literature [8] |
| 49. Crocetin-dihexoside 1 | 49.58 | 651.2673 ( **[M-H]** $^-$) 697.2722 ( **[M + HCOOH-H]** $^-$) 675.2621 ( **[M + Na]** $^+$) | 697.2722 → 489.2148, 369.1719, **327.1606**, 283.1725, 207.0521, 161.0468 675.2621 → 513.2094, 351.1570 | Level 2 Literature [8] |
| 50. Crocetin-dihexoside-sinapoyl-dihexoside | 49.69 | 1181.4281 ( **[M-H]** $^-$) 1205.4250 ( **[M + Na]** $^+$) | 1181.4281 → 857.3149, 651.2674, 529.1540, **327.1585**, 146.9675 1205.4250 → 937.6451, 693.2277, 531.1699, 513.1603, 369.1158, **207.0654** | Level 2 Literature [8] |
| 51. unknown crocin 2 | 50.19 | 1007.3778 ( **[M-H]** $^-$) | 1007.3778 → 683.2688, 146.9679 | Level 3 |

| Compounds | LC retention time (min) | MS adducts ($m/z$) | Key fragments ($MS^2$, $m/z$) | Level of identification* |
|---|---|---|---|---|
| 52. Crocetin-dihexoside-dihexoside 3 | 51.11 | 975.3715 ( **[M-H]** $^-$)<br>994.4115 ( **[M + NH$_4$]** $^+$)<br>999.3666 ( **[M + Na]** $^+$) | 975.3715 → 651.2675, 341.1104, **327.1618**<br>994.4115 → 649.2184, 487.1665, **329.1753**, **325.1134**, 311.1647, 293.1542, 289.0928, 163.0609<br>999.3666 → 488.1711, **329.1757**, **325.1135**, 311.1643, 163.0611 | Level 2<br>Literature [8] |
| 53. unknown crocin 3 | 51.76 | 1021.3922 ( **[M-H]** $^-$)<br>1067.3985 ( **[M + HCOOH-H]** $^-$) | 1021.3922 → 697.2891, 651.2768, 341.1133, **323.0998**, 225.0776, 179.0577, 146.9679<br>1067.3985 → 1021.3910, 697.2916, 341.1078, 323.0965, 179.0583, 146.9676 | Level 3 |
| 54. Crocetin-dihexoside-caffeoylquinic acid | 52.13 | 987.3500 ( **[M-H]** $^-$)<br>1011.3471 ( **[M + Na]** $^+$) | 987.3500 → 825.3200, 663.2434, 501.2173, 146.9672<br>1011.3471 → 635.2745, 473.2190, **325.1121**, 311.1643, 163.0611 | Level 2<br>Literature [8] |
| 55. Crocetin-dihexoside 2 | 52.20 | 651.2689 ( **[M-H]** $^-$)<br>697.2471 ( **[M + HCOOH-H]** $^-$)<br>670.3080 ( **[M + NH$_4$]** $^+$)<br>675.2625 ( **[M + Na]** $^+$) | 651.2689 → 369.1728, **327.1618**, **323.0985**, 283.1722, 263.0777, 239.1820, 221.0700, 179.0581<br>697.2471 → 651.2687, 369.1740, **327.1618**, **323.1001**, 283.1720, 239.1822, 221.0685, 179.0581<br>670.3080 → 675.2621, 347.0957, **329.1751**, 311.1652, 293.1542, 283.1708, 275.1441, 265.1587, 229.1229, 163.0610, 145.0503<br>675.2625 → 347.0955 | Level 2<br>Literature [8] |
| 56. Crocetin-dihexoside-hexoside 1 | 52.52 | 813.3203 ( **[M-H]** $^-$)<br>859.3241 ( **[M + HCOOH-H]** $^-$)<br>832.3598 ( **[M + NH$_4$]** $^+$)<br>837.3150 ( **[M + Na]** $^+$) | 813.3203 → 651.2682, 489.2147, **327.1621**, 179.0568, 146.9691<br>832.3598 → 837.3137, 473.2168, 355.0710, **329.1749**, **325.1130**, 311.1643, 293.1540, 283.1712, 229.1253, 163.0617, 145.0508<br>837.3150 → 675.2532 | Level 2<br>Literature [8] |
| 57. Crocetin-dihexoside-hexoside 2 | 52.62 | 813.3209 ( **[M-H]** $^-$)<br>832.3592 ( **[M + NH$_4$]** $^+$)<br>837.3148 ( **[M + Na]** $^+$) | 813.3209 → 651.2686, 489.2150, 327.1619, 179.0574, 146.9687<br>832.3592 → 837.3121, 473.2164, 355.0687, **329.1744**, **325.1131**, 311.1642, 293.1538, 283.1684, 229.1231, 163.0606, 145.0497 | Level 2<br>Literature [8] |

| Compounds | LC retention time (min) | MS adducts ($m/z$) | Key fragments ($MS^2$, $m/z$) | Level of identification* |
|---|---|---|---|---|
| 58. Crocetin-hexoside | 55.19 | 489.2153 ( **[M-H]** $^-$)<br>535.2205 ( **[M + HCOOH-H]** $^-$)<br>490.2198 ( **[M + H]** $^+$)<br>513.2099 ( **[M + Na]** $^+$) | 489.2153 → 387.7939, **327.1593**, 283.1708, 239.1823<br>535.2205 → 489.2208, 369.1739, **327.1599**, 283.1727, 265.1599, 239.1803<br>513.2099 → 351.1571, 185.0427 | Level 2<br>Literature [3,8] |
| 59. Crocetin-dihexoside 3 | 56.38 | 651.2673 ( **[M-H]** $^-$)<br>675.2620 ( **[M + Na]** $^+$) | 651.2673 → 369.1748, **327.1615**, **323.0990**, 283.1706, 239.1827, 221.0672, 179.0569, 161.0486<br>675.2620 → 347.0950 | Level 2<br>Literature [8] |
| 60. Crocetin-dihexoside 4 | 56.89 | 651.2672 ( **[M-H]** $^-$)<br>675.2619 ( **[M + Na]** $^+$) | 651.2672 → 369.1714, **327.1606**, **323.0992**, 283.1709, 239.1799, 221.0670, 179.0581<br>675.2619 → 347.0962 | Level 2<br>Literature [8] |

* Identification levels are assigned according to Metabolomics Standards Initiative (MSI) guidelines: Identified compounds confirmed with authentic standards (Level 1), identified compounds based on previous research (Level 2), and putatively characterized compounds (Level 3).
Reference literature includes: 1. Fu et al., 2014; 2. Zhou et al., 2010; 3. Bergonzi et al., 2012; 4. Tian, Kriisa, et al., 2022; 5. Liu et al., 2021; 6. Tian et al., 2017; 7. Tian, Qin, et al., 2022; 8. Ni et al., 2017; 9. Shan et al., 2019

$m/z$ 353, and [M-H-162-162]$^-$ at $m/z$ 191 (W. He et al., 2010). Compound 40 ($C_{31}H_{32}O_{16}$) was defined as the hydroxy-methylglutaroyl derivative of di-caffeoylquinic acid. The precursor ion ([M-H]$^-$ at $m/z$ 659) sequentially lost one caffeoyl unit ([M-H-162]$^-$ at $m/z$ 497), one hydroxy-methylglutaroyl group ([M-H-162-144]$^-$ at $m/z$ 353), and one caffeoyl unit ([M-H-162-144-162]$^-$ at $m/z$ 191).

