

## Research Article

# A Simple Method for the Screening and Measurement of Phenols in *Dendrobium chrysotoxum* by a Miniature Mass Detector Using a Matrix Solid-Phase Dispersion Method

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The present study aims at building a miniature mass method for the simultaneous determination of 12 phenols including the subtypes of bibenzyl, phenanthrene, and fluorenone, which was used to evaluate the quality of *Dendrobium chrysotoxum*. Through the full scan mode, new compounds were elucidated. The new compounds were quantified by carrying out the analysis of the ratio of the standard solution areas to new compound areas versus analyte concentration. The limit of detection (LOD) and limit of quantification (LOQ) for phenols were 0.5 µg/mL–1 µg/mL and 1 µg/mL–2 µg/mL, respectively. Average recoveries of phenols were ranged from 83.2% to 97.5%. Reproducibility represented by the RSD percentage was from 2.3% to 8.7%. The average content of the four analytes, erianin, chrysotobibenzyl, confusarin, and moscatilin, were more than 200 mg/kg, and the content of bibenzyl compounds was found to be the highest in *Dendrobium chrysotoxum*. Among these bibenzyl compounds, erianin was determined as the typical chemical marker from *Dendrobium chrysotoxum*. The newly established UPLC with a miniature mass detector method was found to be an appropriate tool for the quality assessment of *Dendrobium chrysotoxum*.

## 1. Introduction

There are 74 species of *Dendrobium* reported in China [1]; however, only few *Dendrobium* species are edible. *Dendrobium chrysotoxum* is used in traditional or folk Chinese medicine in westsouth China, which can be differentiated from the others only by specialists. And its quality assessment depends mainly on morphology-based authentication, which might be practical in distinguishing different species with distinct features, but is not effective for evaluating the quality of same species from different ecological conditions or at different cultivation stages. In Chinese Pharmacopoeia of 2015, the quality of *Dendrobium chrysotoxum* is assessed by the determination of erianin with high-performance liquid chromatography (HPLC). HPLC has been widely utilized for the analysis of pharmaceutical compounds and medicinal herbs. There are many published

methods for HPLC analysis of bibenzyl and phenanthrene in *Dendrobium* [2–6]. However, these standard compounds can be separated only in laboratory, so it is difficult to use this method in routine analysis.

To overcome such problems, liquid chromatography (LC) coupled with mass spectrometry has been used [7, 8]. It was disadvantageous to these methods, such as complicated operation and expensive instrument. A new technology of miniature mass has been developed for environment pollution and drug analysis [9]. The developments in the medical field are focused on the raw materials and active pharmaceutical ingredients [10–15]. To our knowledge, no research on the qualitative and quantitative analysis of phenols from *Dendrobium chrysotoxum* by a miniature mass detector (MMD) has been previously reported.

Previous studies on the analysis of phenols involved a simple dilution of the sample or one simple extraction

procedure [16, 17]. Matrix solid-phase dispersion (MSPD) is a unique technique, which is especially suitable to the extraction of solid, semisolid, and/or highly viscous food and biological matrices, and achieves the isolation of target analytes by dispersing tissues onto a solid support, thus avoiding many difficulties encountered by employing the classical solid-phase extraction (SPE) approach. The main benefits of MSPD include flexibility, selectivity, and the possibility of minimizing extraction and cleanup steps, resulting in a drastic reduction in the analysis time and lower solvent consumption [18, 19].

Therefore, we developed and validated a miniature mass method for the simultaneous determination of 12 phenols including the subtypes of bibenzyl, phenanthrene, and fluorenone, which was used for subsequent analysis of their content in *Dendrobium chrysotoxum*. Through the full scan mode, new compounds were monitored and quantified based on the ratio of standard solution areas to new compounds. The combination of a fast, low-cost extraction procedure and a rapid detection method gives a reliable screening method that can be applied in the routine laboratory analysis for the determination of these phenols, reducing the cost of analyses and increasing the sample throughput.

## 2. Experimental

**2.1. Chemicals.** Gigantol, erianin, chrysotobibenzyl, tristin, coumarin, naringenin, apigenin, moscatin, and confusarin were of the highest purity (purity > 98%) were supplied by Zhong Ke Technology Co. Ltd. (Beijing, China). The structures of the compounds are shown in Table 1.

