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Application of Time of Flight Mass Spectrometry in the Identification of *Dendrobium devonianum* Paxt and *Dendrobium officinale* Kimura et Migo Grown in Longling Area of Yunnan, China

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Abstract: In this study, in order to protect the characteristic *Dendrobium devonianum* Paxt industry in the Longling area, and promote the healthy development of its characteristic Chinese herbal medicines in Yunnan Province, China, the identification of *Dendrobium devonianum* Paxt and *Dendrobium officinale* Kimura et Migo from Longling county was discussed using time of flight mass spectrometry. The data of 13 *Dendrobium devonianum* and 7 *Dendrobium officinale* in the Longling area were collected by TOF MS-IDA-15 MS/MS mode, and the collected data were analyzed by PCA and T-test using MarkerView software, and the difference markers were searched using the database to confirm their compound structures. In positive and negative ion modes, 3645 and 2344 peaks were detected, respectively; 64 positive ion compounds and 60 negative ion compounds, for a total of 124 compounds were identified, mainly including organic acids, polyphenols, alkaloids, amino acids and their derivatives, benzene and its derivatives, and other compounds. The score plot and loading plot analyzed by PCA show that *Dendrobium devonianum* and *Dendrobium officinale* collected in the Longling area can be effectively identified and differentiated by high-resolution mass spectrometry with the 15 different markers in positive ion mode and 17 markers in negative ion mode, respectively. The successful identification of *Dendrobium devonianum* and *Dendrobium officinale* fully demonstrates that TOF MS can be effectively used in the identification of *Dendrobium* and related Chinese herbal medicines with broadly application foreground.

Keywords: Time of flight mass spectrometry; identification; *Dendrobium devonianum*; Longling area

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1. Introduction

Dendrobium nobile Lindl. is a famous Chinese herbal medicine, including *Dendrobium devonianum* Paxt and *Dendrobium officinale* Kimura et Migo. *Dendrobium officinale* is a synonym of *Dendrobium catenatum* Lindl [1], but the name *Dendrobium officinale* is generally used in China [2,3]. Research has been performed on *Dendrobium officinale*, due to its positive biological health care effects [4–7]. *Dendrobium devonianum* is a characteristic *Dendrobium* in the Longling area of Yunnan Province, China. It has been continuously favored by consumers in the Chinese market due to its anti-oxidant [8,9], antibacterial [10], immune regulation [11], and other functions. Therefore, many *Dendrobium devonianum* not produced in Longling often pretend to be *Dendrobium devonianum* produced in Longling. Because the medicinal effect of Chinese herbal medicine is closely related to the environment in

which it grows, the medicinal effect of *Dendrobium devonianum* produced in Longling is greater than that of products not produced in Longling area. On the other hand, the *Dendrobium officinale* produced in Longling is not very effective because the area is not its place of origin. Therefore, in the Longling area, *Dendrobium officinale* often pretends to be *Dendrobium devonianum*; especially when it is dried or pulverized into powder, it is difficult to distinguish between *Dendrobium devonianum* and *Dendrobium officinale*. This has resulted in a great negative impact on the standardized development of *Dendrobium devonianum* in Longling, Yunnan.

At present, there are few literature reports on the identification of *Dendrobium devonianum*, and the relevant literature reports mainly focus on *Dendrobium officinale*. In the Chinese pharmacopoeia and related literatures [12,13], methods such as appearance evaluation and thin layer chromatography are used to identify *Dendrobium officinale*. These methods only rely on the appearance, shape, and color, subject to human visual disturbance. *Dendrobium officinale* and its mixed varieties can also be distinguished by fluorescence microscopy [14], but the instruments used have strong specificity, and the sample pretreatment is complicated and the applicability is narrow. Molecular identification technology is a commonly used identification method with good reproducibility and high sensitivity [15,16], but it has high technical requirements and long analysis time. Mid-infrared (MIR) and near-infrared (NIR) spectra are also commonly used methods [17,18], these methods have the advantages of simple operation and quick acquisition of characteristic spectra of samples, but the later data processing technology requires high requirements and does not have universal applicability.

With the development of liquid chromatography technology, liquid chromatography-ultraviolet fingerprint method is also commonly used in the identification of *Dendrobium officinale* [19–21], but the fingerprint method is only judged by similarity, with no exact basis for the evaluation of the similarity; moreover, the characteristic peaks cannot be identified by compound structure. At the same time, the ultraviolet scanning is greatly disrupted by the complex chemical impurities in *Dendrobium officinale*, resulting in poor accuracy. Since the high-precision analysis and high-resolution mass spectrometry can effectively overcome the interference of ion suppression, fragmentation, and the presence of isomers in the process of complex matrix analysis, more information on compound structures can be obtained [22]. Combined with the data analysis of chemometrics, this technique can be better and more useful for the identification of *Dendrobium officinale* [23–25].

The use of *Dendrobium officinale* produced in the Longling area to counterfeit *Dendrobium devonianum* is a new phenomenon, and there are few studies on this phenomenon at present. Therefore, the study aimed at this phenomenon, using time-of-flight mass spectrometry, combined with multivariate analysis, aiming to characterize the metabolic difference among *Dendrobium devonianum* and *Dendrobium officinale* grown in Longling area of Yunnan, China.