Other hydroxycinnamic acids found in the extracts were presented mostly in the form of sugar esters, such as feruloyl- or sinapoyl-hexoside (compounds 33–36). These esters shared a similar MS fragmentation pattern, all producing [M-H-162]$^-$ in the $MS^2$ spectra due to hexoside cleavage. The ions of [M-H-162]$^-$ at $m/z$ 193 (for compound 33) and 223 (compounds 34, 35, and 36) suggested the acid moieties were ferulic acid and sinapic acid, respectively (Tables 1 & 2).

### 3.2.3. Flavonols

The major flavonols presented in GF and GFV extracts were glycosides of quercetin (compounds 41–43). The ions at $m/z$ 303 were observed in the $MS^2$ spectra of all these compounds, proving the presence of quercetin (Tables 1 & 2). The structures of compounds 42 (defined as quercetin 3-*O*-rutinoside) and 43 (quercetin 3-*O*-glucoside) were determined by comparing fragmentation pattern with authentic standards. Compound 41 was identified as quercetin-hexoside-deoxyhexoside. It had [M + H]$^+$ at $m/z$ 611 and [M + H-162-146]$^+$ at $m/z$ 303 that were similar to quercetin 3-*O*-rutinoside.

### 3.2.4. Crocins

Compounds 44–60 were defined as crocins due to maximum UV absorption at around 440 nm and typical ions of crocetin unit (detected at $m/z$ 329 and 325 under ESI$^+$ mode or $m/z$ 327 and 323 under ESI$^-$ mode, Table 2).

Crocin I (Compound 44) produced the ions at $m/z$ 999 ([M + Na]$^+$), 675 ([M + Na-162-162]$^+$), and 329 ([M + H-162-162-162-162]$^+$), which indicated a gentiobiose substituted at each site of crocetin backbone (Xiao et al., 2017). Compounds 45, 48, and 52 were identified as crocin I isomers ($C_{44}H_{64}O_{24}$; crocetin-dihexoside-dihexoside 1, 2, and 3), displaying different MS fragmentation patterns from crocin I (Table 2). Unfortunately, their structural arrangement and substituted sugar moieties were not able to determine with mass spectrometry only.

Compounds 47, 56, and 57 ($C_{38}H_{54}O_{19}$) were isomers of crocetin-dihexoside-hexoside. All these compounds had molecular ions of [M-H]$^-$ at $m/z$ 813 and [M + Na]$^+$ at $m/z$ 837 (Table 2). Other negative ions were also observed at $m/z$ 651 ([M-H-162]$^-$), 489 ([M-H-162-162]$^-$), and 327 ([M-H-162-162-162]$^-$). Compound 47 was further defined as crocin II based on the same fragmentation pattern as authentic standard.

Compounds 49, 55, 59, and 60 ($C_{32}H_{44}O_{14}$) were found in the samples ([M + Na]$^+$ at $m/z$ 675, [M-H]$^-$ at $m/z$ 651; Table 2) with a similar

molecular weight of crocin III, a *β-D*-gentiobiosyl-*trans*-crocetin ester (652.7 g/mol). Nevertheless, due to lack of authentic standard, these compounds were tentatively identified as crocetin-dihexoside isomer 1–4, respectively.

In addition to glycosylation, the crocetin in *G. jasminoides* can also conjugate to hydroxycinnamic acids and form acylated derivatives (Table 2). The acylation occurred either on the hydroxy group of sugar moieties (such as crocetin-dihexoside-sinapoyl-dihexoside, compound 50) or on the carboxyl group of crocetin (crocetin-dihexoside-caffeoylquinic acid, compound 54). Compound 50 had the $[M\text{-}H]^-$ ion at *m/z* 1181 and $[M\text{-}H\text{-}162\text{-}162\text{-}206]^-$ at *m/z* 651 (loss of two hexoside groups and a sinapoyl group). Compound 54 (with $[M\text{-}H]^-$ at *m/z* 987) produced the fragment ions at *m/z* 663 as lack of a di-hexoside group. The difference between the *m/z* 501 and 147 ions indicated the loss of a caffeoylquinic acid unit.

### 3.3. Chemical composition of hulls and dehulled fruits

The concentration of each identified compound in extracts is given in Supplemental Table 4–6. Three extraction solvents, 50% aqueous methanol, 80% aqueous methanol, and absolute methanol, had different effects on these chemical components. For most of identified compounds, their contents in the 100% methanolic extracts were remarkably lower than those found in samples extracted with 50% or 80% methanol. Higher extraction efficiency with aqueous methanol compared to pure methanol has been observed in previous research (Kyriakoudi et al., 2012; Tian, Kriisa, et al., 2022). This can be mechanistically explained by solvent polarity effects. Since crocins, iridoid glycosides, hydroxycinnamic acids, and flavonol glycosides are all highly polar compounds, the presence of water increases the polarity of the extraction solvent, enhancing solubilization and release of polar compounds from plant tissues. Therefore, in the following sections, the comparison among extracts or phytochemicals was made only based on the extracts using 50% and 80% methanol.

Fig. 1 shows the total contents of iridoids, crocins, hydroxycinnamic acids, and flavonols in GF and GFV extracts. The total content was calculated as the sum of the concentrations of identified compounds within the same group. Iridoids were the primary phytochemicals presented in both GF and GFV samples. The total content of iridoids ranged from 70.9 ± 0.4 to 74.6 ± 1.0 mg/g dry weight (DW) in dehulled fruits and from 61.4 ± 0.7 to 65.6 ± 0.3 mg/g DW in hulls (Fig. 1a). Crocins were the second most abundant phytochemicals. The highest level of crocins were found in the extract of GF fruits at a total concentration of 19.4 ± 1.8 mg/g DW (in 80% methanol extract, MeOH) and 21.2 ± 1.2 mg/g DW (50% MeOH). It was followed by GF hulls (16.4 ± 0.2 mg/g DW in 50% MeOH to 16.5 ± 0.3 mg/g DW in 80% MeOH), GFV fruits

