separations

MDPI

Article

Exploratory Study on Distinguishing Dendrobium Stem and Five Species of Dendrobium Using Heracles Neo Ultra-Fast Gas Phase Electronic Nose

Yuping Dai [1,2,3,†], Dan Huang [1,3,4,†], Ye He [1,2], Yun Xiang [1,*] and Shunxiang Li [1,3,4,*]

1 State Key Laboratory of Chinese Medicine Powder and Medicine Innovation in Hunan (Incubation), Science and Technology Innovation Center, Hunan University of Chinese Medicine, Changsha 410208, China; daiyuping397@163.com (Y.D.); huangdan110@hnucm.edu.cn (D.H.); hy070915@126.com (Y.H.)
2 Hunan Fenghuang Lanke Traditional Chinese Medicine Co., Ltd., Changsha 410208, China
3 Hunan Engineering Technology Research Center for Bioactive Substance Discovery of Chinese Medicine, School of Pharmacy, Hunan University of Chinese Medicine, Changsha 410208, China
4 Hunan Province Sino-US International Joint Research Center for Therapeutic Drugs of Senile Degenerative Diseases, Changsha 410208, China
* Correspondence: xiangyun@hnucm.edu.cn (Y.X.); lishunxiang@hnucm.edu.cn (S.L.)
† These authors contributed equally to this work.

Abstract: Dendrobium stem is a valuable food with medicinal and edible properties. Due to its high medicinal value and price, closely related *Dendrobium* varieties are often sold as imitations on the market. Therefore, there is an urgent need to develop new methods that can quickly identify Dendrobium stem and its closely related species. The Heracles Neo ultra-fast gas phase electronic nose was used in this study to determine and analyze the composition and contents of volatile organic compounds (VOCs) in Dendrobium stem and samples of five other species closely related to it. A total of 20 VOCs were identified, and a fingerprint map of the VOCs was constructed. Principal component analysis (PCA), Euclidean distance, and other methods were used to comprehensively process and analyze the obtained VOC information. The AroChemBase database was also used for qualitative analysis of the compounds. The results showed that there are significant differences in the odor fingerprint spectra of Dendrobium stem and the five other closely related species. The main types of compounds in Dendrobium stem and its five closely related species were organic esters, aldehydes, ketones, and olefins. Among them, 3-methylbutanal and n-butanol were characteristic compounds of the Dendrobium stem sample, while the VOCs acetonitrile and trometamol were present in the five related *Dendrobium* species samples. The Heracles Neo ultra-fast gas phase electronic nose can quickly and accurately identify Dendrobium stem and its five closely related species. It can also be used for the quality evaluation of Dendrobium stem, providing a theoretical reference for reducing the phenomenon of medicinal confusion in the Dendrobium stem market.

Keywords: Dendrobium stem; *Dendrobium*; Heracles Neo ultra-fast gas phase electronic nose; volatile organic compounds; PCA; Euclidean distance

Citation: Dai, Y.; Huang, D.; He, Y.; Xiang, Y.; Li, S. Exploratory Study on Distinguishing Dendrobium Stem and Five Species of Dendrobium Using Heracles Neo Ultra-Fast Gas Phase Electronic Nose. *Separations* **2024**, *11*, 211. https://doi.org/10.3390/separations11070211

Academic Editors: Paraskevas D. Tzanavaras and Susanne K. Wiedmer

Received: 13 June 2024
Revised: 30 June 2024
Accepted: 9 July 2024
Published: 10 July 2024

1. Introduction

Dendrobium officinale Kimura et Migo (Fam. Orchidaceae) is a herbaceous plant that has been the subject of research for many years [1]. Dendrobium stem is the dried stem of *Dendrobium officinale* Kimura et Migo (Fam. Orchidaceae). It has been widely used as a medicinal and edible product for thousands of years, and it is listed as a top-grade traditional Chinese medicine along with *Ganoderma lucidum*, Ginseng, and *Cordyceps sinensis*. At the same time, Dendrobium officinale is often used as an ingredient in food. Common Dendrobium stem foods include wine, yogurt, and extract [2].

Dendrobium stem benefits the stomach and fluid generation. It is commonly used for heat-related conditions consuming fluids like dry mouth, irritation, and thirst [3].

Dendrobium is a collective term for various medicinal plants in the Dendrobium genus, Orchidaceae family. Besides Dendrobium stem, common medicinals include *Dendrobium nobile* Lindl, *Dendrobium huoshanense* C.Z.Tang et S.J.Cheng, *Dendrobium chrysotoxum* Lindl, *Dendrobium fimbriatum* Hook, and fresh/dried stems of similar species in the same genus. Dendrobium stem, known as the head of the "Nine Immortal Grasses of China," is expensive due to its scarce wild resources and high medicinal value.

Modern pharmacological research has shown that plants of the *Dendrobium* genus are rich in polysaccharides, alkaloids, volatile oils, various beneficial amino acids, and trace elements for humans [4–6]. They provide pharmacological activities such as antioxidant, anti-tumor, hypoglycemic, liver protection, and bone enhancement properties and the improvement of endocrine and metabolic disorders and bowel movements [7–11]. The seeds of Dendrobium stem have a low germination rate and slow growth under natural conditions. In addition, due to long-term overharvesting and other reasons, the wild resources of Dendrobium stem are scarce [12]. Due to the rich nutritional value and high price of Dendrobium stem, closely related species such as *Dendrobium fimbriatum* Hook. and *Dendrobium chrysotoxum* Lindl., which have similar appearances and significant differences in medicinal value, are often sold as Dendrobium stem on the market.

At present, Dendrobium stem is typically identified using methods such as source identification, microscopic identification, physicochemical identification, and PCR-RFLP DNA technology [13–16]. The first two methods can be carried out quickly but require the evaluators to have extensive experience, professional knowledge, and strong subjectivity. The latter two have high accuracy and good precision; however, the processes are cumbersome and costly, making it difficult to achieve rapid identification.

The electronic nose, also known as the artificial olfactory system, is an emerging analytical instrument that simulates human olfaction. It is specifically used to detect, analyze, and identify complex flavors and volatile organic compounds (VOCs) [17]. Its principle is that when complex gases touch the embedded gas sensor inside, the sensor begins to detect and recognize the gas components, generating an odor fingerprint, thereby achieving the purpose of distinguishing and verifying the authenticity of different samples [18].