2. Materials and Methods

2.1. Sample Collection and Preparation

20 samples (3-year-old, artificial cultivation) of *Dendrobium*, including 13 *Dendrobium devonianum* Paxt and 7 *Dendrobium officinale* Kimura et Migo, were collected from the Longling area of Yunnan, China (Figure 1). Sample collection time was November 2020, all samples were collected from farmers' markets with the permission of local management personnel, which are legally registered with their local authority. The collected samples were quickly transferred to the laboratory, the stems (Length about 15 cm) were selected, dried at 60 °C, pulverized and passed through a 0.28 μm sample sieve, and stored at 4 °C in the dark [26].

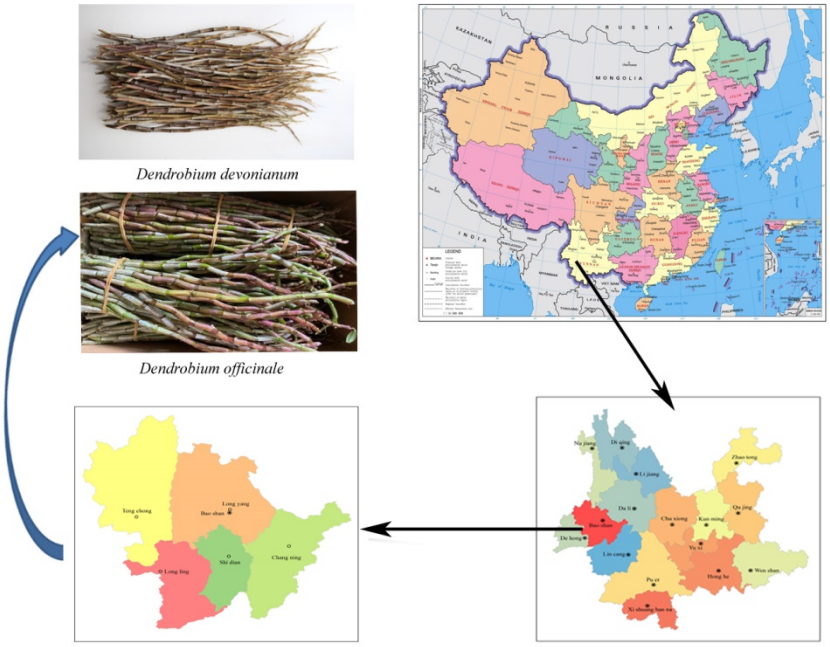

Figure 1. Location map of different cultivation modes of *Dendrobium devonianum* and *Dendrobium officinale.*

2.2. Chemicals and Reagents

Isopropanol and methanol of HPLC grade were obtained from Merck KGaA (Darmstadt, Germany). Highly purified water was prepared by a Milli-Q water purification system (Bedford, MA, USA). Ammonium acetate (≥99.995%) and formic acid of HPLC grade were purchased from Millipore Sigma Company (St. Louis, MO, USA).

2.3. Sample Preparation and Analysis

2.3.1. Sample Preparation Method

The weighed 2 g sample was put into a 50 mL centrifuge tube, and then 20 mL methanol-water solution (V:V = 90:10) was added, vortexed for 1 min, and ultrasonically extracted for 30 min, centrifuged at 5000 r/min for 5 min. The supernatant was filtered through a 0.22 μm filter membrane before analysis.

2.3.2. Instrumental Analysis Method

SCIEX X500R QTOF system was used for data acquisition along with ExionLC AD ultra-high performance liquid chromatography (Framingham, MS, USA) and Waters ACQUITY UPLC BEH C18 column (2.1 × 100 mm, 1.7 μm, Waters, MA, USA). Solvent A was 2 mM ammonium acetate in ultrapure water with 0.01% formic acid and B was the mixed solution of acetonitrile, isopropanol, and water (V:V:V = 47.5:47.5:5) containing 2 mM formic acid and 0.01% formic acid. The flow rate for UHPLC was 0.4 mL/min with the following gradient: 10% B (0~5.0 min), 10% B~50% B (5.0~6.0 min), 50% B~95% B (6.0~15.0 min), 95% B~100% B (15.0~20.0 min), 100% B (20.0~35.0 min), 100% B~5% B (35.0~35.1 min), 5% B (35.1~40.0 min). The injection volume was 10 μL. The electrospray ionization (ESI) source was operated in positive (ESI^+) and nositive (ESI^-) mode. The TOF MS-IDA-15 MS/MS mode was used for data acquisition and the MS source conditions were used: CUR = 35 psi, GS1 = 55 psi and GS2 = 55 psi, CAD = 11, IS =5500/−4500 V, TEM = 550 °C, DP = 70 V/−70 V, CE = 40 V/−40 V, CES = 20. MS scan range: 100~1500 m/z, MS IDA scan range: 50~1500 m/z.

