Analysis of the Essential Oils of *Coriandrum sativum* Using GC-MS Coupled with Chemometric Resolution Methods

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The essential oils extracted from *Coriandrum sativum* L. were analyzed by GC-MS coupled with chemometric resolution methods. Through the chemometric resolution methods, peak clusters were uniquely resolved into the pure chromatographic profiles and mass spectra of each component. Qualitative analysis was performed by comparing the pure mass spectra with those in the NIST 05 mass spectral library. Quantitative analysis was performed using the total volume integration method. A total of 118 constituents were detected, of which 104 were identified, accounting for 97.27% of the total content. The results indicate that GC-MS combined with chemometric resolution methods can greatly enhance the capability of separation and the reliability of qualitative and quantitative results. The combined method is an economical and accurate approach for the rapid analysis of the complex essential oil samples in *Coriandrum sativum* L.

Key words *Coriandrum sativum*; chemometric resolution method; essential oil; GC-MS

Coriandrum sativum L. (CSL), also called Chinese parsley in China, is a famous spice and is widely used in cooking due to its pleasant and delicate aroma. In China, CSL is not only an important spice in cuisine but is also a key traditional medicine. CSL is often used to treat headaches, measles, and rectal prolapse, and to prevent cancer.[1)] Numerous studies have been carried out regarding the chemical compositions and pharmacological activities of the essential oils of CSL fruits/seeds.[2—8)] However, the fresh immature CSL plant is in fact the part most consumed by humans and most often used as medicine. The essential oils extracted from the CSL plant contain important bioactive compounds and have been proven to have antimicrobial[9—12)] and anti-oxidative effects.[10)]

Several studies have been done on the essential oil composition of CSL plants grown in different places.[13—20)] However, the identification of components was performed only through retention indices or direct similarity searches in the mass spectral libraries attached to the GC-MS instruments. So far, only a few components have been identified and the results may even be unreliable or may have been misidentified because heteroscedastic noise and overlapping peaks are always a problem in the analysis of essential oils. Using two-dimensional gas chromatography combined with time-of-flight mass spectrometry (GC×GC-TOF-MS), Eyres *et al.*[18)] detected and identified more components among the essential oils of CSL leaves in Fiji. However, the overlapping peaks are inevitable for the analysis of a complex sample even under optimum conditions. Furthermore, the GC×GC-TOF-MS is expensive and not readily available at present. Therefore, methods that are more economical should be developed for the rapid analysis of the essential oils of CSL.

In this study, the essential oils of CSL were separated and detected by GC-MS. Then a chemometric method called heuristic evolving latent projections (HELP) was applied to resolve the overlapped peaks. The pure chromatogram and spectrum of each component were accessible through the resolution of HELP method. Qualitative and quantitative analyses were then performed on account of the pure chromatograms and mass spectra.

Experimental

Materials Fresh plants of *C. sativum* L. were harvested in a local vegetable farm in Guangzhou, China. Undecane, linalool, nonanal, 1-hexanol, 1-dodecanol, dodecanal, 1-octadecanol, and 1-heptadecanol were purchased from Dr. Ehrenstorfer of GmbH (Augsburg, German) and for use as standards. The purities of the standards were all above 99.5%.

Extraction of Essential Oil About 400 g of fresh whole CSL was cut into about 0.5 cm lengths at room temperature and then transferred immediately into a standard essential oil extractor to which 300 ml deionized water was added. The essential oils were extracted using the standard steam distillation method according to the Chinese Pharmacopeia.[21)] The total of 1.88 g essential oils were obtained with a yield of 0.47% (w/w).

Detection of Essential Oil GC-MS analyses were performed on a Shimadzu 2010 gas chromatography instrument coupled to a Shimadzu QP2010 plus mass spectrometer (Kyoto, Japan). Compounds were separated on a Rtx-5MS analytical capillary column (30 m×0.25 mm i.d., 0.25 μm-film thickness). The oven temperature was maintained at 50 °C for 2 min and then programmed at 10 °C/min to 280 °C and held for 10 min. Helium (99.999%) was used as the carrier gas at a flow rate of 1.0 ml/min. The injector temperature was set at 230 °C. About 0.5 μl of the essential oil of CSL was injected, and the splitting ratio was 1 : 50. The spectrometer was operated in electron-impact (EI) mode with an ionization energy of 70 eV. The mass range was scanned from m/z 41 to 400 amu. The scan rate was 0.15 s/scan. The temperatures of the transfer line and ionization source were set at 250 °C.

Data Analysis Data analysis was performed on a personal computer. Programs relating to the chemometric resolution methods were coded in MATLAB 6.5. The essential oil components were identified by matching their mass spectra with those of the reference compounds in the National Institute of Standards and Technology version 2005 (NIST 05) mass spectral library.