The Heracles Neo electronic nose uses two gas chromatography columns with different polarities to separate odor substances. The chromatographic peaks obtained from the gas phase are used as sensors and processed using appropriate models to qualitatively or quantitatively analyze volatile compounds in the sample [19]. Compared with ordinary gas detection, its advantages lie in its extremely short analysis time, high sensitivity, real-time detection, high throughput, etc. Its retention index qualitative library, combined with n-alkane calibration, converts retention time into retention index and can qualitatively analyze odor components [20,21].

To establish an accurate and efficient identification method for Dendrobium stem and related species, this study compared differences in volatile organic compounds (VOCs) between Dendrobium stem and samples of five closely related species using the Heracles Neo ultra-fast electronic nose, AroChemBase professional database, principal component analysis (PCA), Euclidean distance analysis, and compound qualitative analysis. Sensory descriptions of flavor characteristics for Dendrobium stem and the five Dendrobium samples are additionally provided.

2. Materials and Methods

2.1. Materials

Dendrobium stem and the five Dendrobium samples were identified by Prof. Zhaoming Xie at the Hunan University of Chinese Medicine. A voucher specimen (HNUCM2023-SH01) was deposited in Science and Technology Innovation Center of Hunan University of Chinese Medicine. *Dendrobium officinale* Kimura et Migo (collected from Fenghuang, China, referred to as TPSH), *Dendrobium nobile* Lindl (collected from Chishui, China, referred to as JCSH), *Dendrobium huoshanense* C.Z.Tang et S.J. Cheng (collected from Huoshan, China, referred to as HSSH), *Dendrobium chrysotoxum* Lindl (collected from Jinghong, China, re-

ferred to as GZSH), *Dendrobium fimbriatum* Hook (collected from Wuming, China, referred to as LSSH), and *Dendrobium denneanum* Kerr (collected from Xingyi, China, referred to as DQSH) were selected as samples in this study in order to explore and study the VOCs of different varieties of Dendrobium.

2.1.1. Sample Preparation

Different varieties of Dendrobium stem and five types of *Dendrobium* samples were crushed in sequence, passed through a No. 3 sieve, sealed, and refrigerated for later use. The preparation of the samples for Heracles Neo ultra-fast gas phase electronic nose detection was as follows: First, 1.0 g of Dendrobium stem or Dendrobium sample was weighed and placed into a 20 mL headspace bottle attached to the electronic nose and then sealed with PTFE spacers. For each sample, we set up five parallel samples in order to prevent accidental errors and ensure the accuracy of the experiment. The prepared samples were placed on an automatic sampler device for further analysis.

2.1.2. Heracles Neo Ultra-Fast Gas Phase Electronic Nose Analysis Conditions

The detection conditions for the Heracles Neo were determined by optimizing the detection parameters used in previous research: a 20 mL sample bottle; sample weight of 1.0 g; incubation temperature of 80 °C; incubation time of 20 min; initial temperature of the trap of 40 °C; final temperature of the trap of 240 °C; trap diversion rate of 0 $mL \cdot min^{-1}$; capture duration of 55 s; injection port temperature of 200 °C; injection volume of 5000 μL; injection speed of 250 μL/s; injection duration of 25 s; initial temperature of the column of 40 °C; column temperature program heating method of 0.5 °C/s −150 °C and 3 °C/s to 250 °C; collection time of 290 s; detector temperature of 260 °C; and FID gain of 12. Calibration was performed using a standard solution of n-alkanes (nC6 nC16), and the retention time was converted into a retention index. The chromatographic information was recorded within 275 s. There are two chromatographic columns in the Heracles Neo ultra-fast gas phase electronic nose (Alpha MOS Corporation, Toulouse, France), namely, the low-polarity MXT-5 column and the medium-polarity MXT-1701 column (Alpha MOS Corporation, Toulouse, France). After deducting the blank running reference, the odor chromatograms of Dendrobium stem and the other *Dendrobium* species could be obtained. Qualitative analysis of the compound was then performed using the AroChemBase database.

2.2. Statistical Analysis

Principal component analysis (PCA) and compound qualitative analysis of experimental data were performed using AlphaSoft 17.0 (Alpha MOS Corporation, Toulouse, France), and bar charts were drawn using Origin Pro 2023 software (OriginLab Corporation, Northampton, MA, USA).

3. Results

3.1. Heracles Neo Analysis

The six samples of Dendrobium stem and related species were detected and analyzed using the optimized electronic nose detection parameters mentioned above. Figures 1 and 2 show the different samples represented by different colors. From the gas chromatography overlay graphs, it can be intuitively seen that the detection results of the two chromatography columns are generally similar. There are differences in retention time and peak area among the Dendrobium stem and *Dendrobium* samples. In the spectrum, the blue color represents a prominent chromatographic peak in the HSSH sample between 0 and 50 s, and there is a characteristic peak near 50–100 s. The yellow color represents a higher chromatographic peak in the TPSH sample than in the other five *Dendrobium* samples, and the red color represents a lower chromatographic peak in the GZSH sample. The peak height is relatively low between 100 s and 300 s, with the green JCSH sample showing a significant difference in peak height, which is higher than that of the other samples at different peak times. Through the analysis of the original spectra, it can be concluded that

the differences in the six Dendrobium stem and *Dendrobium* samples are mainly reflected in the changes in peak height, which indicates the difference in VOCs. Overall, there are significant differences in odor among the Dendrobium stem and *Dendrobium* samples, which can be effectively distinguished through odor fingerprint spectra. To further verify the differences between sample groups, PCA statistics were first used to identify the odor differences between sample groups in this study. The differential chromatographic peaks were determined, and then the specific chromatographic peaks were qualitatively analyzed through searching the AroChemBase database.