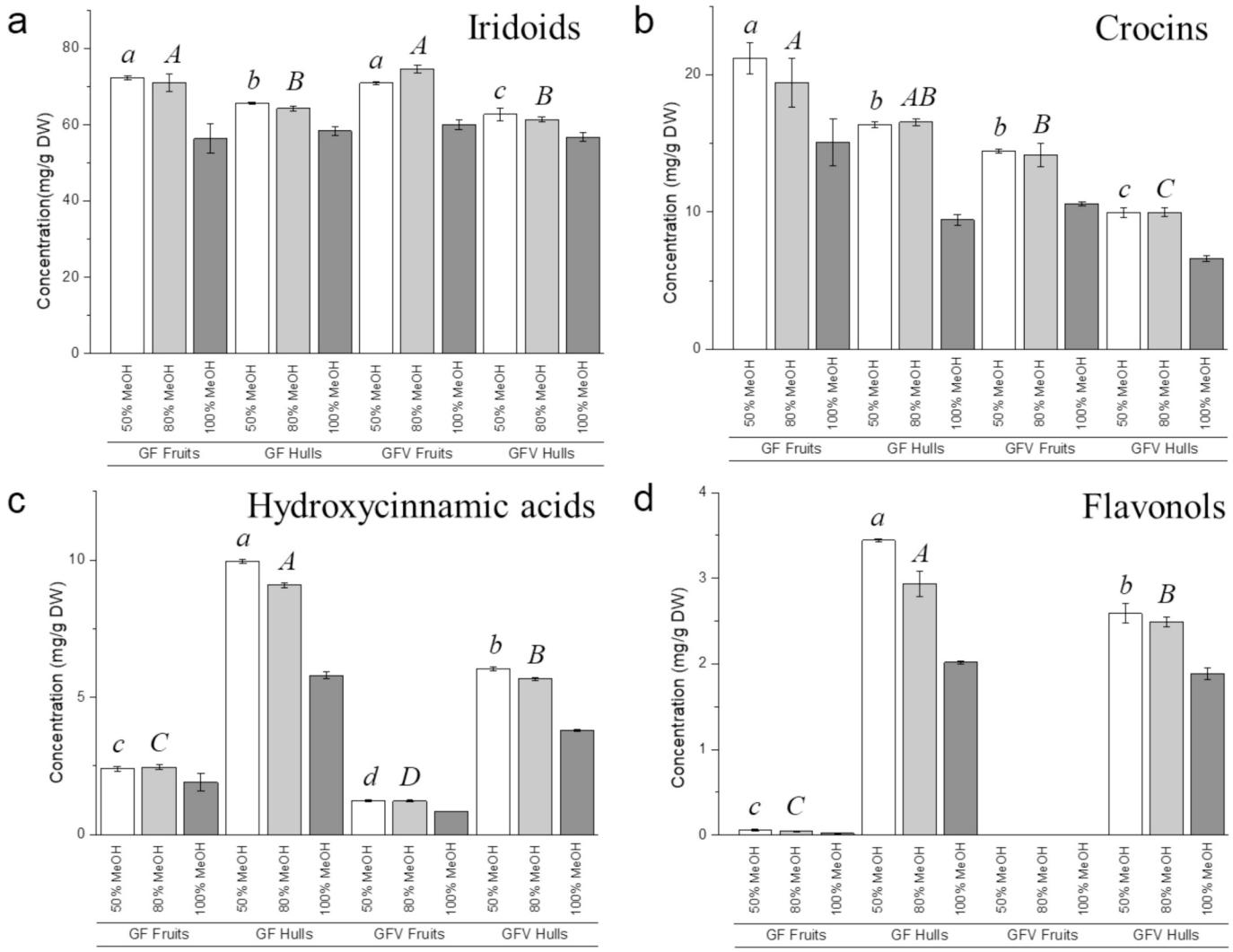



**Fig. 1.** Total contents of iridoids (a), crocins (b), hydroxycinnamic acids (c), and flavonols (d) in the different extracts of dehulled fruits and hulls. Statistical differences are based on one way-ANOVA and Tukey's *post hoc* test ($p < 0.05$). The differences among 50% or 80% methanol extracts are shown with letters *a-d* or *A-D*, respectively. Results represent mean values of three biological replicates ($n = 3$); corresponding SD values are provided in Supplemental Table 4–6.

(14.5 ± 0.1 mg/g DW in 50% MeOH and 14.1 ± 0.8 mg/g DW in 80% MeOH), and GFV hulls (10.0 ± 0.3 mg/g DW in both extracts, Fig. 1b).

As the minor groups, the contents of hydroxycinnamic acids and flavonols varied widely among extracts. The compounds from these two groups were present predominantly in the fraction of hulls rather than fruits. Among the GF extracts, the hulls contained 9.1 ± 0.1 to 10.0 ± 0.1 mg/g DW of hydroxycinnamic acids, which was approximately four times higher than that detected in the fruits. A similar result was also observed in the GFV samples. The total concentration of hydroxycinnamic acids was up to 6.0 ± 0.1 mg/g DW in hulls and 1.23 ± 0.03 mg/g DW in dehulled fruits, respectively (Fig. 1c). Higher content of flavonols were measured from the hull extracts of GF and GFV (3.44 ± 0.02 mg/g DW and 2.6 ± 0.1 mg/g DW, respectively), whereas only a trace amount of which was presented in the corresponding fruits (Fig. 1d).

Iridoids may accumulate preferentially in the fruits as part of defense and signaling functions, while phenolic acids and flavonols are enriched in hulls where they serve as protective antioxidants against UV radiation and microbial stress. Such tissue-targeted accumulation of specialized metabolites reflects the differential regulation of secondary metabolic pathways across plant tissues, with biosynthetic enzymes showing distinct spatial expression patterns that drive metabolite partitioning and ecological function (Erb & Kliebenstein, 2020). Minor components such as dicaffeoyl-hydroxy-methylglutaroyl-quinic acid (diCa-hmg-QA) and quercetin glycosides were concentrated in hulls, suggesting that these by-products might have significant value as sources of antioxidative phenolics. This supports the potential for fraction-specific utilization rather than discarding hulls as waste. Crocins, glycosylated carotenoids responsible for color and potential antioxidant activity, were more abundant in GF than GFV, indicating a genotype effect. The higher crocin content in GF may relate to upregulated carotenoid cleavage dioxygenases or glycosyltransferases in this variety, as suggested by previous transcriptomic studies of *Gardenia* fruits. From a functional perspective, these differences could impact the antioxidative activities and color-related properties of extracts, which are relevant for food and nutraceutical application (Xu et al., 2023).