2.3.3. Data Processing and Marker Identification Methods

Sample data were acquired by SCIEX OS (Version 2.0) software using dynamic background subtraction (DBS). Data processing steps such as data import, peak extraction,

metabolite information extraction, metabolite structure prediction, and database search were processed by MarkerView software (SCIEX, MS, USA). The main parameters were set as: mass deviation: 5×10^{-6} (5 ppm), signal-to-noise ratio (S/N) maximum window was 5, unknowns determination retention time deviation window was 5%, and identification database was XIC. The identified target substances were clustered on the MetaboAnalyst online platform, and subjected to multivariate statistical analysis such as principal component analysis (PCA). The T-test was used to screen the difference components through the Natural Products-TCM Library_1.0 established by SCIEX and online ChemSpider database (HMDB, Massbank, Pubmed, etc.) for structural search and alignment.

3. Results and Discussion

3.1. Optimum Selection of Extraction Solvents

The extraction effect of methanol to water ratios (90:10, 70:30, 50:50, and 30:70) was investigated. The results show that when the proportion of water in the extract is larger (greater than 30%), the color of the extract is darker, and a large number of water-soluble polysaccharides, pigments, and other substances which would interfere with mass spectrometry analysis were extracted in *Dendrobium* samples. Finally, a methanol: water ratio of 90:10 was optimally selected. Under this condition, the cells of the *Dendrobium* samples would be infiltrated by water, more intracellular substances could be fully extracted by methanol, and the extraction amount of large-polarity polysaccharides and pigment substances were also reduced to a certain extent. As shown in Figure 2, when the ratio of methanol: water was 30:70, the TIC chromatogram contains more large polar extracts in about 1 min, and when the extraction solution ratio of methanol: water was 90:10, more moderately polar compounds can be extracted in the range of 2–15 min.

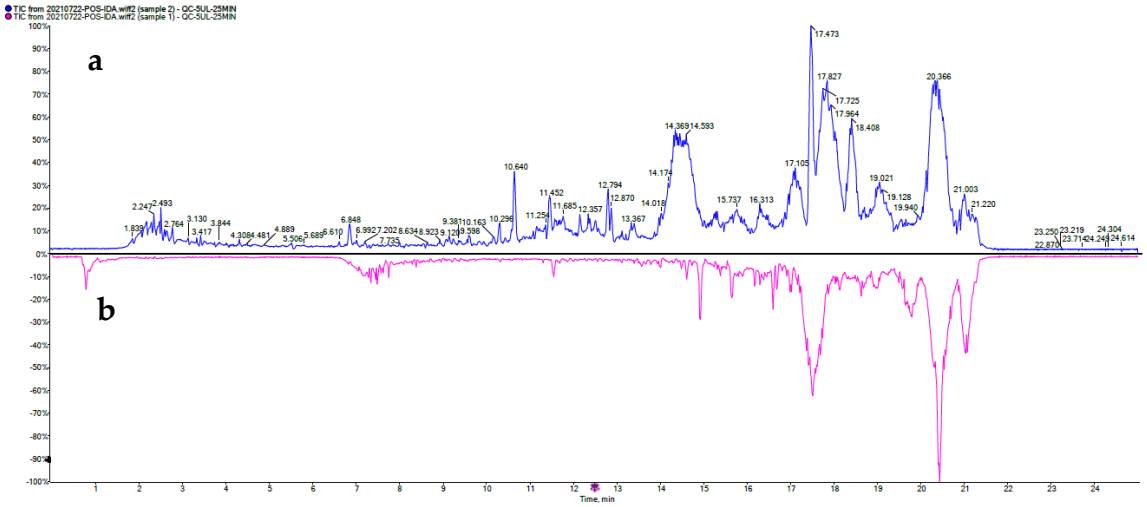

Figure 2. TIC chromatograms of different extraction solvents (**a**) methanol: water ratio of 90:10, (**b**) methanol: water ratio of 30:70.

3.2. Stability and Repeatability of Instrument

100 µL of each sample of the 20 samples in this experiment were mixed to make a quality control sample (QC). During the injection process, a QC sample was run before every 4foursamples. A total of five QC samples were run in this experiment to monitor the sensitivity and stability of the instrument and for subsequent data analysis and correction. As shown in Figure 3, the overlapped graphs of the five QC samples were consistent, indicating that the instrument has good repeatability. On the other hand, among the five QC samples, three representative m/z values at different retention times were selected to compare the response intensities. As shown in Figure 4, the deviations of the response intensities of the three m/z values in the five QC samples were small, indicating that the

performance of the instrument was robust and rugged, and the data obtained were stable and reliable.