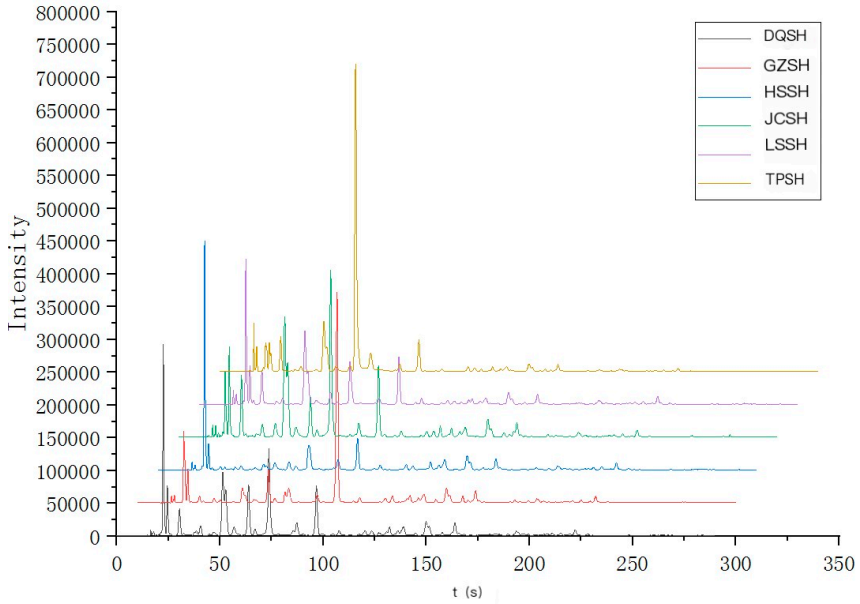

Figure 1. MXT-5 gas chromatogram overlay diagram.

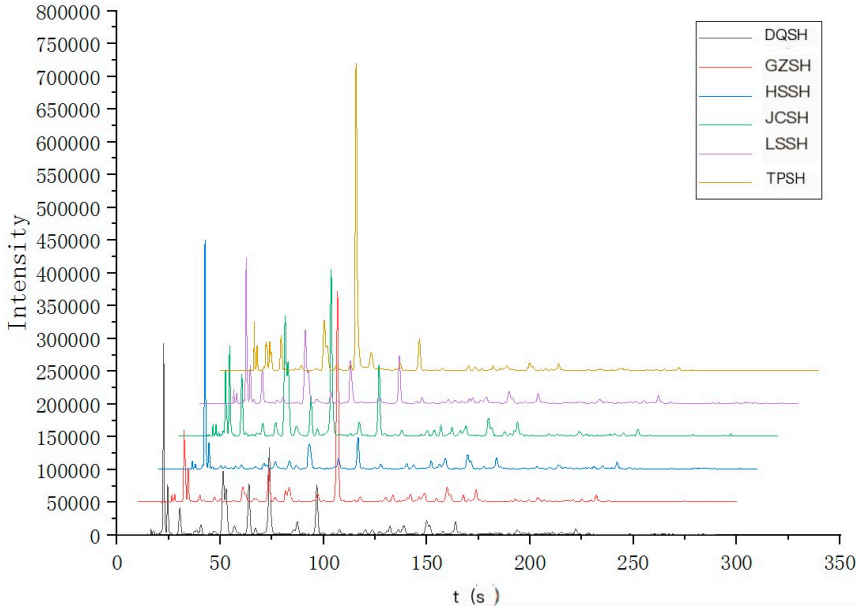

Figure 2. MXT-1701 gas chromatogram overlay diagram.

3.2. Principal Component Analysis (PCA)

Principal component analysis (PCA) is a multivariate statistical method that obtains the maximum difference between data groups based on the original data of the sample without knowledge of their characteristics. After dimensionality reduction and linearization, the data are presented intuitively as two- or three-dimensional graphs [22].

Figure 3 shows the PCA of Dendrobium stem and the five *Dendrobium* samples. The horizontal and vertical coordinates represent the contribution rates of the first principal component (PC1) and the second principal component (PC2) obtained via PCA, respectively. From the figure, it can be seen that the sum of the contribution rates of the first principal component (PC1) and the second principal component (PC2) reaches 79.158%, which can better reflect the actual situation of the sample. A recognition index between 80 and 100 indicates effective differentiation. The recognition index of the sample on the electronic nose principal component analysis chart reaches 93, indicating that the difference in odor can effectively distinguish Dendrobium stem and the five *Dendrobium* samples. The position distribution and distance of Dendrobium stem and the five *Dendrobium* samples in the PCA chart reflect the degree of odor difference between samples. It can be seen that the degree of odor difference between the samples is different. In the PCA chart, the closer the distance, the smaller the sample difference, and the farther the distance, the greater the sample difference. The TPSH sample is located in the left area of the figure, while the other *Dendrobium* samples are located in the right area, indicating a significant difference in overall odor between Dendrobium stem and the other *Dendrobium* samples. The close distribution of LSSH and DQSH indicates that the overall odor difference between the two groups of samples is relatively small. The farthest distance between GZSH and JCSH indicates the greatest difference in VOCs between the two.

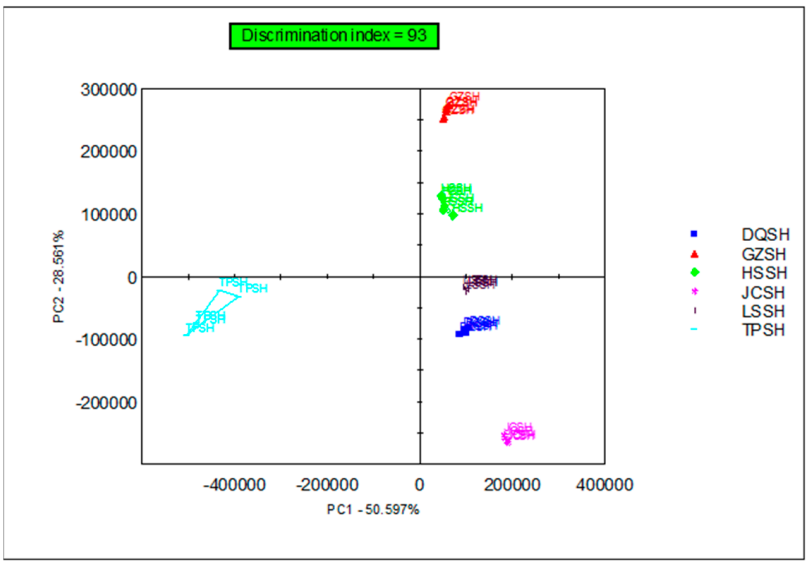

Figure 3. Principal component analysis of Dendrobium stem and five *Dendrobium* samples.