Data Resolution by HELP The HELP method, developed by Liang and Kvalheim,[22—26)] is an efficient curve resolution method for 2-dimensional data obtained from hyphenated instruments and had been successfully applied to resolve several complex traditional Chinese medicine samples.[27—31)] For the detailed theory of HELP, the reader can refer to references.[22—26)] The procedure of HELP method to resolve GC-MS data can be summarized into the following four steps: (1) determination and correction of background and baseline drift[22,23,32)]; (2) identification and confirmation of the number of components in each peak cluster, the pure selective regions, zero-concentration regions, and overlapped regions of each component by elution sequence information, rank maps,[33)] and evolving latent projective graphs (ELPGs)[22,23,25)]; (3) unique resolution of 2-dimensional data into pure chro-

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matographic profiles and pure mass spectra was performed *via* the full rank resolution technique with selective regions, and zero-concentration regions[22,25]; and (4) justification of the reliability of the resolved results by reconstructing the 2-dimensional data.

Results

Qualitative Analysis of Essential Oils The total ion chromatogram (TIC) of the essential oils extracted from CSL plants is shown in Fig. 1. It is obviously a complicated system with a large number of peaks. Some peaks are obviously overlapping (for example, peak cluster B in Fig. 1), whereas some peaks seem to be single with different mass spectra at different positions but are actually overlapping (for example, peak cluster A in Fig. 1). If the mass spectra of these peaks were directly searched using the standard mass in the mass spectral library, the similarity indices will be quite low. On the other hand, components with low content are also difficult to identify correctly due to the effect of background and noise. In these situations, qualitative and quantitative analyses are difficult to perform, and the results may be not accurate and reliable. Therefore, background correction and the resolution of the overlapping or low-content peaks should be performed before the qualitative and quantitative analysis.

To resolve the complicated data, the original chromatogram obtained by GC-MS was converted into a format that can be manipulated with MATLAB software. The original chromatogram was a very large matrix with 11000 rows and 360 columns; hence, it was divided into sub-matrices according to the baseline separated. To explain how the HELP method works, peak cluster A [8.843—9.032 min, (scan points: 2538—2614)] and B [12.7225—13.060 min, (scan points: 4090—4225)] in Fig. 1 were selected as examples to illustrate the resolution process.

Both parts I and II of peak cluster A (Fig. 2a) appear as a single peak. However, at different positions of part I, the mass spectra are different. This indicates that part I of peak cluster A is not a single component. If the conventional method is performed, qualitative and quantitative analysis is difficult or even impossible. Part IV of peak cluster B (Fig. 2b) is severely overlapping. There are many other peak clusters similar to peak clusters A and B in the original chromatogram. Hence, it needs to be resolved into chromatographic profiles and mass spectra for better qualitative and quantitative analysis.

Before the resolution of the data, evolving latent projection graphs (ELPGs) were used to confirm whether background exists in the data.[22,32] If the ELPGs fail to start and end at the origin (zero concentration regions), this indicates that background is present in the data. Before background correction, there are obvious shifts from the origin in the ELPGs of peak clusters A and B (figure not shown), indicating that both peak cluster A and B are influenced by background. After the determination of the background, the correction of background and baseline shifts was then performed.[22,32] After background correction, the start and end points of both peak clusters A and B were at the origin (Fig.

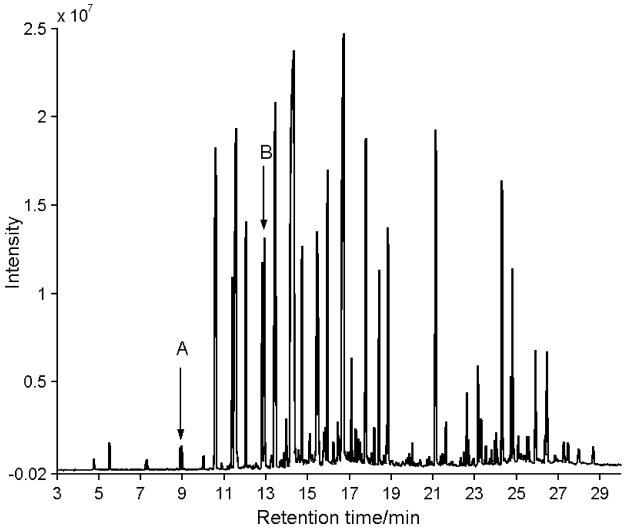

Fig. 1. Total Ionic Chromatograms of the Essential Oils of *Coriandrum sativum* L. Fresh Plants