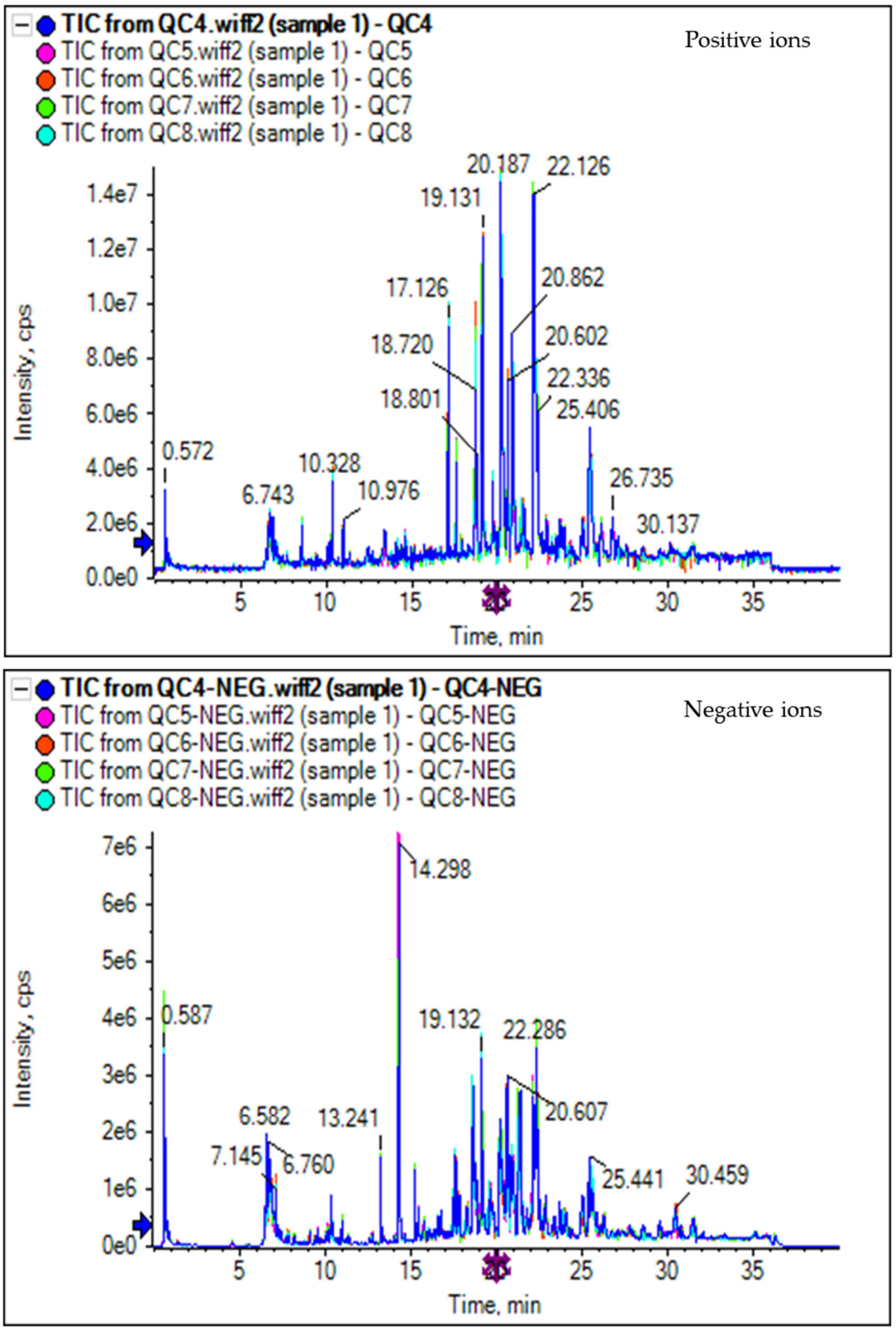

Figure 3. The overlapped graphs of the five QC samples.

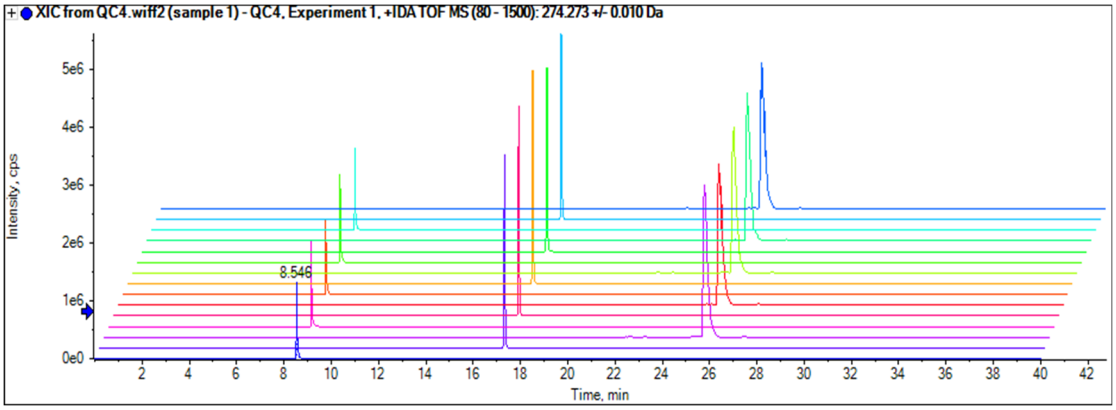

Figure 4. Stacked plot of response intensities for three *m/z* values of five QC samples.

3.3. Identification of Dendrobium devonianum and Dendrobium officinale

In positive and negative ion modes, 3645 and 2344 peaks were detected, respectively. The collected *Dendrobium devonianum* and *Dendrobium officinale* data were searched using the database, and a total of 64 positive ion compounds and 60 negative ion compounds were identified in both *Dendrobium devonianum* and *Dendrobium officinale*, a total of 124 compounds, mainly including organic acids, polyphenols, alkaloids, amino acids and their derivatives, benzene and its derivatives, and other compounds, similar to the composition reported in the related literature [27,28], as shown in Figure 5.

