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Determination of Volatile Components in Black Cardamom with Gas Chromatography-Mass Spectrometry and Chemometric Resolution

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***Abstract*— Volatile components of black cardamom essential oil was analyzed by chromatography-mass spectrometry (GC-MS) with the help of multivariate curve resolution (MCR) approach. The GC-MS data analysis revealed that forty nine components exist in black cardamom essential oil, however, after applying MCR approach this numbers extended to eighty two components with concentration higher than 0.01%. MCR approaches overcome the problem of background and overlapped peaks. The most important constitutes are 1,8-Cineole (36.66%), β-Pinene (8.55%), α-Terpineol (8.44%), 1R-α-Pinene (5.10%) ,and Limonene (4.51%).**

Keywords—Cardamom; Multivariate curve resolution; Gas chromatography-mass spectrometry; Chemometrics

I. INTRODUCTION

The large cardamom belongs to the family Zingiberaceae, and is also known by the names 'greater Indian cardamom' or 'Nepal cardamom'. It is native to the Eastern Himalayan region. In India, it is cultivated in Sikkim, Darjeeling and the Assam hills and it is also cultivated in Nepal, Bhutan and, to some extent, in some of the south-east Asian countries such as Thailand, Indonesia and Laos[1]. Large cardamom is one of the major spices grown in India[2-3]. The pods are used as a spice, in a manner similar to the green Indian cardamom pods, but it has a drastically different flavor, so it cannot be substituted in the same recipes, unless a different flavor is acceptable. Its strong, smoky flavor and aroma are derived from the traditional drying procedure, which involves drying over open flames. Black cardamom is the dried fruit of a perennial herbaceous plant. It is valued for its acceptable taste, flavor and aroma. The spice is used in rice preparations and meat dishes, besides a wide range of beverages and sweets[4]. Various authors have studied the chemical composition of the essential oil of large cardamom by GC and GC-MS [5-11]. A work carried out by Gurudutt et al [5] on the steam-distilled essential oil of black cardamom, using GC-MS, reported 40 components. The major compounds were 1,8-cineole (61.31%), β-pinene (8.85%), α-terpineol (7.92%), α-pinene (3.79%) and allo-aromadendrene (3.17%). The absence of α-terpinyl acetate was also reported. Shankaracharya et al [11] reported α-pinene, β-pinene, 1,8-cineole, myrcene, γ-terpinene, limonene, p-cymene, terpinene 4-ol, terpineol and nerolidol, as major constituents of large cardamom oil. Gas chromatography–mass spectrometry (GC–MS) is one of the most successful techniques for the determination of the components of essential oils [12-15]. In GC–MS technique, the components are qualitatively and quantitatively analyzed, but their identifications are performed only through the direct similarity searches in the MS databases attached to the GC–MS instruments. Even under the best experimental conditions, the probability of overlapped peak in chromatographic separations can become quite severe, especially for highly complex samples. This is due to the existence of the background, baseline offset, and some overlapping/embedded peaks. Fortunately, with the development of chemometric resolution techniques, the extraction of required information about the components in a complex mixture has become possible. Multivariate curve resolution (MCR) methods have been used for the analysis of unresolved peaks in chromatographic separations coupled to multichannel detection such as high performance liquid chromatography–diode array detector (HPLC–DAD), liquid chromatography–mass spectrometry (LC–MS), and GC–MS [16]. In present work, hydrodistillation method in a full glass Clevenger type apparatus has been used to extract the volatile components of black cardamom essential oils. GC-MS has been used for the determination of essential oil's components. Moreover, due to the complexity of essential oils and existence of overlapping peaks, chemometric resolution techniques was used for resolving the co-eluted GC-MS peak clusters.

II. EXPERIMENTAL

A. Materials and reagents

Indian Black cardamom was purchased. Normal hexane and anhydrous sodium sulfate with purity higher than 99% were purchased from Merck (Germany).

B. Extraction of volatile components by hydrodistillation

100 g of dried and beaten black cardamom submerged in 1 L water in a round bottom flask and hydrodistilled in a full glass Clevenger type apparatus. The extraction was completed in 4h. Then the system was cooled down and the essential oil was collected in a dark glass bottle. The essential oil was dried by the use of anhydrous sodium sulfate, then it was stored at 4˚C until GC-MS analysis.