The stock solutions of the reference compounds were prepared by dissolving the compounds in methanol, and the working standard solutions were prepared daily from stock solutions by diluting the solution with the appropriate volume of the mobile phase. All solutions were stored in a refrigerator at  $-20^{\circ}\text{C}$ . HPLC-grade acetonitrile and methanol were provided by Tedia Company Inc. (OH, USA). Water was purified using a Milli-Q system (Millipore, Bedford, USA). The other solvents, purchased from Shanghai Chemical Factory (Shanghai, China), were of analytical grade.

### 2.2. Sample Preparation

**2.2.1. Plant Material.** Four fresh samples (three kilograms) of *Dendrobium chrysotoxum* were supplied by Professor Shouling Li from Ruili *Dendrobium* Field Genebank, Yunnan Province, China. The samples were dried at  $50^{\circ}\text{C}$  for one week and grounded to powder using a Waring (Hunan, China) HD100 blender at high speed (20,000 rpm).

**2.2.2. Matrix Solid-Phase Dispersion.** A 500 mg portion of the dried sample was put into a 50 mL beaker, and 1 g of Florisil and 0.5 g of C18 were added. The mixture was then blended with a glass pestle until it become homogeneous, after which the samples were allowed to stand for 15 min.

The samples containing absorbent were introduced into the cartridge (6 mL volume capacity). The cartridge was

washed with 10 mL hexane and discarded. Ten milliliter of methanol was added, and the elution was collected in a 10 mL graduated tube. A  $2\mu\text{L}$  portion of the elution was analyzed by UPLC.

### 2.2.3. UPLC-Miniature Mass Detector (MMD) Analysis.

An Acquity UPLC™ System (Waters, Milford, MA, USA), with a binary solvent manager and a sample manager, combined with a QDa detector (MMD), was used for analyzing the phenolic fraction separation and identification of the phenolic acids. The column used was a Waters Acquity UPLC BEH C18 ( $100\text{ mm} \times 2.1\text{ mm} \times 1.7\mu$ ). The column temperature was set at  $30^{\circ}\text{C}$ , and the injection volume was  $5\mu\text{L}$ . The solvents used were acetic acid 0.1% in water (mobile phase A) and methanol (mobile phase B). The gradient was as follows: 0–1 min 90% (A) and 10% (B), 1–10 min 35% (A) and 65% (B), and 10–12 min 10% (A) and 90% (B).

The MMD condition is explained in Section 2.2.4.

### 2.2.4. Newly Elucidated Compound Analysis

**(1) Full-Scan Spectra of Standards: MMD Conditions.** The ESI source conditions were as follows: source temperature was set at  $350^{\circ}\text{C}$ . The full-scan mode was performed in the range of 50–400 Da, the scan time rate was 8 pin/sec, and the capillary voltage was set to 0.8 kV, while the cone voltage was at 15 V. The positive and negative modes were simultaneously recorded (Table 1).

**(2) Full-Scan Spectra of Sample: MMD Conditions.** The ESI source conditions were as follows: source temperature was set at  $350^{\circ}\text{C}$ . The full-scan mode was performed in the range of 50–400 Da, the scan time rate was 8 pin/sec, and the capillary voltage was set to 0.8 kV, while the cone voltage was at 15 V. The positive and negative modes were simultaneously recorded.

**(3) Quantification Determination: MMD Conditions.** The ESI source conditions were as follows: source temperature was set at  $350^{\circ}\text{C}$ . The MMD mass spectrometer was operated in the selected ion mode (SIM), and the experimental conditions were the same as those described in Step 2. Newly elucidated compound quantification was built by carrying out an analysis on the ratio of the family standard solution areas to newly elucidate compound areas versus analyte concentration (see Table 2).

**2.3. Method Validation.** The calibration curve with matrix-matched standards of gigantol, erianin, chrysotobibenzyl, tristin, moscatin, confusarin, coumarin, naringenin, and apigenin was obtained. Calibration curves ranging from 2 to  $100\mu\text{g/mL}$  were constructed from serial dilutions of the standard. Six concentrations for each of the standard solutions were injected in triplicate, and then the calibration curves were constructed by plotting the peak areas versus the concentration of the corresponding standard. The limits of detection (LOD) and the limits of quantification (LOQ) were

TABLE 1: UPLC-MMD mass condition.