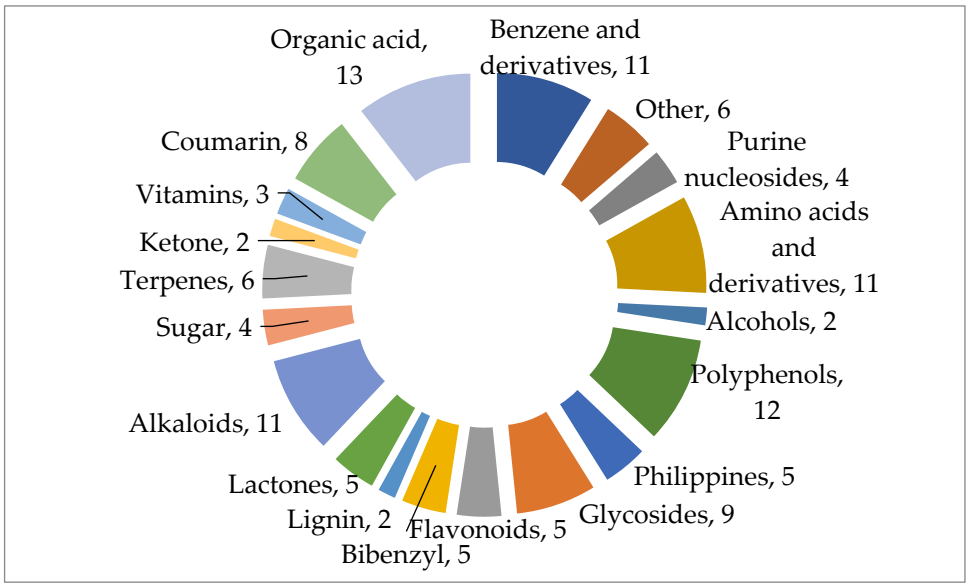

Figure 5. Compounds identified using the database in *Dendrobium devonianum* and *Dendrobium officinale.*

Using MarkerView software to conduct PCA analysis, Score Plot and Loading Plot, it can be seen that *Dendrobium devonianum* and *Dendrobium officinale* from the Longling area can be clearly distinguished, indicating that high-resolution mass spectrometry can effectively identify *Dendrobium devonianum* and *Dendrobium officinale* from the same place, Figure 6. The volcano plot in Figure 7 shows that the closer the ions were to the two ends of the X-axis, the greater the difference was.

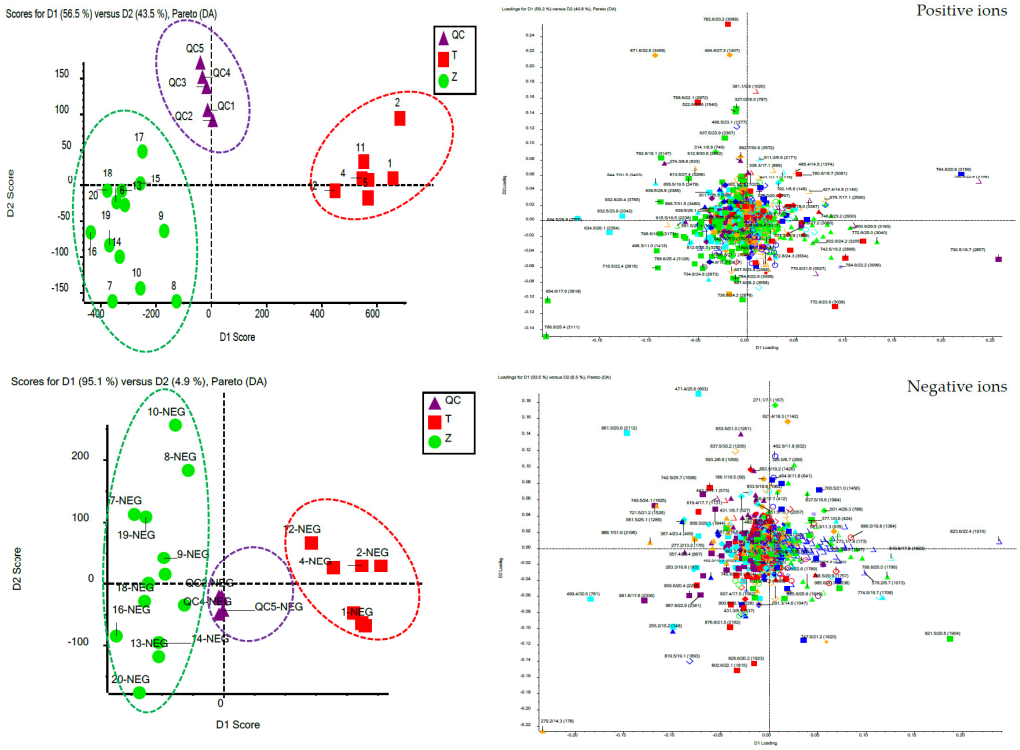

Figure 6. Score plot and loading plot of PCA of *Dendrobium devonianum* and *Dendrobium officinale* (T: *Dendrobium officinale*, Z: *Dendrobium devonianum*, QC: quality control sample).