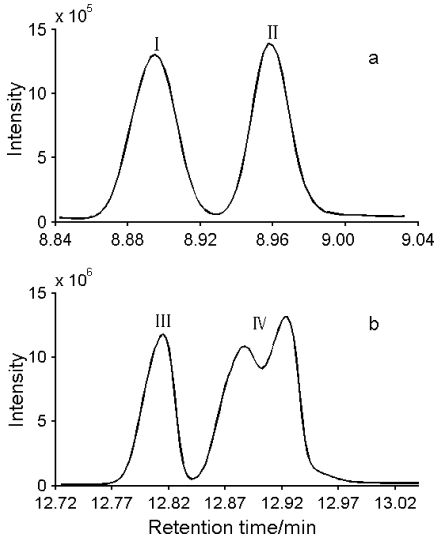

Fig. 2. Total Ionic Chromatograms of Peak Clusters A (a) and B (b) in Fig. 1

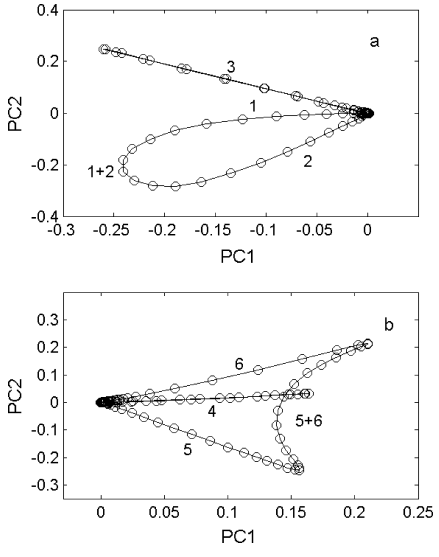

Fig. 3. Evolving Latent Projection Graphs (ELPGs) for Peak Cluster A (a) and Peak Cluster B (b) after Background and Baseline Correction

The straight lines 1, 2, and 3 in (a) represent the pure region of components 1, 2, and 3, whereas curve 1+2 represents the overlapping region of components 1 and 2. The straight lines 4, 5, and 6 in (b) represent the pure region of components 4, 5, and 6, whereas curve 5+6 represents the overlapping region of components 5 and 6.

3). Background correction is very important, without which the accurate resolution of overlapping peaks and the identification of low-content peaks would be impossible.

After background correction, the ELPGs[22] and rank map[25,33] were plotted. The number of components in each peak cluster, pure selective region, and zero-concentration region, as well as the overlapping regions of each component, was evaluated by ELPGs and rank maps.

The ELPGs are actually principal component projective curves from spectral spaces. In ELPGs, based on the chromatographic direction, the straight-line sections indicate the pure selective region of one component, whereas the curved sections show the overlapping region of two or more components. In the ELPGs of peak cluster A (Fig. 3a), straight lines 1 and 2 represent the selective regions of components 1 and 2, whereas the curve 1+2 between straight lines 1 and 2 is the overlapping region of components 1 and 2. Straight line 3 starts almost from the origin and returns to the start point, which indicates it is an almost pure component (component 3) and almost baseline separated from component 2. Hence, there are 3 components in peak cluster A. From the ELPGs of peak cluster B (Fig. 3b), straight line 4 starts from the origin and returns almost to the origin point, which denotes that it is almost a pure component (component 4). Straight lines 5 and 6 represent the pure selective regions of components 5 and 6, whereas the curve line 5+6 represents the overlapping region of components 5 and 6. Therefore, 3 components are also present in peak cluster B.

The rank maps were obtained from fixed size moving window evolving factor analysis[33] or so-called eigenstructure tracking analysis.[25] In rank maps, one curve represents one logarithmic eigenvalue of the matrix. The noise level (below dotted lines in Fig. 4) is characterized by the curves that have smaller values and that appear together at the bottom. Curves higher than the noise level (above dotted lines in Fig. 4) represent the local ranks of the data matrix and denote the appearance of new components. If one curve is higher than the noise level, that is, the local rank is one, then only one component is present during the retention time. If two curves are higher than the noise level, the local rank is two, and there are two components. Hence, the component numbers in the peak cluster, the elution sequence of components, the pure selective regions, the zero-concentration regions, and the overlapping regions of each component were easily obtained from the rank maps. Figure 4 illustrates the rank maps with a window size of 5 of peak clusters A and B after background and baseline correction. As shown in Fig. 4a, the zones marked as 1, 2, and 3 have one curve higher than the noise level present. Therefore, the local rank was one, respectively, that is, only one component appears at zones 1, 2, and 3. Hence, the zones marked as 1, 2, and 3 are the pure selective regions of components 1, 2, and 3. There are two curves higher than the noise level at the zones marked as 1+2 and 2+3, indicating that there are two components at zones 1+2 and 2+3, which are the overlapping regions of components 1 and 2, and component 2 and 3, respectively. Therefore, there are three components in peak cluster A. As shown in Fig. 4b, peak cluster B also has three components. The pure regions and overlapping regions are marked as 4, 5, 6, and 4+5, 5+6. The results are consistent with those of ELPG analysis. And the results of rank map analysis verified those of ELPG analysis, too.