C. Gas chromatography-mass spectrometry analysis (GC-MS)

GC-MS analysis were performed with the use of HP-Agilent 6890 GC that has been coupled with a HP-Agilent 5973 mass selective detector and was equipped with RTX-5 capillary fused silica column (30 m, 0.25 mm i.d. and 0.25-µm film thickness). Temperature programming has been preformed under following condition: the oven temperature was held at 50 ˚C for 5 min, then programmed at 4 ˚C min^{-1} to 250 ˚C, held for 5 min. Other operating conditions were as follows: carrier gas, He (99.99 %); injector type, splitless. In MS, voltage and ionization source temperature were 70 eV and 220 ˚C, respectively.

D. Identification

The essential components were identified by calculating their Kovats retention indices (RIs) and comparing them with RIs and mass spectra of standard compounds stored in NIST mass spectral database.

E. Data analysis and software requirements

MCRC software [17] was used for preprocessing, chemical rank determination and local rank analysis. preprocessing methods such as baseline correction, denoising and smoothing have been done on input data in order to obtain more accurate results, in addition chemical rank determination and local rank analysis have been performed prior to resolution step. In The resolution step MCR-ALS has been used to extract the pure mass spectrum and chromatographic profile of each component from the original GC-MS data matrix. Finally, the essence of each pure component can be determined by comparing its resolved mass spectrum with those of mass libraries and the relative percentage of each component can be calculated [18].

A software G1701DA MSD ChemStation version D.00.01 was used to collect data and conversion to ASCII format. Programs of the chemometric resolution methods were coded in MATLAB R2009a by authors. library searches and spectral matching of the resolved pure components were conducted using the NIST MS database.

III. THEORY

The resolution of a multicomponent system involves the description of the variation of measurements as an additive model of the contributions of their pure constituents [19–28]. To do so, relevant and sufficiently informative experimental data are needed. These data can be obtained by analyzing a sample with a hyphenated technique (e.g., HPLC-DAD , GC-MS). In the resolution of any multicomponent system, the main goal is to transform the raw experimental measurements into useful information. By doing so, we aim to obtain a clear description of the contribution of each of the components present in the mixture or the process from the overall measured variation in our chemical data. All resolution methods mathematically decompose a instrumental response of mixtures into the contributions linked to each of the pure components in the system. This global response is organized into a matrix D containing raw measurements about all of the components present in the data set. Resolution methods allow for the decomposition of the initial mixture data matrix D into the product of two data matrices C and S^T, each of them containing the pure response profiles of the *n* mixture or process components associated with the row and the column directions of the initial data matrix, respectively. In matrix notation, the expression for all resolution methods is:

$$D = CS^T + E \quad (1)$$

Where D (r×c) is the original data matrix, C (r×n) and S^T (n×c) are the matrices containing the pure-component profiles related to the data variation in the row direction and in the column direction, respectively, and E (r×c) is the error matrix. The variables r and c represent the number of rows and the number of columns of the original data matrix, respectively, and n is the number of chemical components in the mixture or process. C and S^T often refer to concentration profiles and spectra [29]. The field of curve resolution was born in response to the need for a tool to analyze multivariate experimental data from multicomponent dynamic systems. The common goal of all curve-resolution methods is to mathematically decompose the global instrumental response into the pure-component profiles of each of the components in the system. The use of these methods has become a valuable aid for resolving complex systems, especially when obtaining selective signals for individual species is not experimentally possible, too complex, or too time consuming. Two pioneering papers on curve resolution were published by Lawton and Sylvestre early in the 1970s [29, 30]. Whenever the goals of curve resolution are achieved, the understanding of a chemical system is dramatically increased and facilitated, avoiding the use of enhanced and much more costly experimental techniques. Through multivariateresolution methods, the ubiquitous mixture analysis problem in chemistry (and other scientific fields) is solved directly by mathematical and software tools instead of using costly analytical chemistry and instrumental tools, for example, as in sophisticated "hyphenated" mass spectrometry-chromatographic methods. Resolution methods are often divided in iterative and noniterative methods. Most noniterative methods are one-step calculation algorithms that focus on the one-at-a-time recovery of either the concentration or the response profile of each component. Once all of the concentration (**C**) or response (**S**) profiles are recovered, the other member of the matrix pair, **C** and **S**, is obtained by least-squares according to the general CR model, $\mathbf{D} = \mathbf{CS^T}$. Iterative resolution methods obtain the resolved concentration and response matrices through the one-at-a-time refinement or simultaneous refinement of the profiles in **C**, in $\mathbf{S^T}$, or in both matrices at each cycle of the optimization process. The profiles in **C** or $\mathbf{S^T}$ are "tailored" according to the chemical properties and the mathematical features of each particular data set. The iterative process stops when a convergence criterion is fulfilled. The method of multivariate curve resolution-alternative least square (MCR-ALS) calculates the concentration and pure spectral profiles in an iterative way. This algorithm starts with initial estimates obtained by using the techniques of EFA,