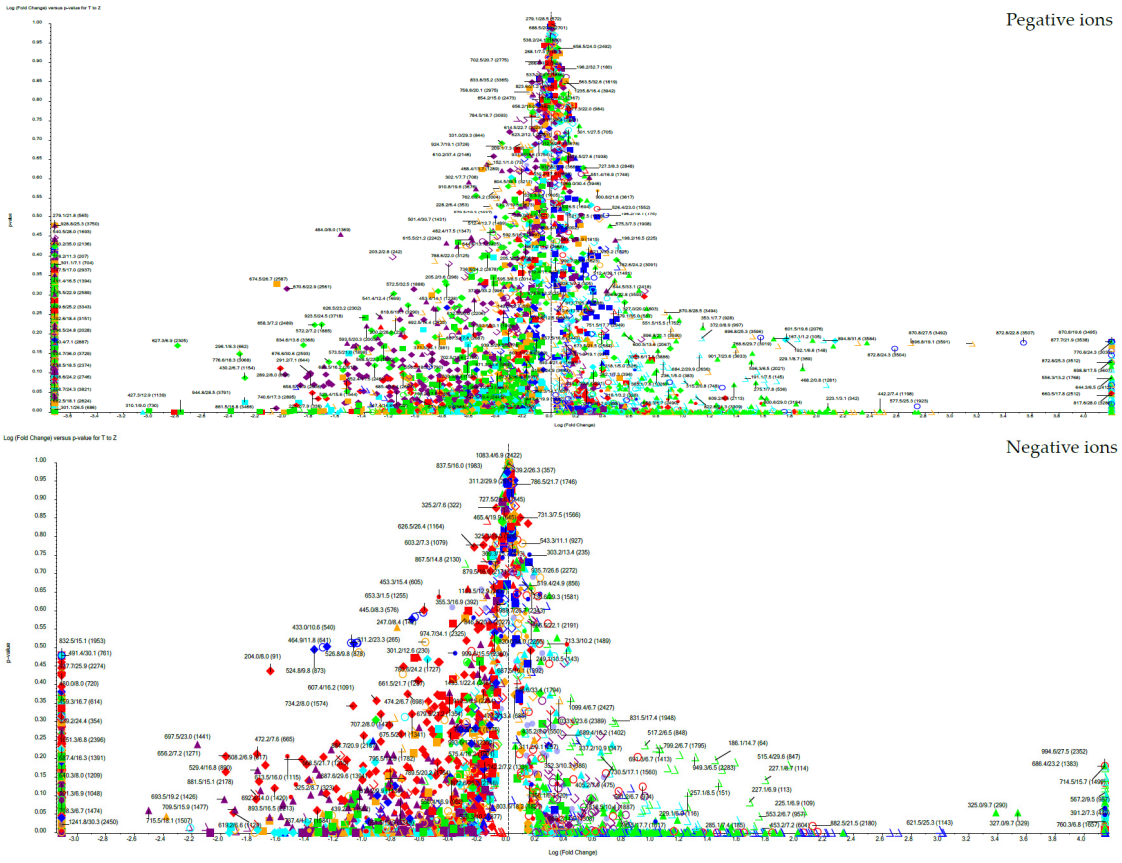

Figure 7. The volcano plot of *Dendrobium devonianum* and *Dendrobium officinale*.

Through the analysis of loading plot and volcano plot, the 3645 and 2344 peaks detected were screened for differential compounds. Then, differential markers compounds were screened by T-test; differential marker compounds can be identified when $p < 0.01$ and fold change (FC) ≥ 2 or FC ≤ 0.5. Combined with the database comparison and reports in the literature [4,28–30], it was confirmed that there were 15 differential markers in the positive ion mode and 17 in the negative ion mode, as shown in Table 1. In the heatmap (Figure 8), the blue part indicates that the relative content of metabolites is low, and the red part indicates that the relative content is high. It can be seen that the relative content of compounds such as citric acid, shikimic acid, phenprobamate, protocatechuic aldehyde, caffeic acid, daphnetin, p-anisic acid, raspberry ketone, germacrone, curcumol, (+)-nootkatone in *Dendrobium devonianum* was higher than that of *Dendrobium officinale*. The relative content of 6,7-dimethoxycoumarin, vanillic acid, eriodictyol, dendrocandin B, 4-methoxy-2,5,9-trihydroxy-9,10-dihydrophenanthrene, amoenylin, (+)-lirioresinol B and other compounds in *Dendrobium officinale* was higher than that in *Dendrobium devonianum*, which may be related to the difference of its varieties.

Table 1. Difference marker in *Dendrobium devonianum* and *Dendrobium officinale* analyzed by UHPLC-TOF-MS.