Fig. 2 represents the detailed compound profiles in the 50% aqueous methanolic extracts. In the dehulled GF fruits (Fig. 2a), iridoids were presented predominantly as geniposide (Gpo, 43.9 ± 0.9 mg/g DW), which accounted for 46% of the total content of identified phytochemicals. Crocin I (Cri I, 16.1 ± 1.0 mg/g DW), as the second abundant compound, represented 17% of total phytochemicals. Genipin gentiobioside (Gpi-Gen) and its coumaroyl derivative (coumaroyl-genipin gentiobioside, co-Gpi-Gen) were also detected at high amounts (6.6 ± 0.8 mg/g DW and 4.1 ± 0.5 mg/g DW, respectively). The hull fraction of GF mainly contained Gpo (28.0 ± 0.6 mg/g DW), Gde (gardenoside, 18.6 ± 0.2 mg/g DW), and Cri I (11.2 ± 0.1 mg/g DW) (Fig. 2b). These

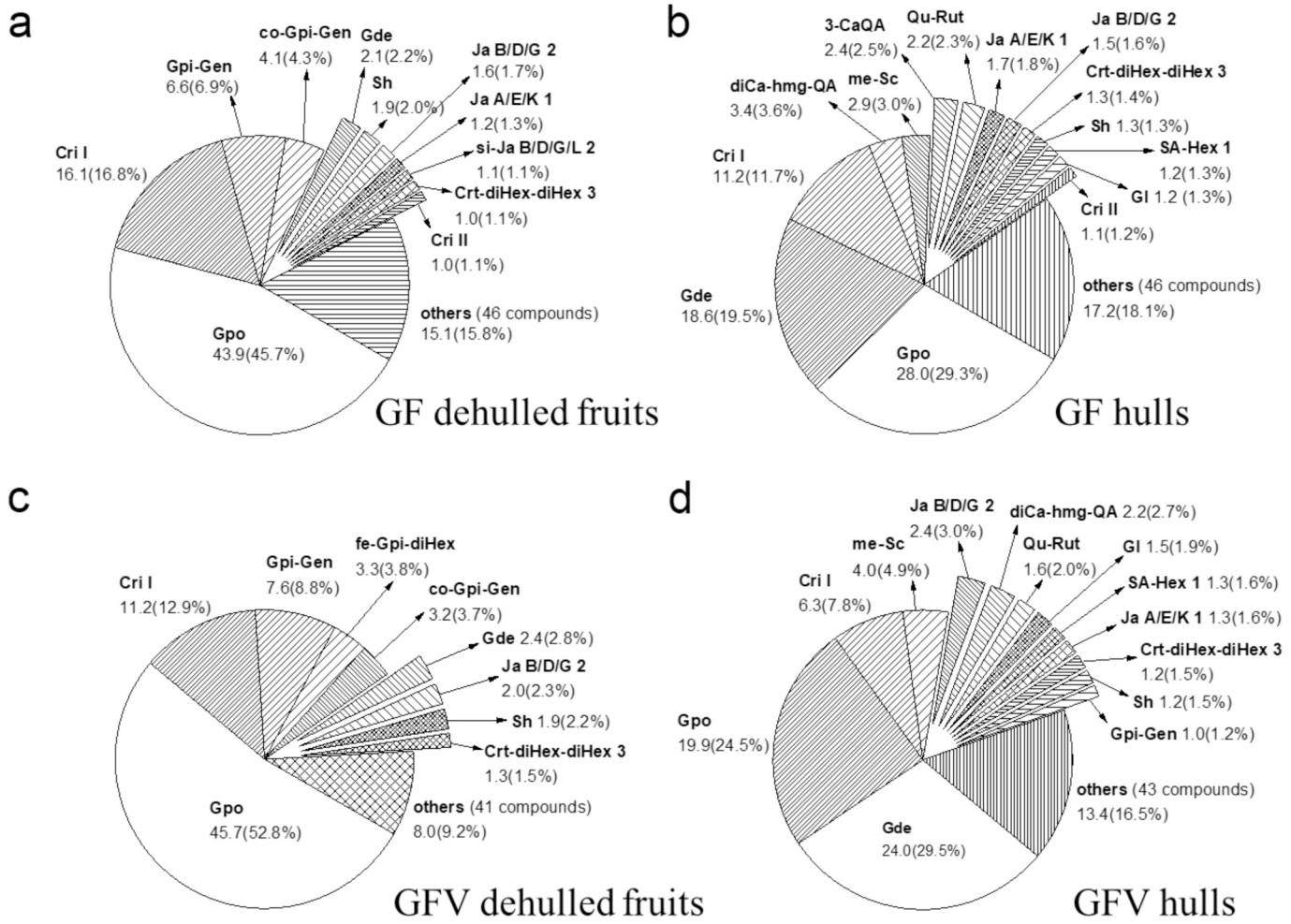
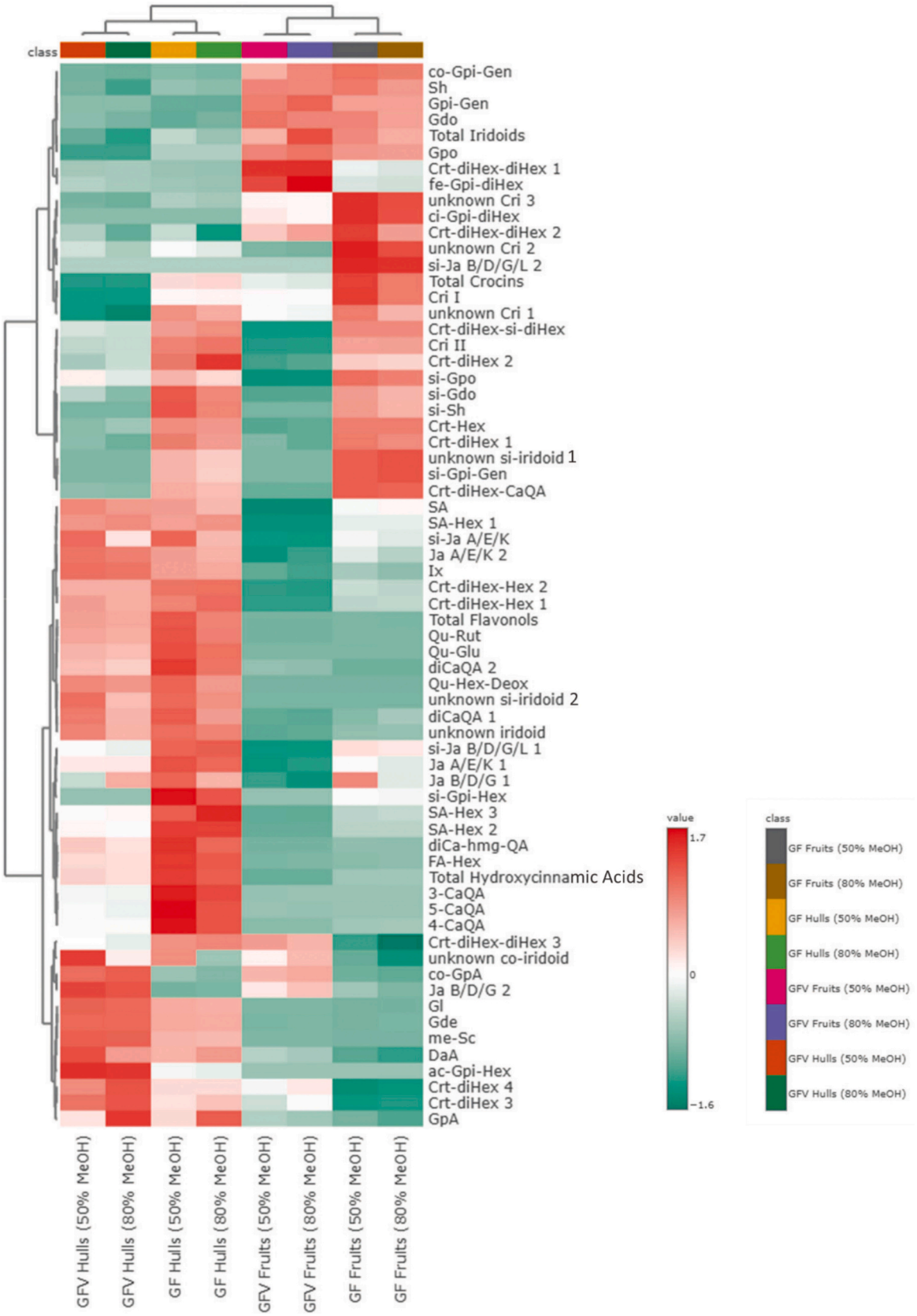