SIMPLISMA or OPA and proper constraints (e.g. non-negativity, unimodality, normalization and selectivity) can be applied during ALS optimization until the concentration and pure spectra optimally fit in the experimental data matrix[26].

IV. RESULT AND DISCUSSION

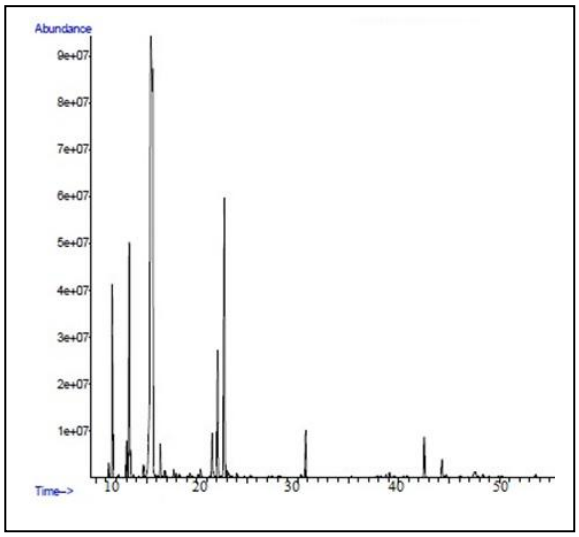

Fig.1 . The total ion chromatogram (TIC) of the black cardamom essential oil

A. Qualitative analysis of black cardamom essential oil

The total ion chromatogram (TIC) of the black cardamom essential oil is shown in Fig.1. The complexity of such a mixture which is due to several overlapped and embedded peaks is illustrated in this figure. The traditional searching based on MS database would fail if the overlapped peaks could not be resolved. By resolving embedded peaks into pure chromatographic profiles and mass spectra more accurate result will be obtained. In present work, TIC of black cardamom was divided to 71 peak clusters, using zero component regions along with elution sequence for the essential oil. According to the morphological score method [30] some of these sub-matrices are single component peaks. These peaks can be easily identified and quantified by direct library searches and peak integration in ChemStation software. In order to show the resolution procedure, as an example, one peak cluster from TIC of black cardamom is selected from retention times of 38.88-39.30 min. The local TIC of this peak cluster is shown in Fig.2. This peak cluster was extracted using MSD ChemStation software and was changed to ASCII format that was compatible with MATLAB software. Direct library search for this peak cluster before performing resolution procedure showed that, only one component of α-Selinene with MF values of 922 exists in this peak cluster. First, the background and noise are removed in order to avoid the effect of them in measured data. The background correction in this work was performed using the method of Liang et al. [31-32]. In this method, adequate information for uni-variate linear regression can be provided by the local rank analysis of zero component regions