Peak	Retention Time/Min	Component Name	Formula	Found At Mass	Mass Error (ppm)	Adduct/Charge	*p*-Value	Fold Change
1	0.53	Citric acid	$C_6H_8O_7$	191.0199	0.8	$[M-H]^-$	8.37×10^{-4}	0.3676
2	0.57	Shikimic acid	$C_7H_{10}O_5$	173.0457	0.9	$[M-H]^-$	3.73×10^{-4}	0.3967
3	1.09	Vanillic acid	$C_8H_8O_4$	169.0495	−0.3	$[M+H]^+$	1.38×10^{-8}	18.185
4	1.23	Ethyl gallate	$C_9H_{10}O_5$	199.0602	0.7	$[M+H]^+$	2.48×10^{-8}	7.5549
5	1.30	Phenprobamate	$C_9H_{11}NO_2$	164.0716	−0.7	$[M-H]^-$	8.43×10^{-3}	0.3215
6	1.59	4′-Hydroxyacetophenone	$C_8H_8O_2$	137.0602	3.6	$[M+H]^+$	1.08×10^{-7}	4.2651
7	1.78	4-Hydroxybenzoic acid	$C_7H_6O_3$	139.0388	−1.2	$[M+H]^+$	1.35×10^{-10}	5.7547
8	2.16	3-O-Caffeoylquinic acid methyl ester	$C_{17}H_{20}O_9$	369.1167	−3.6	$[M+H]^+$	1.16×10^{-8}	15.996
9	2.98	Protocatechuic aldehyde	$C_7H_6O_3$	137.0245	0.5	$[M-H]^-$	1.35×10^{-10}	5.7547
10	3.49	Caffeic acid	$C_9H_8O_4$	179.0355	2.7	$[M-H]^-$	3.14×10^{-4}	0.3564
11	3.59	Orcinol glucosid	$C_{13}H_{18}O_7$	285.0969	−3.9	$[M-H]^-$	6.06×10^{-10}	5.9221
12	4.24	Daphnetin	$C_9H_6O_4$	177.0193	−0.3	$[M-H]^-$	3.70×10^{-5}	0.2891
13	4.73	Cantharidin	$C_{10}H_{12}O_4$	197.0812	2.0	$[M+H]^+$	8.30×10^{-9}	3.2472
14	5.38	Topotecan	$C_{23}H_{23}N_3O_5$	420.1583	4.2	$[M-H]^-$	1.71×10^{-7}	11.844
15	5.68	Genipin	$C_{11}H_{14}O_5$	227.0920	2.5	$[M+H]^+$	2.09×10^{-10}	5.7112
16	6.51	p-Anisic acid	$C_8H_8O_3$	153.0548	1.0	$[M+H]^+$	1.48×10^{-5}	0.1837
17	6.56	Acanthoside B	$C_{28}H_{36}O_{13}$	581.2220	−1.5	$[M+H]^+$	2.65×10^{-12}	36.214
18	6.69	4-Acetoxy-3-methoxycinnamic acid-H	$C_{12}H_{12}O_5$	235.0603	−3.7	$[M-H]^-$	8.99×10^{-4}	0.4932
19	6.70	6, 7-Dimethoxycoumarin	$C_{11}H_{10}O_4$	207.0653	0.3	$[M+H]^+$	2.93×10^{-9}	5.8539
20	6.70	(+)-Lirioresinol B	$C_{22}H_{26}O_8$	417.1542	−3.2	$[M-H]^-$	2.19×10^{-4}	2.0176
21	6.84	Raspberry ketone	$C_{10}H_{12}O_2$	165.0909	−0.4	$[M+H]^+$	1.30×10^{-5}	0.1281
22	6.84	Ethyl caffeate	$C_{11}H_{12}O_4$	207.0660	−1.4	$[M-H]^-$	3.84×10^{-3}	2.1844
23	6.95	Eriodictyol	$C_{15}H_{12}O_6$	287.0561	0.1	$[M-H]^-$	3.24×10^{-8}	3.5502
24	7.37	Germacrone	$C_{15}H_{22}O$	219.1746	1.3	$[M+H]^+$	3.11×10^{-3}	0.0930
25	7.37	Curcumol	$C_{15}H_{24}O_2$	237.1850	0.3	$[M+H]^+$	2.74×10^{-3}	0.0770
26	7.37	(+)-Nootkatone	$C_{15}H_{22}O$	219.1746	1.3	$[M+H]^+$	3.11×10^{-3}	0.1936
27	7.39	Amoenylin	$C_{17}H_{20}O_5$	303.1230	−2.5	$[M-H]^-$	3.31×10^{-3}	7.5125
28	7.42	4-Methoxy-2, 5, 9-trihydroxy-9, 10-dihydrophenanthrene	$C_{15}H_{14}O_4$	257.0815	−1.8	$[M-H]^-$	3.89×10^{-11}	5.6239
29	7.77	Nobilonine	$C_{17}H_{27}NO_3$	294.2051	−4.2	$[M+H]^+$	9.19×10^{-5}	3.2548
30	7.96	Kaempferide	$C_{16}H_{12}O_6$	299.0554	−2.4	$[M-H]^-$	5.25×10^{-3}	2.6050
31	8.11	Denbinobin	$C_{16}H_{12}O_5$	283.0605	−2.6	$[M-H]^-$	4.09×10^{-6}	127.68
32	8.66	Dendrocandin B	$C_{27}H_{30}O_8$	481.1847	−4.4	$[M-H]^-$	5.34×10^{-10}	5.0332