**Fig. 2.** Concentration (> 1 mg/g DW) and percentage of major compounds in the 50% aqueous methanolic extracts of GF (a, dehulled fruits; b, hulls) and GFV (c, dehulled fruits; d, hulls): The compounds include **Sh** (shanzhiside), **me-Sc** (scandoside methyl ester), **Gde** (gardenoside), **Gl** (galioside), **Ja B/D/G 2** (jasminoside B/D/G 2), **Gpi-Gen** (genipin gentiobioside), **Gpo** (geniposide), **Ja A/E/K 1** (jasminoside A/E/K 1), **co-Gpi-Gen** (coumaroyl-genipin gentiobioside), **fe-Gpi-diHex** (feruloyl-genipin-dihexoside), **si-Ja B/D/G/L 2** (sinapoyl-jasminoside B/D/G/L 2), **3-CaQA** (3-*O*-caffeoylquinic acid), **SA-Hex 1** (sinapic acid-hexoside 1), **diCa-hmg-QA** (dicaffeoyl-hydroxy-methylglutaroyl-quinic acid), **Qu-Rut** (quercetin 3-*O*-rutinoside), **Cri I** (crocin I), **Cri II** (crocin II), **Crt-diHex-diHex 3** (crocetin-dihexoside-dihexoside 3). Percentages represent mean values of three biological replicates (n = 3); corresponding SD values are provided in Supplemental Table 4.




(caption on next page)

**Fig. 3.** Hierarchical clustering heatmap for comparison among different extracts: The compounds include **DaA** (deacetylasperulosidic acid), **Gdo** (gardoside), **Sh** (shanzhiside), **GpA** (geniposidic acid), **me-Sc** (scandoside methyl ester), **Gde** (gardenoside), **Ja B/D/G 1** (jasminoside B/D/G 1), **Ix** (ixoroside), **Gl** (galioside), **Ja B/D/G 2** (jasminoside B/D/G 2), **Gpi-Gen** (genipin gentiobioside), **Gpo** (geniposide), **Ja A/E/K 1** (jasminoside A/E/K 1), **Ja A/E/K 2** (jasminoside A/E/K 2), **co-GpA** (coumaroyl-geniposidic acid), **unknown co-iridoid** (unknown coumaroyl iridoid), **si-Sh** (sinapoyl-shanzhiside), **si-Gdo** (sinapoyl-gardoside), **si-Gpi-Hex** (sinapoyl-genipin-hexoside), **co-Gpi-Gen** (coumaroyl-genipin gentiobioside), **si-Gpi-Gen** (sinapoyl-genipin gentiobioside), **unknown si-iridoid 1** (unknown sinapoyl iridoid 1), **fe-Gpi-diHex** (feruloyl-genipin-dihexoside), **si-Ja B/D/G/L 1** (sinapoyl-jasminoside B/D/G/L 1), **si-Ja B/D/G/L 2** (sinapoyl-jasminoside B/D/G/L 2), **si-Gpo** (sinapoyl-geniposide), **ci-Gpi-diHex** (cinnamoyl-genipin-dihexoside), **si-Ja A/E/K** (sinapoyl-jasminoside A/E/K), **ac-Gpi-Hex** (acetyl-genipin-hexoside), **unknown si-iridoid 2** (unknown sinapoyl iridoid 2), **5-CaQA** (5-*O*-caffeoylquinic acid), **3-CaQA** (3-*O*-caffeoylquinic acid), **4-CaQA** (4-*O*-caffeoylquinic acid), **FA-Hex** (ferulic acid-hexoside), **SA-Hex 1** (sinapic acid-hexoside 1), **SA-Hex 2** (sinapic acid-hexoside 2), **SA-Hex 3** (sinapic acid-hexoside 3), **SA** (sinapic acid), **diCaQA 1** (dicaffeoylquinic acid 1), **diCaQA 2** (dicaffeoylquinic acid 2), **diCa-hmg-QA** (dicaffeoyl-hydroxy-methylglutaroyl-quinic acid), **Qu-Hex-Deox** (quercetin-hexoside-deoxyhexoside), **Qu-Rut** (quercetin 3-*O*-rutinoside), **Qu-Glu** (quercetin 3-*O*-glucoside), **Cri I** (crocin I), **Crt-diHex-diHex 1** (crocetin-dihexoside-dihexoside 1), **unknown Cri 1** (unknown crocin 1), **Cri II** (crocin II), **Crt-diHex-diHex 2** (crocetin-dihexoside-dihexoside 2), **Crt-diHex 1** (crocetin-dihexoside 1), **Crt-diHex-si-diHex** (crocetin-dihexoside-sinapoyl-dihexoside), **unknown Cri 2** (unknown crocin 2), **Crt-diHex-diHex 3** (crocetin-dihexoside-dihexoside 3), **unknown Cri 3** (unknown crocin 3), **Crt-diHex-CaQA** (crocetin-dihexoside-caffeoylquinic acid), **Crt-diHex 2** (crocetin-dihexoside 2), **Crt-diHex-Hex 1** (crocetin-dihexoside-hexoside 1), **Crt-diHex-Hex 2** (crocetin-dihexoside-hexoside 2), **Crt-Hex** (crocetin-hexoside), **Crt-diHex 3** (crocetin-dihexoside 3), and **Crt-diHex 4** (crocetin-dihexoside 4). Results represent mean values of three biological replicates (n = 3); corresponding SD values are provided in Supplemental Table 4 and Supplemental Table 5. Hierarchical clustering was performed with Ward's linkage and Euclidean distance. Color scale (shown at right) indicates normalized concentration levels (green = low, red = high). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

compounds accounted for close to 60% of total phytochemicals identified in GF hulls. On the contrary to the fruits, higher levels of diCa-hmg-QA (3.45 ± 0.01 mg/g DW), 3-*O*-caffeoylquinic acid (3-CaQA, 2.42 ± 0.03 mg/g DW), and quercetin 3-*O*-rutinoside (Qu-Rut, 2.226 ± 0.004 mg/g DW) were found in GF hull extracts.