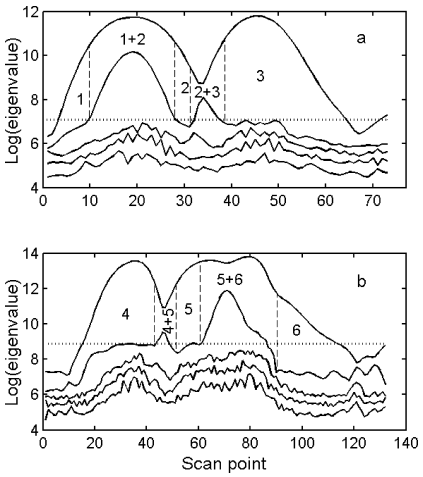

Fig. 4. Rank Maps of Peak Cluster A (a) and Peak Cluster B (b) after Background and Baseline Correction with a Window Size of 5

The zones marked as 1, 2, and 3 in (a) represent the pure region of the components 1, 2 and 3, whereas the zones marked as 1+2 and 2+3 represent the overlapping regions of the components 1 and 2, and components 2 and 3, respectively. The zones marked as 4, 5, and 6 in (b) represent the pure region of components 4, 5, and 6, whereas the zone marked as 4+5 and 5+6 represents the overlapping regions of components 4 and 5, and components 5 and 6, respectively. Lines below the dotted line represent noise level, and lines above dotted line represent the local ranks (component numbers).

Using the pure selective regions and zero-concentration regions of one component, the 2-dimensional data were then resolved into the unique pure chromatographic profiles and pure mass spectra for each component by the full rank resolution technique.[22,25] The resolved chromatographic profiles of peak clusters A and B are shown in Fig. 5. The pure mass spectra of peak cluster A are shown in Fig. 6 as an example. Using the same procedures, the 2-dimensional data were uniquely resolved into the pure chromatographic profiles and mass spectra for all components.

After the unique resolution of the data, the correction of the resolution results should be justified. To justify the resolution results, the resolved pure chromatograms and spectra were reconstructed by summing their inner product, which were then compared with the actual data. By plotting the re-

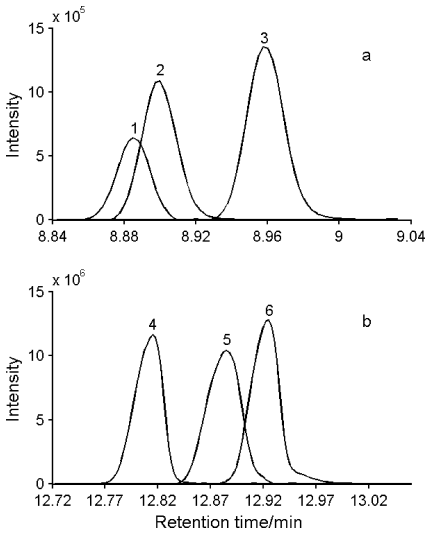

Fig. 5. Resolved Chromatographic Profiles of Peak Clusters A (a) and B (b)

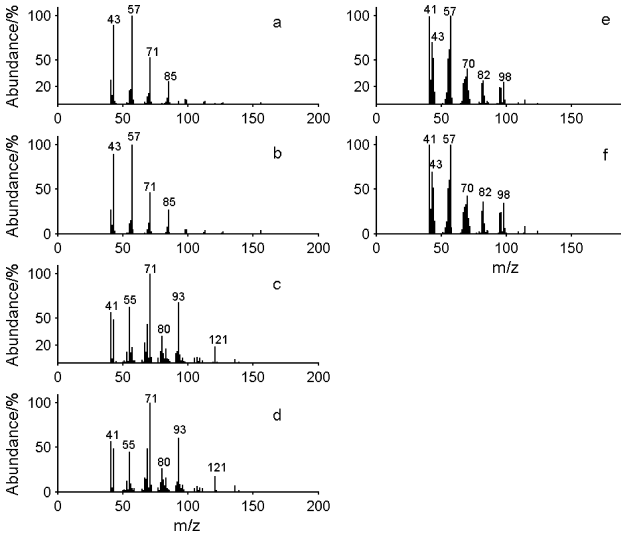

Fig. 6. Resolved Mass Spectra and Standard Mass Spectra of the Components in Peak Cluster A: Resolved (a) and Standard (b) Mass Spectrum of Undecane (Component 1); Resolved (c) and Standard (d) Mass Spectrum of Linalool (Component 2); Resolved (e) and Standard (f) Mass Spectrum of Nonanal (Component 3)

constructed data and the actual data (after background correction), the peak positions and profiles were found to be consistent (figure not shown). Therefore, based on the comparison, the resolution is reasonable.

After the data were uniquely resolved into pure chromatograms and mass spectra, the pure mass spectra were identified by comparison with the standard mass spectra in the NIST 05 mass spectral library. The resolved pure spectra and standard spectra of the components in peak cluster A are shown in Fig. 6. The components 1, 2, and 3 resolved from peak cluster A were identified as undecane, linalool, and nonanal with similarity indices of 96%, 95%, and 97%, respectively. Comparing the resolved mass spectra and standard spectra in Fig. 6, the resolved results are quite reasonable. Likewise, peak cluster B was resolved, and the pure mass spectra of the components 4, 5, and 6 were identified as 2-undecenal, (2*E*)-2-tridecen-1-ol, and 1-undecanol, respectively.