3.3. Euclidean Distance Analysis

Table 1 and Figure 4 show the Euclidean distance of Dendrobium stem and the five *Dendrobium* samples. The larger the distance value, the greater the difference, and the smaller the distance value, the smaller the difference. The distance between DQSH and LSSH samples is the smallest, indicating that these samples have the least difference. The distance between JCSH and TPSH is the largest, indicating that these samples have the most difference, which is consistent with the results of the visual analysis in the PCA diagram. The second and third largest distances are between HSSH and LSSH and DQSH and HSSH, respectively. The first three components with the smallest distance are composed of DQSH, LSSH, and HSSH samples in pairs, indicating that these three samples have the least difference in VOCs and the most similar odor. Similarly, the components with the second- and third-smallest relative distance are GZSH and TPSH and HSSH and TPSH, respectively. Among the three components with the largest distance, TPSH has the largest difference in VOCs compared to the other three samples.

Table 1. Euclidean distance between samples of Dendrobium stem and the five *Dendrobium* samples.

No	Samples	Reference Samples	Distances
1	DQSH	LSSH	156,238.38
2	HSSH	LSSH	218,794.38
3	DQSH	HSSH	258,579.73
4	DQSH	JCSH	274,603.97
5	JCSH	LSSH	347,958.44
6	GZSH	HSSH	383,406.91
7	GZSH	LSSH	390,504.59
8	DQSH	GZSH	415,967.47
9	HSSH	JCSH	507,226.97
10	GZSH	JCSH	542,578.25
11	DQSH	TPSH	503,096.31
12	LSSH	TPSH	575,097.00
13	HSSH	TPSH	576,347.06
14	GZSH	TPSH	626,721.75
15	JCSH	TPSH	685,332.94

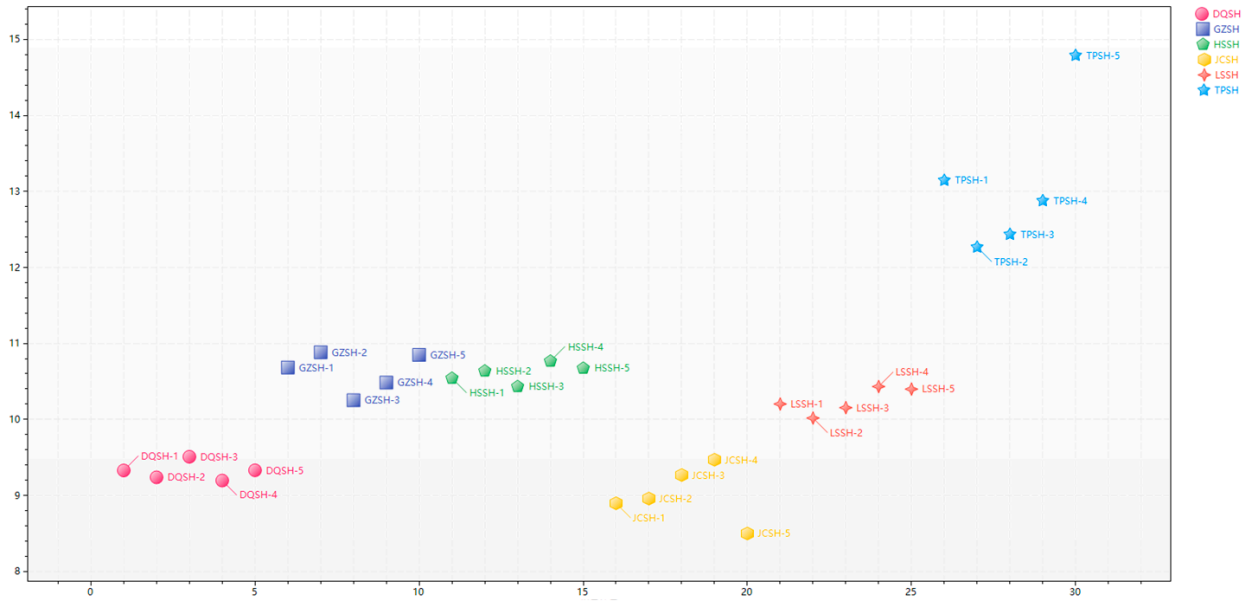

Figure 4. Euclidean distance between samples of *Dendrobium*.

A loading plot was added based on PCA in order to further investigate the differences in odor between different samples. It was determined that chromatographic peaks with good separation effect, high discrimination ability (discrimination ability > 0.900, peak area > 1000), and clear peak sample differentiation would be the most important. The closer the factor is to the sample, the greater the contribution rate. The experimental results are shown in Figure 5. Based on the chromatographic peak screening, the sample's overall distribution trend remained the same as that of Figure 3, indicating that the chromatographic peaks selected reflect the sample's overall odor. The chromatographic peaks were searched in the AroChemBase database based on their retention indices. These chromatographic peaks were analyzed qualitatively to determine the compounds that caused the differences between Dendrobium stem and *Dendrobium* samples.

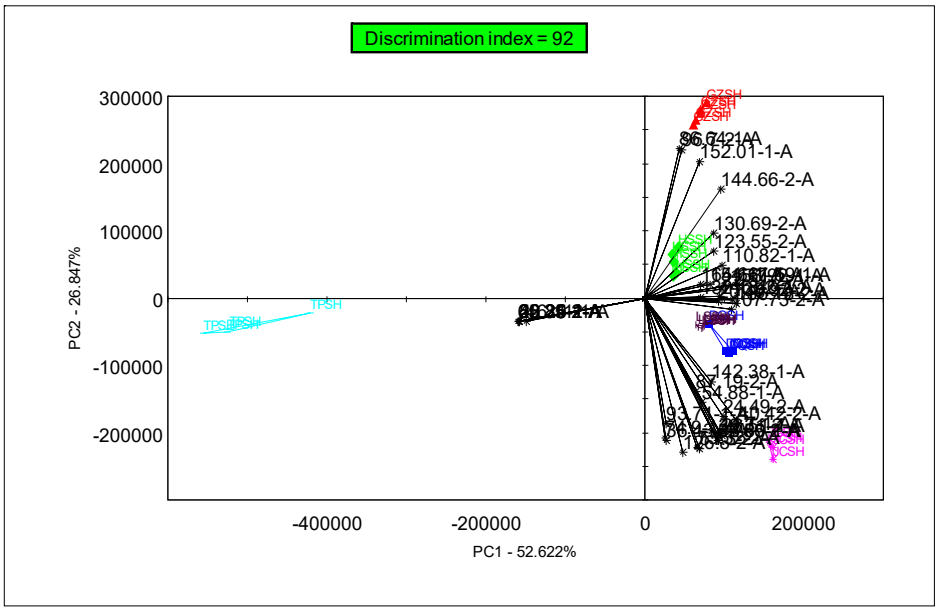

Figure 5. Principal component analysis and loading diagram of Dendrobium stem and five *Dendrobium* samples.