Similarly, Gpo (45.7 ± 0.2 mg/g DW) and Cri I (11.2 ± 0.1 mg/g DW) were rich in the GFV dehulled fruits. Other major compounds were genipin glycosides, such as Gpi-Gen, fe-Gpi-diHex (feruloyl-genipin-dihexoside), and co-Gpi-Gen, presenting at a total content of 14 mg/g of dry fruits (Fig. 2c). In the hull extracts of GFV, Gde, Gpo, Gpo, and Cri I formed the dominating components and together added up to almost 62% of total phytochemicals detected. Hydroxycinnamic acids and flavonols detected in the GFV hulls mainly were diCa-hmg-QA and Qu-Rut, the contents of which were both close to 2 mg/g DW (Fig. 2d).

Current studies on *G. jasminoides* fruits focus merely on major bioactive compounds, and thus, their phytochemical contents have not been thoroughly determined. Lee et al. (2014) studied 68 *G. jasminoides* varieties originated from China and Korea. To pinpoint biomarkers among the fruits, four compounds were extracted with 70% of aqueous methanol and quantified with LC-MS. Among which, geniposide and gardenoside had average contents of 57 and 49 mg/g of fruits, respectively. Yet, geniposidic acid (3 mg/g) and chlorogenic acid (3-*O*-caffeoylquinic acid, 0.7 mg/g) were found at low levels. Chen et al. (2008) measured crocin contents in the ethanol extract of *G. jasminoides* fruits. The results from HPLC showed that crocin I (7%), crocin II (1%), and crocin-3 (1%) together accounted for only 9% of dry extracts, which might have been due to the low extraction efficacy of ethanol. Such differences among these studies may be ascribed to multiple factors, including variations in genotype, fruit maturity at harvest, choice of extraction solvent, and analytical calibration methods. These considerations underscore the importance of standardized extraction and processing protocols when comparing phytochemical data across different studies and highlight the potential for optimizing extraction strategies for industrial applications.

### 3.4. Compositional variation among different extracts of hulls and dehulled fruits

A hierarchical clustering heat map given in Fig. 3 was used to illustrate compositional differences among the GF and GFV samples. As shown in the map, the comparison was made based on the contents of sixty-two identified compounds. The red zones represented the compound of higher amounts, whereas the green zones suggested the lower ones. The extracts of GF and GFV hulls were separated from their corresponding dehulled fruits, indicating a large diversity in phytochemical profile of these two different fractions. Among iridoids, Gpo, Gdo (gardoside), Gpi-Gen, co-Gpi-Gen, Sh (shanzhiside), and ci-Gpi-diHex (cinnamoyl-genipin-dihexoside) were mainly distributed in the dehulled fruits. In contrast, Gde, Gl (galioside), and me-Sc (scandoside methyl ester) formed the majority of iridoids in the hulls of GF and GFV. Some minor iridoids were also presented predominantly in the hull fraction, such as deacetylasperulosidic acid (DaA), geniposidic acid (GpA), and ixoroside (Ix). Hydroxycinnamic acids were concentrated in the hull extracts, which was due to the abundance of various derivatives of caffeoylquinic acid (3-*O*-, 4-*O*-, & 5-*O*-CaQA, diCaQA 1 & 2, and diCa-hmg-QA), sinapic acid (SA and SA-Hex 1, 2, & 3) and ferulic acid (FA-Hex). Moreover, quercetin glycosides (*e.g.*, Qu-Rut, Qu-Glu, and Qu-Hex-Deox) were rich in the hulls rather than the dehulled parts. These results are not completely in accordance with those observed in previous research. He et al. (2006) extracted five key bioactive components from different parts of *G. jasminoides* fruits. Geniposidic acid was concentrated in pericarps (*i.e.*, fruit hulls), but the pulps contained the highest amounts of geniposide, chlorogenic acid, crocin I, and crocin II.

Unlike other studied phytochemical groups varying in the different parts of fruits, our results suggested that the crocin contents were mainly influenced by the *G. jasminoides* variety. Both Cri I and Cri II were mainly concentrated in the GF extracts. This explains why GF hulls and fruits contained higher level of total crocins than their GFV counterparts. In addition to primary crocins, the contents of crocetin-dihexoside (Crt-diHex 1 & 2), crocetin-dihexoside-sinapoyl-dihexoside (Crt-diHex-si-diHex), crocetin-dihexoside-caffeoylquinic acid (Crt-diHex-CaQA), and crocetin-hexoside (Crt-Hex) detected in GF extracts were also significantly higher than those measured from GFVs (Fig. 3).

The effect of variety on phytochemical composition was further investigated with the PCA models (PCA loading values were included in Supplemental Table 7 & 8). The model given in Fig. 4a showed that PC1 and PC2 explained 82% and 6% of the total variance, respectively (cumulative 88%). The fruit extracts of GF and GFV were classified into two categories along PC1 in the score plot. GF fruits positively correlated to most of identified crocins, hydroxycinnamic acids, and flavonols, since these compounds were detected in the fruits at higher contents. For iridoids, GF fruits were associated with sinapic acid-iridoid esters, primarily as sinapoyl-geniposide (si-Gpo), sinapoyl-gardoside (si-Gdo), sinapoyl-genipin gentiobioside (si-Gpi-Gen), and sinapoyl-jasminoside isomers (si-Ja A/B/D/E/G/K/L). On the contrary, Gdo, Gpo, Gpi-Gen, and Ja B/D/G correlated strongly with GFV fruits. Other positive correlation between GFV fruits and iridoids were found with DaA, GpA, Gl, me-Sc, co-GpA (coumaroyl-geniposidic acid), and fe-Gpi-diHex (feruloyl-genipin-dihexoside). Similar results were also observed among hull extracts. The model in Fig. 4b (PC1 and PC2 as 76% and 13%, respectively with a cumulative 89%) suggested that most of identified compounds were rich in GF hulls. The negative associations of GF hulls were mainly with co-GpA, Ja B/D/G, and ac-Gpi-Hex (acetyl-genipin-hexoside).