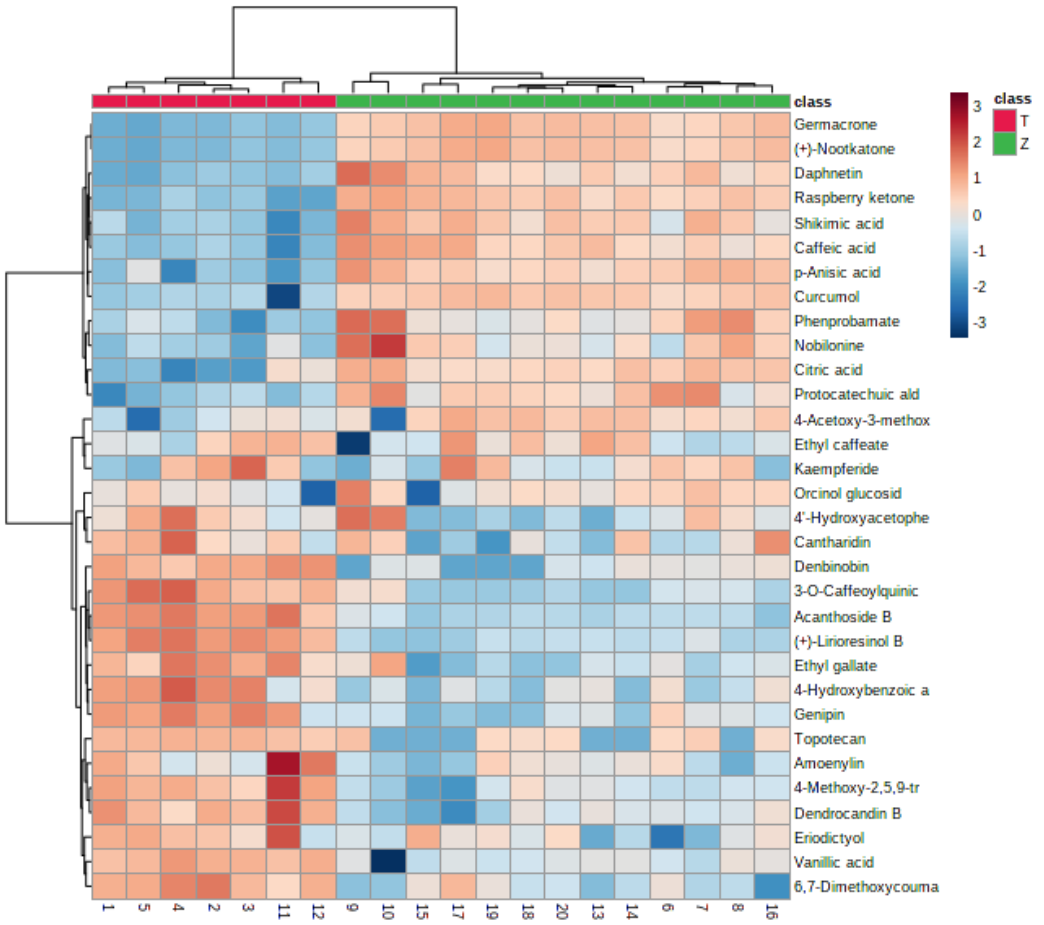

Figure 8. Heatmap of difference markers in *Dendrobium devonianum* (Z) and *Dendrobium officinale* (T).

4. Conclusions

In this study, time-of-flight mass spectrometry was applied to the identification of *Dendrobium devonianum* and *Dendrobium officinale* produced in Longling, Yunnan Province, China. The collected data were analyzed by PCA and T test using MarkerView software to find differential marker compounds, and the structures of the compounds were identified through database search. In positive and negative ion modes, 3645 and 2344 peaks were detected respectively, and 64 and 60 compounds were identified, totaling 124 compounds, mainly including organic acids, polyphenols, alkaloids, amino acids and their derivatives, benzene and its derivatives, and other compounds. The score plot and loading plot analyzed by PCA show that *Dendrobium devonianum* and *Dendrobium officinale* produced in the Longling area can be effectively differentiated by time-of-flight mass spectrometry and 32 different markers analyzed by *t*-test. The successful identification of *Dendrobium devonianum* and *Dendrobium officinale* is of great significance for promoting the characteristic *Dendrobium devonianum* industry in Longling County, Yunnan Province and the orderly development of *Dendrobium* industry in China.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations9050108/s1.

Author Contributions: Conceptualization, T.L. and H.-C.L.; methodology, T.L. and X.-L.C.; software, L.C. and J.W.; validation, Z.-X.H.; formal analysis, X.-L.C.; investigation, L.-J.S.; resources, G.-W.W., J.W. and Z.-X.H.; data curation, L.C.; writing—original draft preparation, T.L.; writing—review and editing, H.-C.L.; supervision, H.-C.L.; funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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