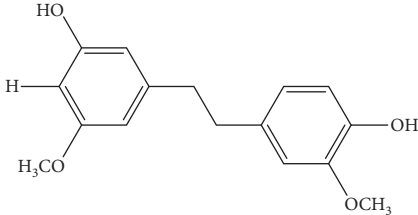
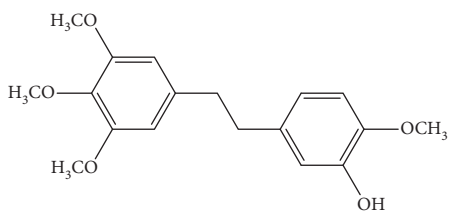
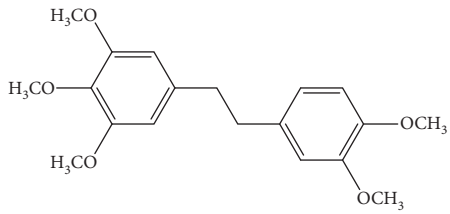
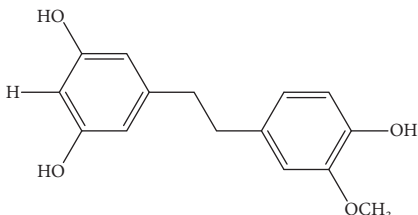
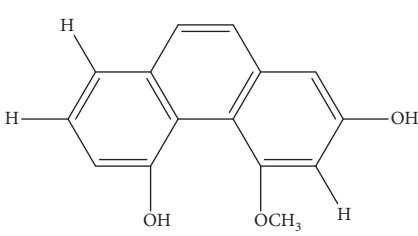
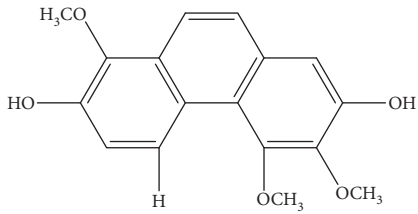
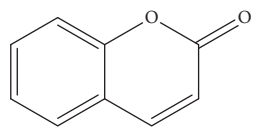
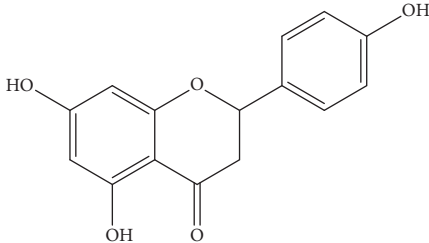
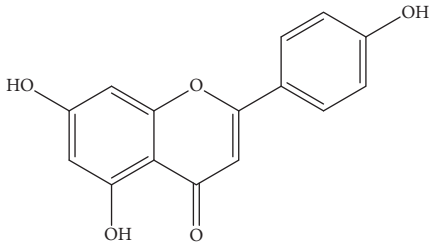
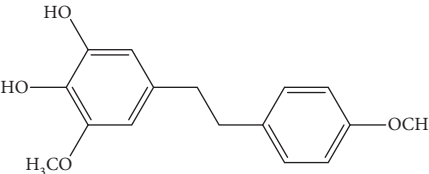
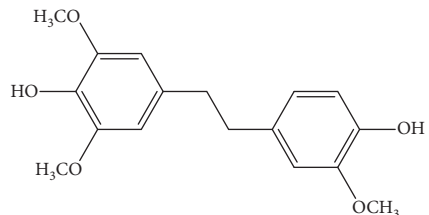
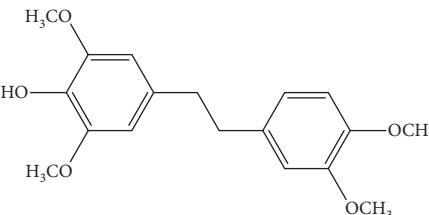
| Compound                | Class         | Formula                                                                              | Molecular weight | $m/z$<br>(% relative abundant)                              |
|-------------------------|---------------|--------------------------------------------------------------------------------------|------------------|-------------------------------------------------------------|
| Gigantol<br>GI          | Bibenzyl      |    | 274              | 297 [M+Na] <sup>+</sup> 100,<br>275 [M+H] <sup>+</sup> 52,  |
| Erianin<br>ER           | Bibenzyl      |    | 318              | 341 [M+Na] <sup>+</sup> 100,<br>319 [M+H] <sup>+</sup> 48   |
| Chrysotobibenzyl<br>CHB | Bibenzyl      |    | 332              | 355 [M+Na] <sup>+</sup> 100,<br>333 [M+H] <sup>+</sup> 35   |
| Tristin<br>TR           | Bibenzyl      |  | 260              | 283 [M+Na] <sup>+</sup> 100,<br>261 [M+H] <sup>+</sup> 46   |
| Moscatin<br>MON         | Phenanthrenes |  | 240              | 241 [M+H] <sup>+</sup> 100,<br>213[M-28+H] <sup>+</sup> 62  |
| Confusarin<br>COF       | Phenanthrenes |  | 300              | 301 [M+H] <sup>+</sup> 100,<br>269 [M-32+H] <sup>+</sup> 48 |
| Coumarin<br>COM         | Coumarin      |   | 146              | 147 [M+H] <sup>+</sup> 90                                   |