3.4. Compound Identification

Following the abovementioned screening, retention times (Rts) were converted to retention indices (RIs) for chromatographic peaks that meet retention conditions. Data from the AroChemBase database were used to qualitatively analyze the chromatographic peaks that show significant differences. The compounds included in the qualitative analysis are shown in Table 2. The threshold values in Table 1 represent the strength of the substance odor. The threshold values in the air medium are in mg/m^3, and those in the oil medium are in mg/kg. For two compounds with the same content, the lower the threshold in the same medium, the stronger the odor. The odor activity value (OAV), which is the ratio of the concentrations of the individual substances in the sample to their threshold concentrations, is used for two substances with different concentrations and thresholds. A high ratio indicates that the odor activity value is high, contributing significantly to the overall odor. A low ratio indicates that the odor activity value is small and contributes little to the overall odor. The odor activity value of each compound (odor contribution value) of the sample can be calculated by determining its content and the odor threshold. This value can be used to adjust the sample's odor and trace the source of the odor.

Table 2. Differential chromatographic peak qualitative results and odor descriptions.

No	Compounds	CAS	RI (RT-5)	RI (RT-1701)	Odor Description	Odor Threshold
1	Ethanol	64-17-5	419	583	Alcoholic; Ethanol; Etheral; Fragrant; Pleasant; Pungent; Strong; Sweet; Weak	1.54×10^2 (air)
2	Propenal	107-02-8	451	607	Acrid; Almond; Cherry; Choking; Hot fat; Pungent; Sharp; Sweet	0.17 (air)
3	Acetonitrile	75-05-8	543	644	Aromatic; Etheral; Sweet	1.76×10^2 (air)
4	1-Butanamine	109-73-9	619	705	Ammoniacal; Fishy	0.36 (air)
5	3-methylbutanal	590-86-3	654	741	Aldehydic; Almond; Apple; Cheese; Chocolate; Fatty; Fruity; Green; Herbaceous; Malty; Peach; Toasted	2×10^{-3} (air)

Table 2. *Cont.*

No	Compounds	CAS	RI (RT-5)	RI (RT-1701)	Odor Description	Odor Threshold
6	But-(E)-2-enal	123-73-9	658	745	Floral; Green; Plastic; Pungent	0.42 (air)
7	N-butanol	71-36-3	664	799	Alcoholic; Amyl alcohol; Banana; Cheese; Fermented; Fruity; Fusel; Harsh; Medicinal; Oil; Rancid; Strong; Sweet	1.12 (air)
8	Trometamol	77-86-1	668	750	Characteristic	-
9	2,3-Pentanedione	600-14-6	703	792	Almond; Apple; Burnt; Butter; Butterscotch; Caramelized; Cheese; Creamy; Diacetyl; Fresh; Fruity; Grain; Malty; Nutty; Oily; Pungent; Sickly; Sweet	0.02 (air)
10	3-Methylbut-2-en-1-ol	556-82-1	765	864	Fruity; Green; Herbaceous; Lavender	0.25 (water)
11	Hexanal	66-25-1	804	894	Acorn; Aldehydic; Fatty; Fishy; Fresh; Fruity; Grassy; Green; Herbaceous; Leafy; Sharp; Strong; Sweaty; Tallowy; Vinous	0.04 (air)
12	2,4-Octadiene	13643-08-8	823	821	Glue; Warm	1.2×10 (oil)
13	M-Xylene	108-38-3	873	927	Aromatic; Cold meat fat; Plastic; Sweet	0.60(air)
14	3-Ethyloctane	5881-17-4	966	975	-	-
15	beta-Pinene	127-91-3	978	985	Dry; Green; Hay; Musty; Pine; Resinous; Sweet; Turpentine; woody; Woody (dry)	3.7×10 (air)
16	1,3,5-trimethylbenzene	108-67-8	994	997	Aromatic; Herbaceous	1.20 (air)
17	Decane	124-18-5	1001	1001	Alkane; Fruity; Fusel; Sweet	1.13×10 (air)
18	()-.-beta-.-Pinene	18172-67-3	1015	1014	Dry; Fresh; Green; Hay; Pine; Resinous; Terpenic; Turpentine; woody; Woody (dry)	2.00 (air)
19	alpha-Phellandrene	99-83-2	1024	1022	Citrus; Green; Minty; Spicy; Terpenic; Turpentine; woody	3.40 (air)
20	1-Methyl-4-isopropenyl-1-cyclohexene	138-86-3	1034	1040	Citrus; Etheral; Fruity; Green; Lemon; Licorice; Orange; Pleasant	-

As shown in Tables 2 and 3, a total of 20 odor components were identified. In order to more intuitively compare the content differences of compounds in Dendrobium stem and *Dendrobium* samples, a bar chart of differential compound contents was drawn based on the data in Table 3, with VOCs as the *x*-axis and average peak area as the *y*-axis, as shown in Figure 6. In the bar chart, we can observe that the most obvious feature is GZSH, represented by red, with hexanal compounds, which are the characteristic compounds of GZSH samples, having the highest content. TPSH, represented by orange, has two characteristic compounds with higher content, namely, 3-methylbutanal and n-butanol. Some volatile organic compounds are generally lower in content than they are in other samples. The purple color represents JCSH, which has higher contents of compounds such as propenal, but-(E)-2-enal, and 2,3-pentanedione compared to the other *Dendrobium* samples. The content changes in DQSH and LSSH samples are relatively similar, and no LSSH components were detected to be higher than in the other *Dendrobium* samples. The

compound content is generally lower than that of other samples. This also reveals that the abovementioned components may be biomarkers for distinguishing odor differences in Dendrobium stem and *Dendrobium* samples.

Table 3. Average peak area of differential chromatographic peaks.