All other peak clusters were resolved and identified in the same way as described above. Table 1 summarizes the chemical components of the essential oils of CSL plants cultured in Guangzhou, China. A total of 118 components were found, of which 104 were identified, accounting for 97.27% of the total content of essential oils. The other 14 compounds cannot be identified in our study, which maybe due to the low signal-to-noise ratio or the absence of their standard mass spectra in the mass spectral library.

Quantitative Analysis of Essential Oils After all peak clusters were resolved, the pure chromatogram and mass spectrum of each component were obtained. Quantitative analysis was carried out using the overall volume integration method[27—29,34,35] which integrates the peak area at every *m*/*z*. Using the overall volume integration method, the total two-way response of each component was obtained and was proportional to the concentration. The relative content of each component was achieved by comparing its two-way response to the total two-way responses of all the components. The method is easy to perform because the pure chromatogram and mass spectrum of each component were obtained *via* the HELP method. The advantage of this quantitative method over conventional peak-area integration using simple peak splitting is that all mass spectral-absorbing points are taken into consideration.[27,28,34,35] The quantitative results are listed in Table 1 by elution time.

To verify the qualitative and quantitative results, the exact standards should be used. Unfortunately, obtaining all the reference components identified is difficult. The components resolved from peak cluster A (undecane, linalool, and nonanal), 1-hexanol, 1-dodecanol, dodecanal, 1-octadecanol, and 1-heptadecanol were verified using standards. These components were detected in the front, middle, and back of the retention time in the TIC of the essential oils (see Table 1). The retention time and the mass spectra of these components resolved from essential oils data are in accordance with their standards (Table 2). The relative errors of quantitative results obtained from the overall volume integration method *versus* those of the standard calibration were between −9.09% and 9.12% (Table 2). The verified results indicated that the overall volume integration method was accurate. However, the results by simple peak splitting cannot be calculated because area of each component and the total area of all the components cannot obtained accurately, which caused by many overlapping peaks that appear to be single (*e.g.* part I of peak cluster A).

Discussion

Compared with the literature,[9,13—17,19,20] more components (total of 118 components were detected and 104 identified) can be analyzed and identified by the GC-MS coupled with the HELP method in our study. Eyres *et al.*[18] separated 98 components and identified 82 of them in cultured CSL by GC×GC-TOF-MS. Deng *et al.*[16] identified 15 compounds in CSL grown in Shanghai, China by solid-phase microextraction and GC-MS. Matasyoh *et al.*[9] detected 27 peaks and identified 24 components from the essential oils of fresh coriander leaves collected in Kenya. Potter and Fagerson[19] detected 41 peaks and identified 37 of them by GC-MS in CSL that grew in Orange, Massachusetts. A total of 35, 8, 19, and 18 components in our study are common with those reported by Eyres *et al.*,[18] Deng *et al.*,[16] Matasyoh *et al.*,[9] and Potter and Fagerson,[19] respectively (Table 1). Differences of the relative contents for each common component were observed among different studies (Table 1).

In addition, the major constituents and their relative contents are also different from those reported in the literature. As shown in Table 1, (2*E*)-2-dodecenal (18.28% of total content) was the most abundant compound, followed by 1-dodecanol (8.59%), (*Z*)-14-methyl-8-hexadecenal (7.25%), and tetradecanal (6.34%). The other important compounds were 1-decanol (5.39%) and decanal (4.41%). However, the major constituents reported by Eyres *et al.*[18] were (2*E*)-2-decen-1-ol (26.00%), 1-decanol (19.64%), (2*E*)-2-decenal (9.12%), (2*E*)-2-tetradecenal (7.03%), decanal (6.56%), (2*E*)-2-dodecenal (5.37%), and (2*E*)-2-dodecen-1-ol (4.6%). (2*E*)-2-Tridecenal (19.29%), 1-decanol (16.52%), (2*E*)-2-decen-l-al (13.99%), (2*E*)-2-decen-l-ol (13.71%), decanal (9.12%), 2-decenal (8.41%) and *E*-8-dodecenyl acetate (5.6%) are the predominant components reported by Deng *et al.*[16] (2*E*)-De-

Table 1. Chemical Components of the Essential Oils from *Coriandrum sativum* L. Fresh Plants