TABLE 1: Continued.

| Compound                                     | Class    | Formula                                                                              | Molecular weight | $m/z$<br>(% relative abundant)              |
|----------------------------------------------|----------|--------------------------------------------------------------------------------------|------------------|---------------------------------------------|
| Naringenin<br>NA                             | Flavone  |    | 272              | $-271^a$ $[M-H]^-$ 100                      |
| Apigenin<br>AP                               | Flavone  |    | 270              | $-269^a$ $[M-H]^-$ 100                      |
| 3,4-Dihydroxy-5,4'-dimethoxy bibenzyl<br>DDB | Bibenzyl |   | 274              | $297$ $[M+Na]^+$ 100,<br>$275$ $[M+H]^+$ 50 |
| Moscatinin<br>MOL                            | Bibenzyl |  | 304              | $327$ $[M+Na]^+$ 100,<br>$304$ $[M+H]^+$ 49 |
| Chrysotoxin<br>CHT                           | Bibenzyl |  | 318              | $341$ $[M+Na]^+$ 83,<br>$319$ $[M+H]^+$ 100 |

<sup>a</sup>Negative mode.

estimated by means of the baseline noise method with a signal three and ten times higher than that of the baseline noise, respectively (see Table 3).

The accuracy and precision of the whole analytical procedure were evaluated by a fortified sample at 50 and 200 mg/kg in five replicates at each level.

### 3. Results and Discussion

**3.1. Optimization of the MSPD Condition.** In the present work, MSPD is used for extraction, and the plant sample is dispersed over deactivated mixture of C18 and Florisil.

Various tests with other solid supports, such as neutral alumina and Florisil, were performed. The recoveries of coumarin were lower than 60%, and the recoveries of confusarin were not satisfied with C18.

Different mixture rates of C18 and Florisil were applied to evaluate the capability of cleaning up from spiked samples. The recoveries of the method are shown in Figure 1. According to the above results, C18/Florisil (1:2) was selected as the final adsorbents used in the following studies.

In order to choose a proper elution for the retained phenols, various organic solvents were studied. When the

TABLE 2: UPLC-MMD parameters at the SIM mode.

| Compound | $t_R$<br>(min) | SIM condition       |                    | Precursor ion<br>( $m/z$ ) | Capillary<br>volt (kV) | Cone<br>volt (v) | Quantification with the<br>corresponding standard |
|----------|----------------|---------------------|--------------------|----------------------------|------------------------|------------------|---------------------------------------------------|
|          |                | Start<br>time (min) | Stop<br>time (min) |                            |                        |                  |                                                   |
| GI       | 5.59           | 3                   | 8                  | 297                        | 0.8                    | 15               | GI                                                |
| ER       | 7.12           | 6                   | 9.5                | 341                        | 0.8                    | 15               | ER                                                |
| CHB      | 1.85           | 0.5                 | 3                  | 355                        | 0.8                    | 15               | CHB                                               |
| TR       | 2.90           | 2                   | 4                  | 283                        | 0.8                    | 15               | TR                                                |
| MON      | 4.12           | 3                   | 7                  | 241                        | 0.8                    | 15               | MON                                               |
| COF      | 5.41           | 4                   | 7                  | 301                        | 0.8                    | 15               | COF                                               |
| COM      | 1.79           | 0.5                 | 3                  | 147                        | 0.8                    | 15               | COM                                               |
| NA       | 4.39           | 3                   | 6                  | -271 <sup>a</sup>          | 0.8                    | 15               | NA                                                |
| AP       | 5.89           | 4.5                 | 9                  | -269 <sup>a</sup>          | 0.8                    | 15               | AP                                                |
| DDB      | 5.62           | 3                   | 8                  | 297                        | 0.8                    | 15               | GI                                                |
| MOL      | 6.84           | 4                   | 8                  | 327                        | 0.8                    | 15               | ER                                                |
| CHT      | 6.97           | 6                   | 9.5                | 341                        | 0.8                    | 15               | ER                                                |

<sup>a</sup>Negative mode.