No	Compounds	CAS	Average Peak Area					
			DQSH	GZSH	HSSH	JCSH	LSSH	TPSH
1	Ethanol	64-17-5	119,106	44,504	138,883	42,433	90,168	17,394
2	Propenal	107-02-8	53,715	34,400	33,137	96,013	41,168	17,780
3	Acetonitrile	75-05-8	32,257	8706	8267	65,322	39,008	0
4	1-Butanamine	109-73-9	7214	1690	1850	18,532	1580	5546
5	3-methylbutanal	590-86-3	0	0	0	0	0	233,691
6	But-(E)-2-enal	123-73-9	80,160	20,714	8733	145,888	91,577	0
7	N-butanol	71-36-3	0	0	0	0	0	132,594
8	Trometamol	77-86-1	54,932	8724	6018	88,517	41,054	0
9	2,3-Pentanedione	600-14-6	72,199	40,390	10,968	175,403	13,140	9402
10	3-Methylbut-2-en-1-ol	556-82-1	12,463	4449	7717	14,522	4966	8173
11	Hexanal	66-25-1	59,134	245,694	47,192	80,454	54,779	37,616
12	2,4-Octadiene	13643-08-8	35,463	20,428	23,021	42,265	17,095	26,329
13	M-Xylene	108-38-3	5615	6488	9261	6811	6800	2775
14	3-Ethyloctane	5881-17-4	7257	5061	6011	7882	4031	4169
15	beta-Pinene	127-91-3	5813	5474	4551	5975	3236	3193
16	1,3,5-trimethylbenzene	108-67-8	3625	4833	2307	1766	1706	1182
17	Decane	124-18-5	10,429	9200	12,370	10,371	6386	5608
18	()-.-beta-.-Pinene	18172-67-3	6399	6363	5990	6897	4208	3856
19	alpha-Phellandrene	99-83-2	15,034	14,971	14,487	16,150	10,487	9003
20	1-Methyl-4-isopropenyl-1-cyclohexene	138-86-3	4291	5194	2176	2179	1755	350

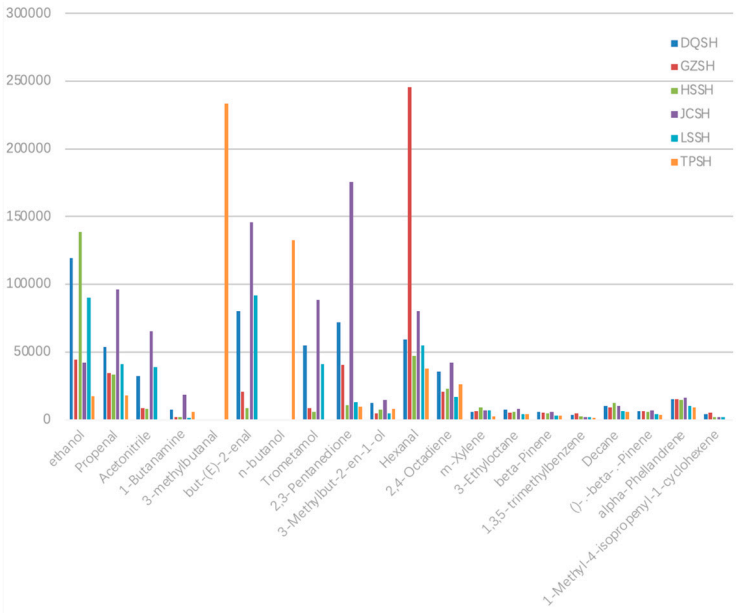

Figure 6. Histogram of differential compound contents.

4. Discussion

Heracles Neo ultra-fast gas phase electronic nose technology was used in this study to conduct in-depth chemical composition analysis of Dendrobium stem and its related species, and 20 compounds were successfully identified. It is worth noting that in the TPSH samples, we found two unique compounds: 3-methylbutanal and n-butanol. The presence of these two compounds may be the key factor leading to significant differences between Dendrobium stem and its related species. In order to further analyze and distinguish the odor characteristics of different *Dendrobium* samples, we established an odor fingerprint map containing *Dendrobium* samples and Dendrobium stem based on the chromatographic peaks of key chemical components that affect their odor. Using these data, a stoichiometric PCA model was also established with a cumulative contribution rate of 79.158% (the sum of the contribution rates of the first principal component (PC1) and the second principal component (PC2)). According to the standards of chemometrics, if the overall contribution rate of a model exceeds 70% to 85%, the model has good discrimination ability. This indicates that the model can quickly distinguish, identify, and analyze the odor of Dendrobium stem and its related species, providing a scientific basis for quality control and source tracing.

In addition, the AroChemBase database was used to qualitatively identify the chromatographic peaks with significant differences, and fingerprint and qualitative substance analyses were performed on Dendrobium stem and the five types of *Dendrobium* samples. Different varieties of *Dendrobium* samples showed differences in component types. By combining the bar charts of differential compound contents, it can be concluded that the composition of Dendrobium stem and the five types of *Dendrobium* samples is complex, which is mainly reflected in the relative contents of ethanol, propylene, 2,3-pentanedione, and hexanal. In the evaluation of flavor characteristics, the main sensory properties of Dendrobium stem and the five related species are fruity, sweet, green, and fresh. 3-Methylbutanal and n-butanol are characteristic compounds of the TPSH sample which endow TPSH with unique malt, nut, and chocolate flavors [23]. Therefore, these two compounds can be used to distinguish Dendrobium stem from other sampled varieties. In addition to these two characteristic compounds, the contents of individual compounds in Dendrobium stem samples are generally lower than those of the other *Dendrobium* samples. But-(E)-2-enal, acetonitrile, and trometamol are differential VOCs with a light aroma found in all five Dendrobium samples but not the TPSH sample. However, their contents are similar in the five Dendrobium samples, so they can only be used to distinguish Dendrobium stem from the other five *Dendrobium* samples. Hexanal is a characteristic compound of GZSH with a special herbal fragrance. Its content is much higher in GZSH samples than in the other five samples. Using a gas chromatography overlay, it can be seen that the peak of this compound appears at around 95 s. This makes hexanal the main characteristic compound distinguishing GZSH from the other *Dendrobium* samples. In addition, 2,4-octadience was detected in all samples. It has a strong herbal odor and is a key substance contributing to the flavor of the *Dendrobium* samples. Based on all the analysis results, it can be concluded that the compound differences in TPSH samples are the greatest, which is consistent with existing studies on the quality evaluation of Dendrobium stem [24].