No.	Retention time/min	Compounds	Formula	Relative content/%	Components reported in literatures*
1	4.694	(3*E*)-3-Hexen-1-ol	$C_6H_{12}O$	0.0032	0.02[a]
2	4.755	*cis*-3-Hexene-1-ol	$C_6H_{12}O$	0.0682	
3	4.850	Unknown		0.0083	
4	4.943	2-Hexen-1-ol	$C_3H_8S_2$	0.0045	0.58[a]
5	4.969	1-Hexanol	$C_6H_{14}O$	0.0050	0.05,[a] 0.29[b]
6	5.500	*n*-Nonane	C_9H_{20}	0.1668	1.53,[a] 1.21,[c] 0.2[d]
7	7.228	*n*-Decane	$C_{10}H_{22}$	0.0297	0.14,[a] 0.25[c]
8	7.276	Octanal	$C_8H_{16}O$	0.0592	0.84,[a] 0.54,[c] 0.5[d]
9	7.335	*cis*-3-Hexenyl acetate	$C_8H_{14}O_2$	0.0243	1.06[b]
10	7.692	1,3,8-*p*-Methatriene	$C_{10}H_{14}$	0.0067	
11	7.717	2-Ethylhexanol	$C_8H_{18}O$	0.0048	
12	7.769	Limonene	$C_{10}H_{16}$	0.0027	0.1[a]
13	8.015	Benzene acetaldehyde	C_8H_8O	0.0044	0.01[a]
14	8.267	Crithmene	$C_{10}H_{16}$	0.0098	
15	8.409	1-Octanol	$C_8H_{18}O$	0.0056	0.15[c]
16	8.707	*p*-Cymene	$C_{10}H_{14}$	0.0018	0.47[a]
17	8.753	1-Undecene	$C_{11}H_{22}$	0.0161	
18	8.885	Undecane	$C_{11}H_{24}$	0.0634	0.09[a]
19	8.900	Linalool	$C_{10}H_{18}O$	0.1300	0.17,[a] 0.32[c]
20	8.958	Nonanal	$C_9H_{18}O$	0.1515	0.2,[a] 0.54[c] 0.2[d]
21	9.974	Tetralin	$C_{10}H_{12}$	0.0311	
22	10.002	1-Nonanol	$C_9H_{20}O$	0.0969	0.12,[a] 0.38[c]
23	10.331	Azulene	$C_{10}H_8$	0.0091	
24	10.580	Decanal	$C_{10}H_{20}O$	4.4075	6.56,[a] 9.12,[b] 14.3,[c] 4.4[d]
25	10.869	3,7-Dimethyl-2-octen-1-ol	$C_{10}H_{20}O$	0.0434	
26	11.169	(*Z*)-2-Decenal	$C_{10}H_{18}O$	0.0292	0.16,[a] 8.4[b]
27	11.271	Lemonol	$C_{10}H_{18}O$	0.0438	
28	11.309	(*Z*)-4-Decen-1-ol	$C_{10}H_{20}O$	0.0426	
29	11.384	(*E*)-2-Decenal	$C_{10}H_{18}O$	1.4815	9.12,[a] 46.1[d]
30	11.480	(*E*)-2-Decenol	$C_{10}H_{20}O$	1.8193	26.0,[a] 13.71,[b] 14.2,[c] 9.2[d]
31	11.560	1-Decanol	$C_{10}H_{22}O$	5.3879	19.64,[a] 16.52,[b] 3.37,[c] 4.3[d]
32	11.593	5-Methyl-4-undecene	$C_{12}H_{24}$	0.1097	
33	11.612	3-Methyl-2-(oxopropyl)-furan	$C_8H_{10}O_2$	0.1117	
34	12.030	Undecanal	$C_{11}H_{22}O$	2.0925	0.98,[a] 3.23,[c] 0.5[d]
35	12.395	Unknown		0.0256	
36	12.815	(2*E*)-2-Undecenal	$C_{11}H_{20}O$	1.6826	1.2,[a] 5.6[d]
37	12.885	(2*E*)-2-Tridecen-1-ol	$C_{13}H_{26}O$	1.8570	0.14[a]
38	12.924	1-Undecanol	$C_{11}H_{24}O$	1.8993	0.32,[a] 2.38,[c] 0.2[d]
39	13.127	Phenylbenzene	$C_{12}H_{10}$	0.0270	
40	13.226	(*Z*)-4-Decenal	$C_{10}H_{18}O$	0.0663	0.16[a]
41	13.261	(*Z*)-4-Tetradecene	$C_{14}H_{28}$	0.1174	
42	13.297	β-Elemene	$C_{15}H_{24}$	0.0434	
43	13.450	Tetradecanal	$C_{14}H_{28}O$	6.3351	0.96,[a] 0.7[d]
44	13.675	(*E*)-2-Nonenal	$C_9H_{16}O$	0.0360	0.04,[a] 0.3[d]
45	13.741	3-(3,3-Dimethylbutyl)-cyclohexanol	$C_{12}H_{24}O$	0.0775	
46	13.842	γ-Elemene	$C_{15}H_{24}$	0.1045	
47	13.957	(*E*)-2-Octenal	$C_8H_{14}O$	0.4326	6.23[c]
48	14.243	(2*E*)-2-Dodecenal	$C_{12}H_{22}O$	18.2820	5.37,[a] 13.99,[b] 15.9,[c] 10.3[d]
49	14.325	1-Dodecanol	$C_{12}H_{26}O$	8.5916	0.19,[a] 13.6[c]
50	14.340	1-Terpinen-4-ol	$C_{10}H_{18}O$	0.9055	
51	14.388	Hexadecanal	$C_{16}H_{32}O$	1.0083	0.07[a]
52	14.597	3-Methoxyhex-1-ene	$C_7H_{14}O$	0.0314	
53	14.645	(*E*)-5-Decen-1-ol	$C_{10}H_{20}O$	0.0524	
54	14.665	(3*E*)-2,2-Dimethyl-3-octene	$C_{10}H_{20}O$	0.0534	
55	14.718	Tridecanal	$C_{13}H_{26}O$	1.5283	0.31,[a] 0.63,[c] 0.1[d]
56	14.752	3,5-Di-*tert*-butylphenol	$C_{14}H_{22}O$	0.0417	
57	15.070	2*E*-9-Methyl-2-undecene	$C_{12}H_{24}$	0.1320	
58	15.095	Unknown	$C_8H_{10}O_2$	0.1869	
59	15.385	3,7,11-Trimethyl-1,6,10-dodecatrien-3-ol	$C_{15}H_{26}O$	0.1105	
60	15.430	*E*-2-Tridecenal	$C_{13}H_{24}O$	1.5712	0.41,[a] 6.75[c]
61	15.452	2-Hydroxy-(*Z*)9-pentadecenyl propanoate	$C_{18}H_{34}O_3$	1.4436	
62	15.473	3-*n*-Hexylthiane, *S*,*S*-dioxide	$C_{11}H_{22}O_2S$	0.1284	
63	15.503	Germacrene B	$C_{15}H_{24}$	1.1129	
64	15.743	2,6,10,14-Tetramethyl-octadecane	$C_{25}H_{52}$	0.0884	
65	15.830	Oleyl alcohol	$C_{18}H_{36}O$	0.2629	
66	15.937	Pentadecanal	$C_{15}H_{30}O$	2.5362	0.09[a]
67	16.220	Unknown		0.1495	
68	16.431	Isopentyl cyclohexanecarboxylate	$C_{12}H_{22}O_2$	0.3720	
69	16.655	(*Z*)-14-Methyl-8-hexadecenal	$C_{17}H_{32}O$	7.2536	
70	16.710	*E*-2-Tetradecen-1-ol	$C_{11}H_{22}O$	2.7224	0.89,[a] 2.12,[c] 0.6[d]
71	16.715	Dodecyl chloroacetate	$C_{14}H_{27}ClO_2$	0.0212	