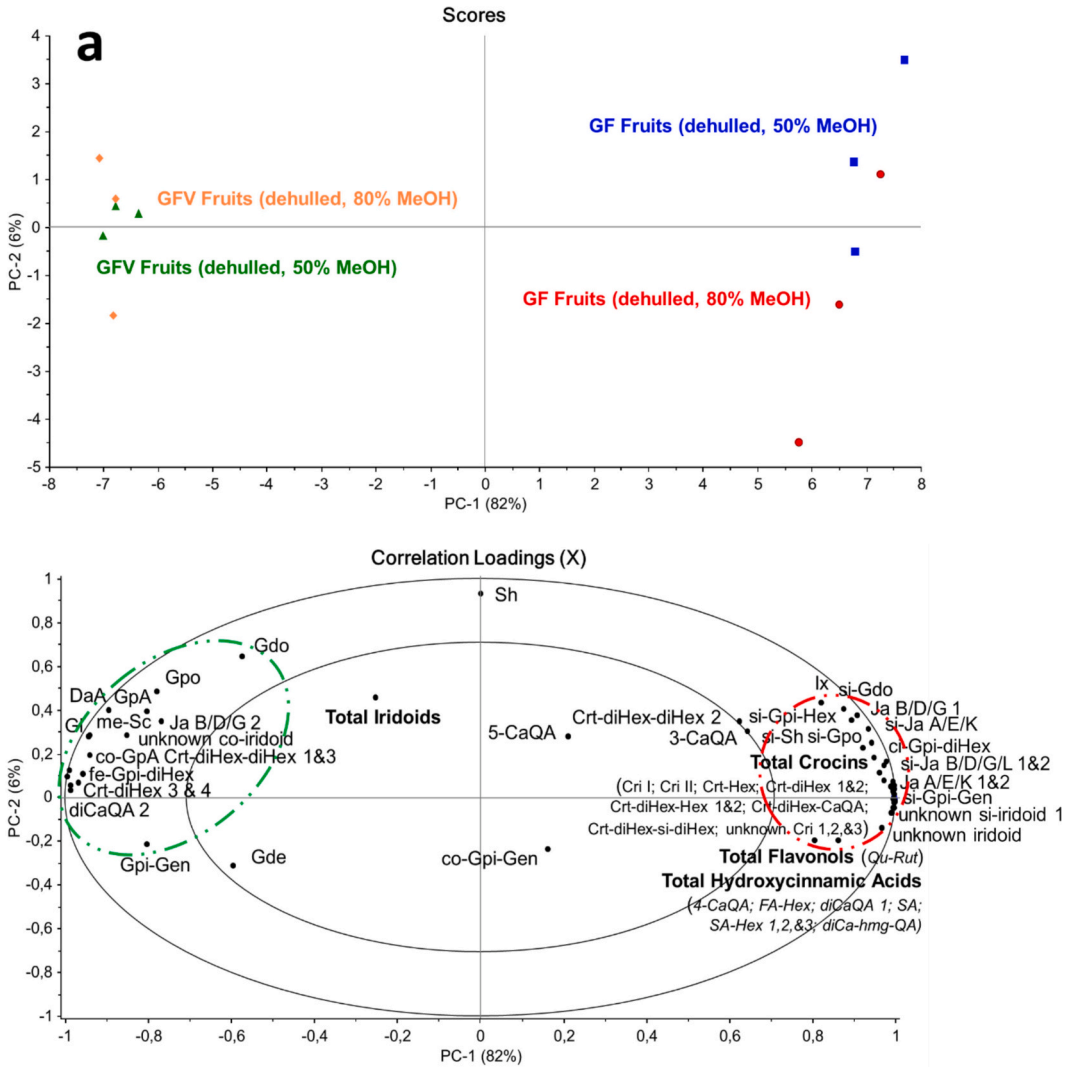



**Fig. 4.** PCA models for comparison among different extracts of dehulled fruits (a) and hulls (b): The compounds in the models include **DaA** (deacetylasperulosidic acid), **Gdo** (gardoside), **Sh** (shanzhiside), **GpA** (geniposidic acid), **me-Sc** (scandoside methyl ester), **Gde** (gardenoside), **Ja B/D/G 1** (jasminoside B/D/G 1), **Ix** (ixoroside), **Gl** (galioside), **Ja B/D/G 2** (jasminoside B/D/G 2), **Gpi-Gen** (genipin gentiobioside), **Gpo** (geniposide), **Ja A/E/K 1** (jasminoside A/E/K 1), **Ja A/E/K 2** (jasminoside A/E/K 2), **co-GpA** (coumaroyl-geniposidic acid), **unknown co-iridoid** (unknown coumaroyl iridoid), **si-Sh** (sinapoyl-shanzhiside), **si-Gdo** (sinapoyl-gardoside), **si-Gpi-Hex** (sinapoyl-genipin-hexoside), **co-Gpi-Gen** (coumaroyl-genipin gentiobioside), **si-Gpi-Gen** (sinapoyl-genipin gentiobioside), **unknown si-iridoid 1** (unknown sinapoyl iridoid 1), **fe-Gpi-diHex** (feruloyl-genipin-dihexoside), **si-Ja B/D/G/L 1** (sinapoyl-jasminoside B/D/G/L 1), **si-Ja B/D/G/L 2** (sinapoyl-jasminoside B/D/G/L 2), **si-Gpo** (sinapoyl-geniposide), **ci-Gpi-diHex** (cinnamoyl-genipin-dihexoside), **si-Ja A/E/K** (sinapoyl-jasminoside A/E/K), **ac-Gpi-Hex** (acetyl-genipin-hexoside), **unknown si-iridoid 2** (unknown sinapoyl iridoid 2), **5-CaQA** (5-*O*-caffeoylquinic acid), **3-CaQA** (3-*O*-caffeoylquinic acid), **4-CaQA** (4-*O*-caffeoylquinic acid), **FA-Hex** (ferulic acid-hexoside), **SA-Hex 1** (sinapic acid-hexoside 1), **SA-Hex 2** (sinapic acid-hexoside 2), **SA-Hex 3** (sinapic acid-hexoside 3), **SA** (sinapic acid), **diCaQA 1** (dicaffeoylquinic acid 1), **diCaQA 2** (dicaffeoylquinic acid 2), **diCa-hmg-QA** (dicaffeoyl-hydroxy-methylglutaroyl-quinic acid), **Qu-Hex-Deox** (quercetin-hexoside-deoxyhexoside), **Qu-Rut** (quercetin 3-*O*-rutinoside), **Qu-Glu** (quercetin 3-*O*-glucoside), **Cri I** (crocin I), **Crt-diHex-diHex 1** (crocetin-dihexoside-dihexoside 1), **unknown Cri 1** (unknown crocin 1), **Cri II** (crocin II), **Crt-diHex-diHex 2** (crocetin-dihexoside-dihexoside 2), **Crt-diHex 1** (crocetin-dihexoside 1), **Crt-diHex-si-diHex** (crocetin-dihexoside-sinapoyl-dihexoside), **unknown Cri 2** (unknown crocin 2), **Crt-diHex-diHex 3** (crocetin-dihexoside-dihexoside 3), **unknown Cri 3** (unknown crocin 3), **Crt-diHex-CaQA** (crocetin-dihexoside-caffeoylquinic acid), **Crt-diHex 2** (crocetin-dihexoside 2), **Crt-diHex-Hex 1** (crocetin-dihexoside-hexoside 1), **Crt-diHex-Hex 2** (crocetin-dihexoside-hexoside 2), **Crt-Hex** (crocetin-hexoside), **Crt-diHex 3** (crocetin-dihexoside 3), and **Crt-diHex 4** (crocetin-dihexoside 4). Results represent mean values of three biological replicates (n = 3); corresponding SD values are provided in Supplemental Table 4 and Supplemental Table 5.