It is important to recognize that odor, as a criterion evaluating medicinal materials and food, is closely related to the intrinsic composition of substances. In the past few decades, new biomimetic sensing technologies have increasingly been applied to quality detection, safety control, and other aspects of life with the development of science and technology [25–28]. In this study, the Heracles Neo ultra-fast gas phase electronic nose was used instead of the human olfactory system. This study confirms the importance of electronic nose technology in the analysis of traditional Chinese medicine odors. The method effectively avoids human factors and increases evaluation accuracy by converting complex odor information into quantifiable data. This approach is in contrast to traditional methods that rely on appearance, color, and the sense of smell to distinguish small differences between samples [29,30].

5. Conclusions

A rapid detection method, Heracles Neo ultra-fast gas phase electronic nose technology, for Dendrobium stem and its closely related species was preliminarily explored in this study. The following conclusions can be drawn:

1. The VOCs of Dendrobium stem and five types of *Dendrobium* samples were analyzed, and a total of 20 odor chemical components were identified. The gas chromatogram results obtained from the MXT-1701 and MXT-5 chromatographic column analysis were similar. It was observed that there are certain differences in the retention time and peak area of the six Dendrobium stem and *Dendrobium* samples.
2. PCA also verified that there are obvious odor differences between Dendrobium stem and its related *Dendrobium* species.
3. According to the Euclidean distance, the difference between the Dendrobium stem sample and the JCSH sample was the largest.
4. The AroChemBase database was used to characterize the screened chromatographic peaks with large differences, and two unique compounds in the Dendrobium stem sample were found: 3-methylbutanal and n-butanol.

This work provides a reference for the classification of the odor patterns, characteristic description, and origin classification of Dendrobium. The results of this study will provide technical support for the identification and quality control of Dendrobium stem and five species of *Dendrobium* and are of great significance for ensuring the quality and value of Dendrobium stem on the market. This study also lays a solid theoretical foundation for the application of Heracles Neo ultra-fast gas phase electronic nose technology in other fields.

Author Contributions: Conceptualization, Y.D. and D.H.; methodology, Y.D. and D.H.; software, Y.H.; formal analysis, Y.H.; investigation, Y.X.; resources, Y.X.; data curation, Y.H. and Y.D.; writing—original draft preparation, Y.D. and D.H.; writing—review and editing, Y.X. and S.L.; supervision, Y.D. and D.H.; project administration, Y.X. and S.L.; funding acquisition, Y.X. and S.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Department of Science and Technology of Xiangxi Tujiazu and Miaozu Autonomous Prefecture (No. 2022JSGG03), Hunan Provincial Natural Science Foundation of China (No. 2024JJ7358), and Hunan University of Chinese Medicine Undergraduate Research Innovation Fund (No. 2023BKS147).

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors would like to acknowledge Yang Ma, Wenxi Xiao & Yafang Du for supporting this work.

Conflicts of Interest: Authors Yuping Dai and Ye He were employed by the company Hunan Fenghuang Lanke Traditional Chinese Medicine Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Zhang, P.; Zhang, X.; Zhu, X.; Hua, Y. Chemical Constituents, Bioactivities, and Pharmacological Mechanisms of *Dendrobium officinale*: A Review of the Past Decade. *Agric. Food Chem.* **2023**, *41*, 14870–14889. [CrossRef] [PubMed]
2. Cha, S.Y.; Park, S.Y.; Lee, J.S.; Lee, K.H.; Kim, J.H.; Fang, Y.; Shin, S.S. Efficacy of Dendrobium candidum polysaccharide extract as a moisturizer. *Cosmet. Dermatol.* **2022**, *7*, 3117–3126. [CrossRef] [PubMed]
3. Chinese Pharmacopoeia Commission. *Pharmacopoeia of the People's Republic of China*; China Medical Science and Technology Press: Beijing, China, 2020; Volume I, p. 295.
4. Wu, W.; Zhao, Z.; Zhao, Z.; Zhang, D.; Zhang, Q.; Zhang, J.; Fang, Z.; Bai, Y.; Guo, X. Structure, Health Benefits, Mechanisms, and Gut Microbiota of *Dendrobium officinale* Polysaccharides: A Review. *Nutrients* **2023**, *23*, 4901. [CrossRef] [PubMed]
5. Bhardwaj, K.; Bhargav, R.; Patocka, J.; Sharma, R.; Navratilova, Z.; Oleksak, P.; Kuca, K. Dendrobine: A neuroprotective Sesquiterpenic Alkaloid for the Prevention and Treatment of Diseases: A Review. *Mini Rev. Med. Chem.* **2024**, *24*, 1395–1408. [CrossRef] [PubMed]