Table 1. (Continued)

No.	Retention time/min	Compounds	Formula	Relative content/%	Components reported in literatures*
72	17.086	Dodecanal	$C_{12}H_{24}O$	0.6778	2.99,[a] 1.06,[b] 4.36,[c] 1.6[d]
73	17.288	Unknown		0.2561	
74	17.421	1,2,3,5,6,7-Hexahydro-inden-4-one	$C_9H_{12}O$	0.1771	
75	17.487	Ledene oxide-(I)	$C_{21}H_{34}O_2$	0.1410	
76	17.567	Unknown		0.0736	
77	17.780	13-Tetradecenal	$C_{14}H_{26}O$	2.5965	0.1[d]
78	17.968	Unknown		0.0358	
79	18.037	*trans*-Decahydro-10*a*-methyl-2(1*H*)-benzocyclooctenone	$C_{13}H_{22}O$	0.0409	
80	18.060	Unknown		0.0814	
81	18.070	Dibenzo[*b*,*e*]7,8-diazabicyclo[2.2.2]octa-2,5-diene	$C_{14}H_{12}N_2$	0.0227	
82	18.085	2,6,10,14,18-Pentamethyleicosane	$C_{25}H_{52}$	0.0224	
83	18.176	*Z*-2-Dodecenol	$C_{12}H_{24}O$	0.2239	4.6[a]
84	18.408	(2*E*)-3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}O$	1.3537	
85	18.835	Unknown		1.3893	
86	18.453	4,4,8-Trimethyl-non-5-enal	$C_{12}H_{22}O$	0.0373	
87	19.670	Citronellyl tiglate	$C_{15}H_{26}O_2$	0.0142	
88	19.790	Hexanoic acid, 3-hexenyl ester	$C_{12}H_{22}O_2$	0.0594	0.11[a]
89	19.845	(8*Z*)-14-Methyl-8-hexadecen-1-ol	$C_{17}H_{34}O$	0.0900	
90	19.996	(2-Nitro-2-propenyl)-cyclohexane	$C_9H_{15}NO_2$	0.1486	
91	21.116	Phytol	$C_{20}H_{40}O$	3.3459	
92	21.380	Unknown		0.0625	
93	21.453	1-(Ethenyloxy)-hexadecane	$C_{18}H_{36}O$	0.0753	
94	21.606	Decyl decanoate	$C_{20}H_{40}O_2$	0.2878	
95	22.311	Unknown		0.0676	
96	22.398	Unknown		0.0420	
97	22.610	1-Octadecanol	$C_{18}H_{38}O$	0.4889	
98	22.692	Heneicosane	$C_{21}H_{44}$	0.1552	
99	23.142	Decyl ether	$C_{20}H_{42}O$	0.6743	
100	23.217	Unknown	$C_{11}H_{22}O_2$	0.1375	
101	23.238	*trans*-Decahydro-9a-methyl-2*H*-benzocyclohepten-2-one	$C_{12}H_{20}O$	0.1509	
102	23.293	Unknown		0.3209	
103	23.518	Unknown		0.1416	
104	23.788	16-Octadecenal	$C_{18}H_{34}O$	0.0945	
105	23.944	2-Hexyl-1-decanol	$C_{16}H_{34}O$	0.1698	
106	24.016	Tridecanedial	$C_{17}H_{34}O$	0.2264	
107	24.288	1-Heptadecanol	$C_{17}H_{36}O$	2.6754	
108	24.723	1,54-Dibromo-tetrapentacontane	$C_{12}H_{25}F$	0.6805	
109	24.792	2-Octadecoxyethanol	$C_{20}H_{42}O_2$	1.6248	
110	25.488	Octadecyl vinyl ether	$C_{20}H_{40}O$	0.1831	
111	25.559	Unknown		0.2363	
112	25.895	1-Heneicosyl formate	$C_{22}H_{44}O_2$	0.9497	
113	26.441	Octadecanal	$C_{18}H_{36}O$	1.0752	
114	27.244	Squalene	$C_{30}H_{50}$	0.2087	
115	27.451	Pentadecanal	$C_{15}H_{30}O$	0.2425	0.1[d]
116	27.966	1-Hexacosanol	$C_{26}H_{54}O$	0.1013	
117	27.970	1-Eicosene	$C_{20}H_{40}$	0.1577	
118	28.659	*cis*-9-Octadecenal	$C_{18}H_{34}O$	0.2192	