TABLE 3: Regression data, limit of detection (LOD), and limit of quantification (LOQ) of the proposed method.

|     | LOD ( $\mu\text{g/mL}$ ) | LOQ (mg/kg) | Calibration equation ( $n = 5$ ) | Determination coefficient, $R^2$ | Linear range ( $\mu\text{g/mL}$ ) |
|-----|--------------------------|-------------|----------------------------------|----------------------------------|-----------------------------------|
| GI  | 1                        | 2           | $y = 632964x - 95693$            | 0.994                            | 2-100                             |
| ER  | 1                        | 2           | $y = 14667x + 3462$              | 0.996                            | 2-100                             |
| CHB | 1                        | 2           | $y = 718654x + 9443$             | 0.994                            | 2-100                             |
| TR  | 1                        | 2           | $y = 474132x - 15725$            | 0.996                            | 2-100                             |
| MON | 1                        | 2           | $y = 874152x + 84434$            | 0.998                            | 2-100                             |
| COF | 1                        | 2           | $y = 364943x + 38924$            | 0.997                            | 2-100                             |
| COM | 0.5                      | 1           | $y = 14793x + 2938$              | 0.995                            | 1-100                             |
| NA  | 0.5                      | 1           | $y = 261143x - 18631$            | 0.993                            | 1-100                             |
| AP  | 1                        | 2           | $y = 914992x - 115674$           | 0.999                            | 2-100                             |

samples and C18/Florisil were blended, which involved washing with hexane and then eluting with ethyl acetate, it was found that, with the exception of methanol, acetone and ethyl acetate could not elute phenols from the cartridge quantitatively. The *n*-hexane could not elute phenols from the cartridge, so *n*-hexane was selected as the clean solvent. Then, the phenols were eluted by methanol (10 mL).

**3.2. Newly Elucidated Compound Confirmation and Quantification.** All reported methods [1-3, 6], with *Dendrobium*, were required for the known compound analysis, but it was limited to obtain all needed standards by the laboratory.

Through the analytical strategy, we can screen the new compounds. First, the full-scan spectra of standards were used and the presence of the signal at the corresponding retention time (RT) was used to identify the target chemical or family of compounds. Second, the precursor ion and other mass spectra in the sample was recorded. If the characteristics of mass spectra were the same with standard and literature, the new compound was confirmed. Third, the new compound was quantified by the standard. Under the same condition, the standard was scanned for both in positive and in negative modes. For phenanthrene and coumarin, MMD in the positive mode

can only give a powerful signal. Although MMD in the positive and negative mode can give a signal for bibenzyl and flavone, the flavone family in the negative mode has a more powerful signal than in the positive mode. However, the result of bibenzyl family was contrary, except for chrysotobibenzyl that lacks hydroxyl group, which did not give a signal in the negative mode. The characterise of bibenzyl was shown to format  $[M + Na]^+$  in the source which was more sensitive than the protonated adduct. Because of a nonvolatile element of sodium that can precipitate in the sampling cone at the laboratory in anyway,  $[M + Na]^+$  was thoroughly detected in the full-scan mode.

The selection of ions for the family of bibenzyl was based on the intensity of  $[M + Na]^+$  in the positive mode as well as the signal in the negative mode.

Figure 2 shows an overview of the full-scan spectra of the sample. For the peak of 5.62 min, the base peak was  $[M + Na]^+ = 327$  and  $[M + H]^+ = 305$  with relative abundant of 48%, and it existed with signals in the positive and negative modes. The result showed that it was a characteristic of bibenzyl. Through searching the literature reported in [1], the compound was found be moscatilin.

For the peak of 6.84 min, it was not matched with the retention time and mass spectra of erianin, the base peak was  $[M + Na]^+ = 341$  and  $[M + H]^+ = 319$  with relative abundant