6. Kirkwood, A.; Fisk, I.; Ayed, C.; Xu, Y.; Yang, N. A flavour perspective of Tiepishihu (*Dendrobium officinale*)—An emerging food ingredient from popular traditional Chinese medicinal plants: A review. *Int. J. Food Sci. Technol.* **2023**, *10*, 4921–4930. [CrossRef] [PubMed]
7. Wang, Z.; Zhao, M.; Zhang, X.; Deng, X.; Li, J.; Wang, M. Genome-wide identification and characterization of active ingredients related β-Glucosidases in *Dendrobium catenatum*. *BMC Genom.* **2022**, *1*, 612. [CrossRef] [PubMed]
8. Wang, Q.T.; Wang, C.F.; Liu, Y.; Zhan, R. Bibenzyl-Phenylpropane Hybrids with Immunosuppressive Activities from Dendrobium Nobile Lindl. *Chem. Biodivers.* **2024**, *21*, e202400283. [CrossRef] [PubMed]
9. Zeng, B.; Yan, Y.; Zhang, Y.; Wang, C.; Huang, W.; Zhong, X.; Chen, Z.; Xie, M.; Yang, Z. Dendrobium officinale Polysaccharide (DOP) inhibits cell hyperproliferation, inflammation and oxidative stress to improve keratinocyte psoriasis-like state. *Adv. Med. Sci.* **2024**, *1*, 167–175. [CrossRef] [PubMed]
10. Zou, J.; Song, Q.; Shaw, P.C.; Zuo, Z. Dendrobium officinale regulate lipid metabolism in diabetic mouse liver via PPAR-RXR signaling pathway: Evidence from an integrated multi-omics analysis. *Biomed. Pharmacother.* **2024**, *173*, 116395. [CrossRef]
11. Luo, D.; Qu, C.; Zhang, Z.; Xie, J.; Xu, L.; Yang, H.; Li, C.; Lin, G.; Wang, H.; Su, Z. Granularity and Laxative Effect of Ultrafine Powder of Dendrobium officinale. *Med. Food* **2017**, *2*, 180–188. [CrossRef] [PubMed]
12. Bao, Y.H. Identification and Evaluation of Germplasm Resources of Dendrobium Officinale. Ph.D. Thesis, Guangzhou University of Chinese Medicine, Guangzhou, China, 2015.
13. Chen, Q.Y.; Huang, Y.T.; Xu, G.H.; Wu, A.Z.; Wei, X.B.; Guo, H. Research progress on active ingredients and identification technology of Dendrobium officinalis. *Stud. Trace Elem. Health* **2022**, *6*, 65–67.
14. Yang, Y.; She, X.; Cao, X.; Yang, L.; Huang, J.; Zhang, X.; Su, L.; Wu, M.; Tong, H.; Ji, X. Comprehensive evaluation of Dendrobium officinale from different geographical origins using near-infrared spectroscopy and chemometrics. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2022**, *277*, 121249. [CrossRef] [PubMed]
15. Liu, J.; He, T.; Chun, Z. DNA molecular identification of Herba Dendrobii and its adulterant species based on ITS sequence analysis. *China J. Chin. Mater. Med.* **2009**, *22*, 2853–2856. [CrossRef]
16. Asahina, H.; Shinozaki, J.; Masuda, K.; Morimitsu, Y.; Satake, M. Identification of medicinal Dendrobium species by phylogenetic analyses using matK and rbcL sequences. *Nat. Med.* **2010**, *2*, 133–138. [CrossRef] [PubMed]
17. Zhang, Y.H.; Li, T.F.; Wei, Z.J.; Qi, L.J.; Gao, W. Construction and application of a fingerprint library of pepper and pepper extract from different origins by ultra-fast gas chromatography electronic nose. *China Food Addit.* **2021**, *9*, 97–104. [CrossRef]
18. Yu, Y.T.; Zhao, Y.M.; Yuan, X.; Chao, L.J.; Li, X.W.; Lu, T.L.; Yan, G.J. Quality evaluation of Astragali Radix from different origins, growth years and harvesting periods by Heracles Neo ultra-fast gas phase electronic nose. *Chin. Tradit. Herb. Drugs* **2022**, *5*, 1328–1337.
19. Sipos, L.; Végh, R.; Bodor, Z.; Zaukuu, J.Z.; Hitka, G.; Bázár, G.; Kovacs, Z. Classification of Bee Pollen and Prediction of Sensory and Colorimetric Attributes-A Sensometric Fusion Approach by e-Nose, e-Tongue and NIR. *Sensors* **2020**, *23*, 6768. [CrossRef] [PubMed]
20. Zhao, Q.L.; Jiang, Q.Y.; Yan, H.; Zhai, C.; Guo, S.; Pan, H. Rapid Identification and Odor Differential Markers of Distinct Origin-Derived Lycium barbarum L. Based on Ultra-Fast Gas Phase Electronic Nose. *J. Nanjing Univ. Tradit. Chin. Med.* **2023**, *6*, 513–522. [CrossRef]
21. Li, M.X.; Qin, Y.W.; Li, Y.; Zhang, J.B.; Ji, D.; Qu, L.Y. Rapid identification and differential markers of Curcumae Radix decoction pieces of different sources based on Heracles Neo ultra-fast gas phase electronic nose. *China J. Chin. Mater. Med.* **2023**, *6*, 1518–1525. [CrossRef]
22. Abdelhafez, O.H.; Othman, E.M.; Fahim, J.R.; Desoukey, S.Y.; Pimentel-Elardo, S.M.; Nodwell, J.R.; Schirmeister, T.; Tawfike, A.; Abdelmohsen, U.R. Metabolomics analysis and biological investigation of three Malvaceae plants. *Phytochem. Anal.* **2020**, *2*, 204–214. [CrossRef]
23. Gupcsó, K.; Kókai, Z.; Bálint, M.; Tavaszi-Sárosi, S.; Németh, É.Z. Studies on Sensory and Phytochemical Characteristics of Poppy (*Papaver somniferum* L.) Varieties for Their Oil Utilisation. *Foods* **2023**, *17*, 3165. [CrossRef] [PubMed]
24. Rao, D.; Zheng, S.G.; Zhao, T.M.; Yan, S.; Hu, Y.D.; Zhao, R.X. Correlation analysis and breeding application of agronomic traits and quality indexes in Dendrobium nobile. *China J. Chin. Mater. Med.* **2021**, *13*, 3330–3336. [CrossRef]
25. Zhao, Y.W.; Jia, W.M.; Wang, Z.J.; Liang, L.D. Synthesis of 2, 3-pentanedione. *Chem. Reag.* **2012**, *5*, 479–480. [CrossRef]
26. Zhang, Q.; Tang, J.; Deng, J.; Cai, Z.; Jiang, X.; Zhu, C. Effect of Capsaicin Stress on Aroma-Producing Properties of *Lactobacillus plantarum* CL-01 Based on E-Nose and GC-IMS. *Molecules* **2023**, *1*, 107. [CrossRef] [PubMed]
27. Jing, W.; Zhao, X.; Li, M.; Hu, X.; Cheng, X.; Ma, S.; Wei, F. Application of Multiple-Source Data Fusion for the Discrimination of Two Botanical Origins of Magnolia Officinalis Cortex Based on E-Nose Measurements, E-Tongue Measurements, and Chemical Analysis. *Molecule* **2022**, *12*, 3892. [CrossRef] [PubMed]
28. Ding, Y.; Dai, Y.D.; Ding, M.; Chen, P.; Wang, Q. The flavor differences of different substrates were analyzed by electronic nose, electronic tongue and HS-SPME-GC-MS. *J. Fungal Res.* **2024**, *536*. [CrossRef]

29. Lu, S.; Han, B.; Yu, B.; Hong, M.; Chen, J.; Chen, J. Comparative Analysis of Morphological and Microscopic Characteristics of *Dendrobium officinale* from 3 Different Producing Areas. *J. Shaoguan Univ. Nat. Sci.* **2023**, *6*, 46–51. [CrossRef]
30. Huang, X.; Zhong, K.; Han, K.; Yang, T.; Liu, X. Traits and microscopic characteristics of Dendrobium nobile from different habitats. *Chin. Tradit. Herb. Drugs* **2020**, *8*, 2226–2231. [CrossRef]