Importantly, these results demonstrate that dehulled fruits and hulls are not chemically homogeneous across cultivars. Beyond descriptive differences, the observed patterns reflect underlying biosynthetic regulation, tissue-specific accumulation, and compound physicochemical properties. From a food chemistry and processing perspective, such systematic differentiation provides a basis for more informed raw material selection and fraction-specific utilization. For instance, dehulled fruits are a more suitable raw material for the targeted extraction of crocins (natural colorants) and geniposide (a key bioactive iridoid), whereas hulls are comparatively richer in hydroxycinnamic acids and flavonol glycosides with strong antioxidant potential. Rather than treating hulls as uniform by-products or fruits as chemically equivalent across cultivars, the present analysis supports a more nuanced allocation of fruit fractions toward different ingredient-oriented or functional application.

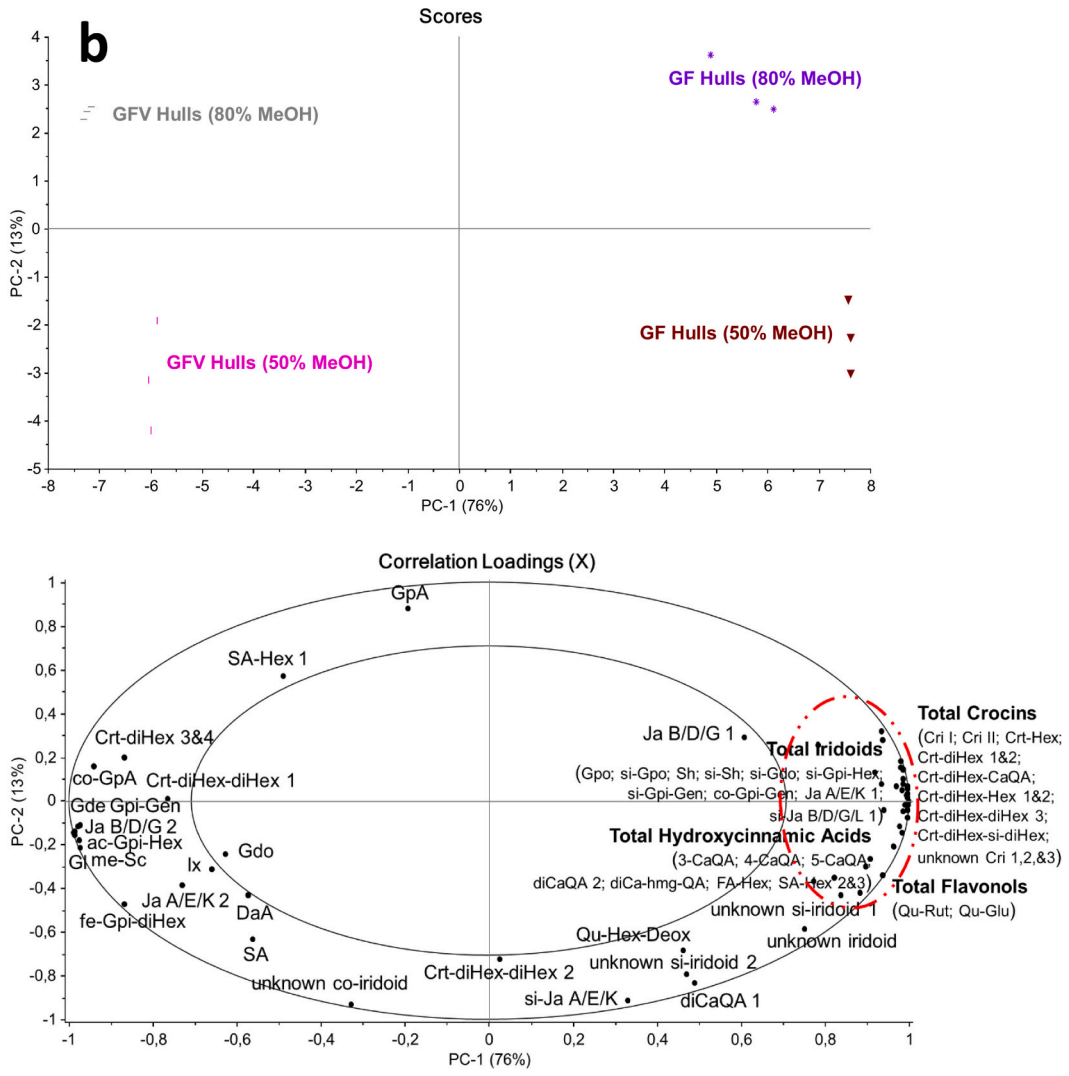



**Fig. 4.** (*continued*).

## 4. Conclusion

This research provides thorough information on phytochemicals in the fruits of *G. jasminoides*. Over 60 compounds were identified covering the groups of iridoids, crocins, hydroxycinnamic acids, and flavonol glycosides. To our knowledge, this study provides one of the most comprehensive LC-MS/MS characterizations in *G. jasminoides* fruits and hulls with two types of mass analyzer (*i.e.*, triple quadrupole and time-of-flight). Two solvents, 50% and 80% aqueous methanol, were confirmed as optimal to extract iridoids, crocins, and phenolic compounds. Moreover, a compositional diversity was observed in different fractions of *G. jasminoides* fruits. Overall, the hulls contained higher levels of hydroxycinnamic acids and flavonols, whereas the dehulled parts were richer sources of iridoids and crocins. The selected varieties, *G. jasminoides* Ellis and *G. jasminoides* var. *radicans* Makino, also showed a large difference in the composition and contents of all identified compounds, which suggested the role of plant genotypes in phytochemical enrichment. By resolving correlation-based compositional patterns across both fruit fractions and cultivars, this study extends beyond descriptive profiling and contributes practical insight into the structured utilization of *G. jasminoides* raw materials for different manufacturing purposes. This knowledge is critical to the pharmaceutical and food industry when selecting optimal materials for different manufacturing purposes. Moreover, a thorough assessment on their processing feasibility, safety/toxicity, and regulatory compliance is required before practical industrial application of these plant materials.

## CRediT authorship contribution statement

**Ye Tian:** Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Conceptualization. **Ying Zhou:** Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Validation. **Youzuo Zhang:** Resources, Conceptualization. **Qinxue Ni:** Writing – review & editing, Resources, Project administration, Conceptualization. **Baoru Yang:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

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Decision No. 337980; and the Academy of Finland's FIRI 2021: Non-roadmap research infrastructures as part of the EU Recovery and Resilience Facility, Decision no. 345916).

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ye Tian reports financial support was provided by Finland-China Food and Health Network. Qinxue Ni reports financial support was provided by China Scholarship Council. Baoru Yang reports equipment, drugs, or supplies was provided by Research council of Finland. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2026.149290.

## Data availability

Data will be made available on request.

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