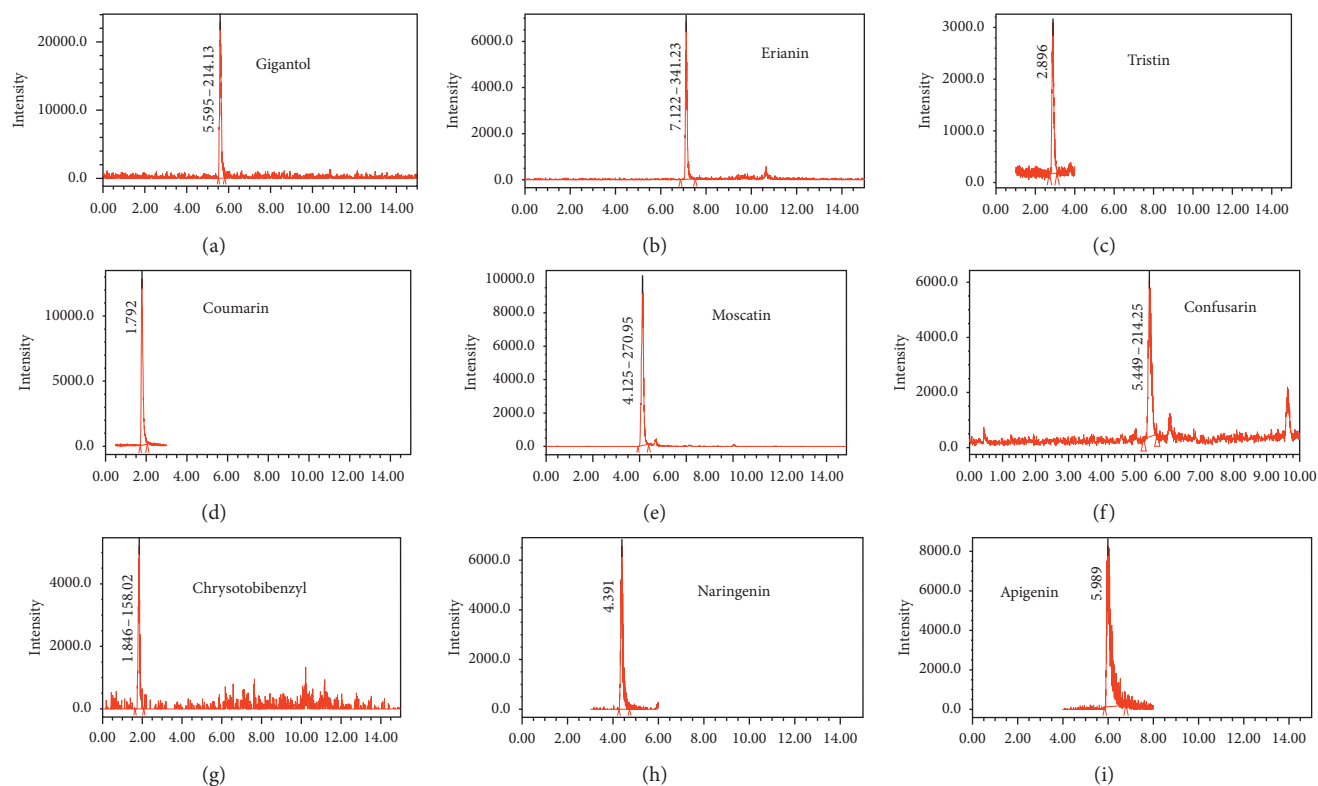


FIGURE 1: SIM chromatogram of the standard.