a—*d*) Components have been reported in refs. 18, 16, 9 and 19.

Table 2. Validation of Qualitative and Quantitative Results

	Retention time/min		Similarity indices		Relative content obtained by overall volume integration (%)	Relative content obtained by standard calibration (%)	Relative error[e]
	t_R[a]	t_R[b]	SI[c]	SI[d]			
1-Hexanol	4.969	4.958	91	94	0.0050	0.0055	−9.09
Undecane	8.885	8.875	96	92	0.0634	0.0595	6.55
Linalool	8.900	8.887	95	96	0.1300	0.1202	8.15
Nonanal	8.958	8.946	97	95	0.1515	0.1402	8.06
1-Dodecanol	14.325	14.317	96	97	8.5916	8.9763	−4.28
Dodecanal	17.086	17.072	94	96	0.6778	0.6239	8.64
1-Octadecanol	22.610	22.586	96	93	0.4889	0.5159	−5.23
1-Heptadecanol	24.288	24.269	93	95	2.6754	2.4518	9.12

a) t_R, retention time of the resolved chromatogram; *b*) t_R, retention time of the standard. *c*) SI, similarity indices of the resolved spectra compared with the NIST 05 mass library; *d*) SI, similarity indices of the resolved spectra compared with those of the standards. *e*) Relative error, which was calculated by (relative content obtained by overall volume integration−relative content obtained by standard calibration)/relative content obtained by standard calibration.

cenal (15.9%), decanal (14.3%), (2*E*)-decen-1-ol *et al.* (14.2%), *n*-decanol (13.6%), (2*E*)-tridecen-1-al (6.75%), (2*E*)-dodecenal (6.23%), dodecanal (4.36%) were the major components reported by Matasyoh *et al.*[9] and (2*E*)-2-decenal (46.1%), (2*E*)-2-dodecenal (10.3%), 2-decenol (9.2%), (2*E*)-2-undecenal (5.6%), *n*-decanal (4.4%), 1-decanol (4.3%), dodecanal (1.6%) were the major components reported by Potter,[13] respectively.

The differences of the component numbers and the relative contents of each component among different reports can be due to differences in climate, geographical location, stages of plant growth, species of plant, or the pretreatment and processing methods used by the researchers. The activities of some enzymes in the CLS plant may also account for the differences.[36] That is, considerable confusion still exits in the volatile compositions of CSL.[36] Therefore, further research is needed to study the essential oils from CSL plants. The GC×GC-TOF-MS is a powerful method for the separation and identification of complicated essential oil samples; however, it is difficult to avail at present, and overlapping peaks are unavoidable because of the large complexity of essential oils.

In this paper, GC-MS coupled with chemometric resolution techniques was successfully applied to resolve the chemical components in the essential oils of CSL plants. Using chemometric resolution methods, the reliability of qualitative and quantitative results was enhanced because the peak clusters were uniquely resolved into pure chromatographic profiles and spectra by making best use of advantages of 2-dimensional data. Furthermore, chemometric resolution methods can also greatly enhance the separation capability of GC-MS. So far, GC-MS coupled with chemometric resolution techniques has proven to be an economical and reliable method for the accurate and rapid determination of very complex essential oil samples.

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