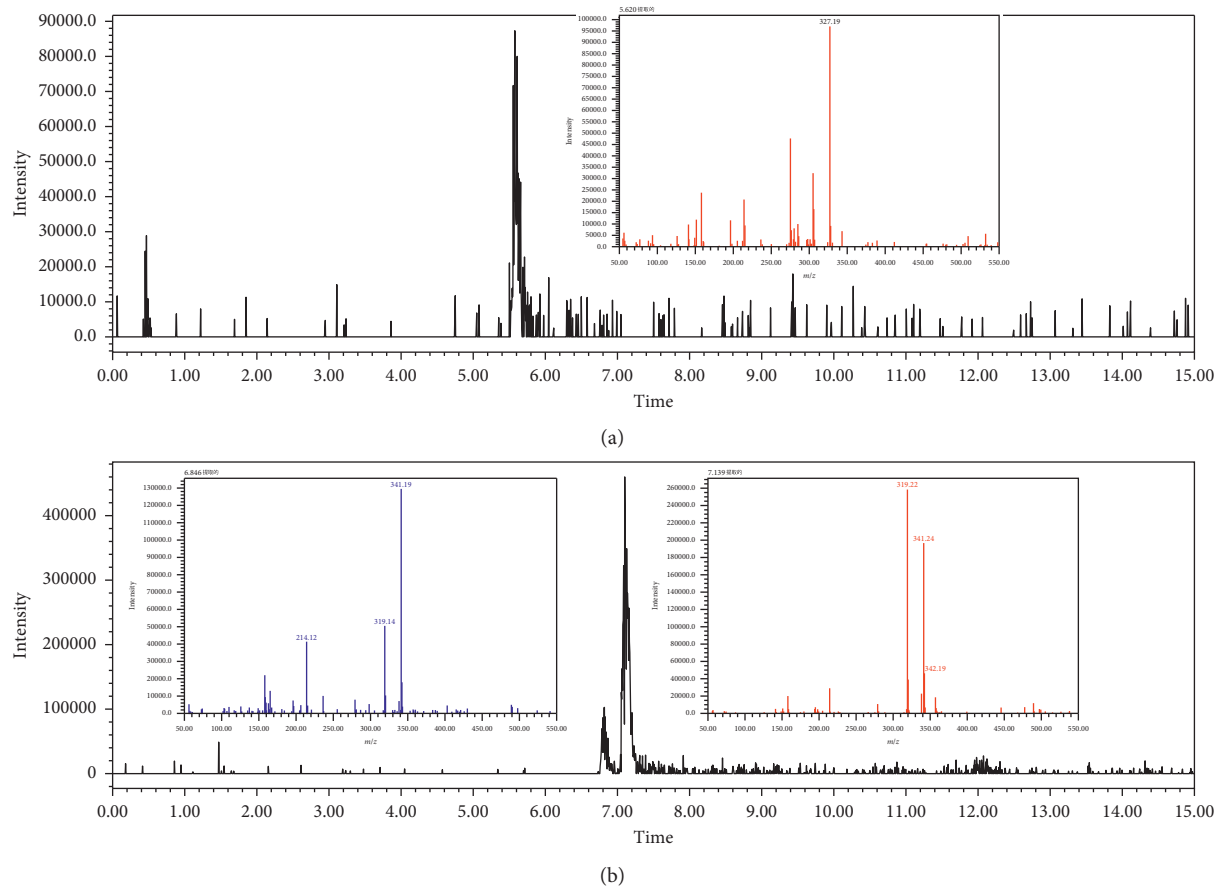


FIGURE 2: Continued.

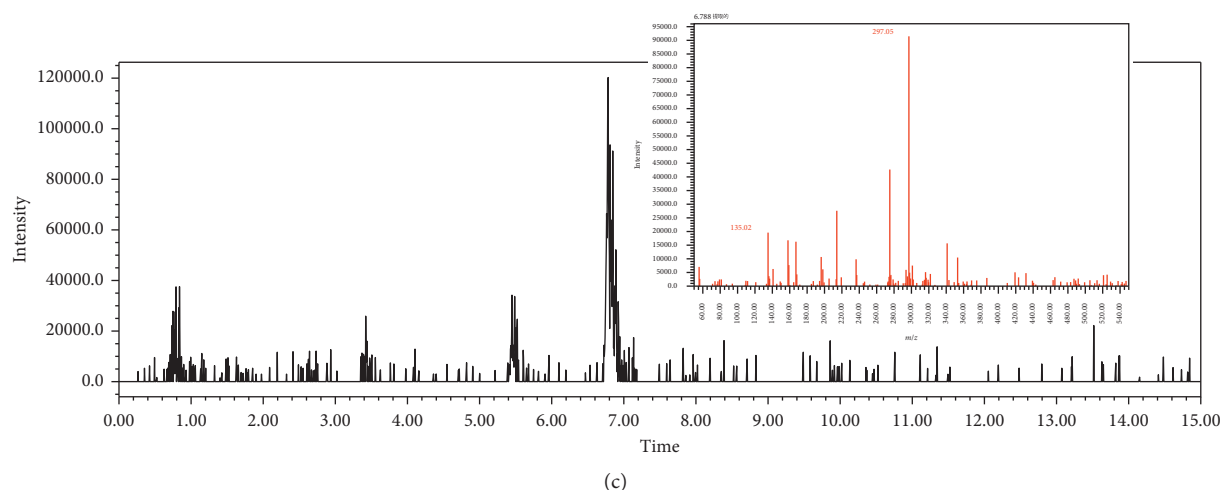


FIGURE 2: Full scan chromatogram and mass spectra of identified bibenzyl in sample (a) moscatilin; (b) chrysotoxin; (c) 3,4-dihydroxy-5,4'-dimethoxybibenzyl.

TABLE 4: The recovery and RSD analyses of spiked samples at two concentrations ( $n = 5$ ).

| Sample |      | Spiked (50 mg/kg) (%) |     | Spiked (200 mg/kg) (%) |     |
|--------|------|-----------------------|-----|------------------------|-----|
|        |      | Recovery              | RSD | Recovery               | RSD |
| GI     | 12.7 | 95.8                  | 4.3 | 83.2                   | 2.3 |
| ER     | 345  | 93.8                  | 4.4 | 97.5                   | 7.2 |
| CHB    | 300  | 82.1                  | 6.8 | 97.2                   | 3.8 |
| TR     | 15   | 91.8                  | 6.1 | 91.5                   | 6.7 |
| MON    | —    | 91.7                  | 8.7 | 91.2                   | 6.5 |
| COF    | 250  | 93.6                  | 6.3 | 89.4                   | 6.2 |
| COM    | —    | 95.4                  | 6.2 | 92.7                   | 6.3 |
| NA     | 6.26 | 90.8                  | 5.2 | 88.5                   | 5.4 |
| AP     | 125  | 88.6                  | 3.6 | 94.2                   | 4.7 |
| DDB    | 16.7 | 92.5                  | 4.2 | 91.5                   | 4.3 |
| MOL    | 220  | 88.7                  | 5.3 | 93.8                   | 5.4 |
| CHT    | 32   | 97.2                  | 3.9 | 91.7                   | 5.8 |

48%, and it existed with signals in the positive and negative modes. Through searching the literature [1], the compound was found be chrysotoxin.

For the peak of 6.97 min, it was the same with gigantol, the base peak was  $[M + Na]^+ = 297$  and  $[M + H]^+ = 275$  with relative abundant of 50%, and it existed with signals in the positive and negative modes. The compound should be 3,4-dihydroxy-5,4'-dimethoxybibenzyl as per the results reported in [7]. These results show the chemical construction elucidated in Table 1. The MMD condition of the SIM and voltage was optimized to achieve the highest sensitivity (Table 2). As seen in Figure 2, the most intense transition was chosen to provide selective detection of phenols in the selective ion mode (SIM).

**3.3. Method Validation.** Calibration curves are obtained for six concentrations associated with triplicate injections. Good linearity was obtained for all analytes with correlation coefficients of  $R^2 > 0.99$  (Table 3). The LOD and LOQ were in the range of  $0.5 \mu\text{g/mL}$ – $1 \mu\text{g/mL}$  and  $1 \text{ mg/kg}$ – $2 \text{ mg/kg}$ ,

respectively. Average recoveries (Table 4) of target compounds at two fortified levels ranged from 83.2% to 97.5%. Repeatability represented by the RSD percentage was from 2.3% to 8.7%.

#### 4. Contents of Phenols in *Dendrobium chrysotoxum*

The developed quantitative methods were applied to evaluate the level of phenols in *Dendrobium chrysotoxum*. The average contents of the four analytes, erianin, chrysotobibenzyl, confusarin, and moscatilin, were more than  $200 \text{ mg/kg}$  (Table 5). The content of bibenzyl was found to be the highest in *Dendrobium chrysotoxum*; the content of phenanthrene and confusarin was higher than that of flavone, but coumarin was not found in *Dendrobium chrysotoxum*. Among the target analytes, erianin was determined as the major component with the highest concentration of  $425 \text{ mg/kg}$  and can be considered as the typical chemical marker for quality evaluation and standardization of the botanical drug derived from *Dendrobium chrysotoxum*.

TABLE 5: The contents of *Dendrobium chrysotoxum* (mg/kg).

|         | Gigantol | Erianin | Chrysotobibenzyl | Tristin | Moscatin | Confusarin | Coumarin | Naringenin | Apigenin | 3,4-Dihydroxy-5, 4'-dimethoxy bibenzyl | Moscatilin | Chrysotoxin |
|---------|----------|---------|------------------|---------|----------|------------|----------|------------|----------|----------------------------------------|------------|-------------|
| 1       | 12.7     | 345     | 300              | 15      | —        | 250        | —        | 6.26       | 8.5      | 16.7                                   | 220        | 32          |
| 2       | 8.9      | 520     | 324              | —       | 35       | 280        | —        | 8.93       | 5.9      | 18.6                                   | 187        | 21          |
| 3       | —        | 450     | 253              | 12.3    | —        | 267        | —        | 15.4       | 12.3     | 22.4                                   | 248        | 26          |
| 4       | 23.4     | 387     | 264              | —       | 24       | 189        | —        | 8.4        | 15.7     | 25.8                                   | 265        | 27          |
| Average | 15       | 425     | 285              | 13.6    | 29.5     | 246.5      | —        | 9.74       | 10.6     | 20.8                                   | 230        | 26.5        |

## Data Availability

The data used to support the findings of this study are included within the article.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

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