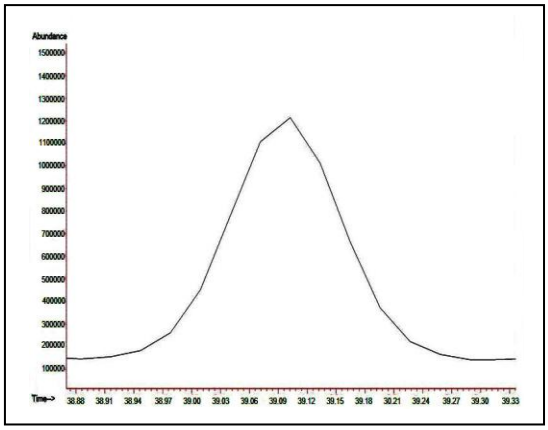

Fig.2 . Total ion chromatogram (TIC) of the selected peak cluster

with respect to retention time and then correcting the baseline. The selected peak cluster after baseline correction is shown in Fig.3. Savitzky-Golay filter [33] was used for noise correction. The selected peak cluster after smoothing is demonstrated in Fig.4 . These steps are essential for achieving reliable results in the resolution procedure. Then, the chemical rank determination was done for all peak clusters using methods of subspace comparison [30] and morphological score. In most methods chemical rank is determined based on PCA or singular value decomposition (SVD), but in systems which are analyzed by hyphenated chromatographic methods (GC-MS, HPLC-DAD, etc), it is difficult to obtain accurate results by using PCA of full data matrix due to noise accumulation. Hence, key spectra instead of full rank matrix would be analyzed by morphological score method in order to avoid accumulation of noise. The results of chemical rank determination for the selected peak cluster are presented in Fig.5. This figure shows the morphological score against the number of components and clearly illustrates the presence of two components in the peak cluster.

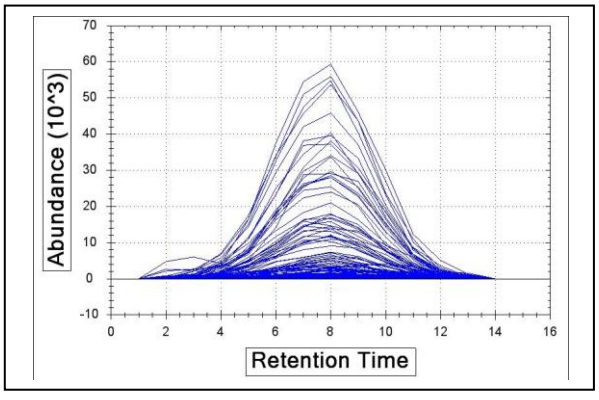

Fig.3 . The selected peak cluster after baseline correction

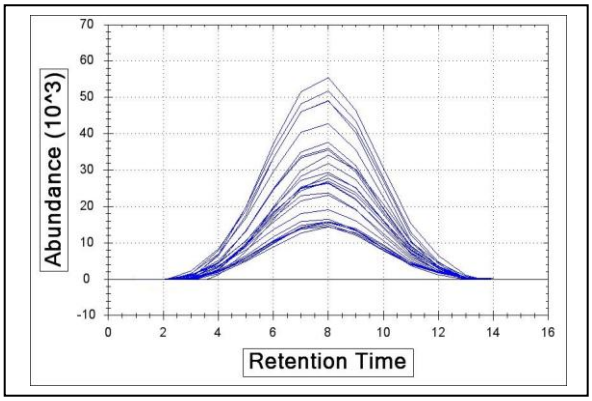

Fig.4 .The selected peak cluster after smoothing and denoising

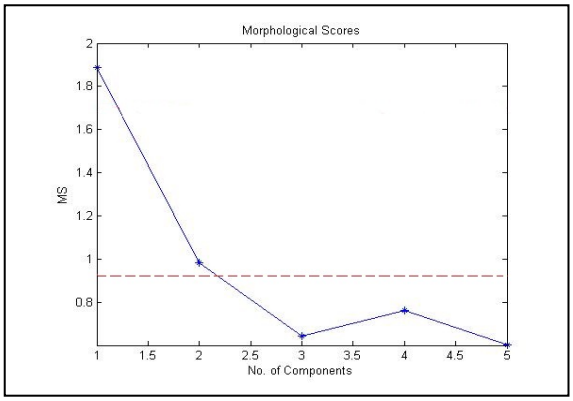

Fig.5 .Chemical rank determination, morphological score plot for the selected peak cluster

To confirm chemical rank which was determined by morphological score, subspace comparison was used which admitted of the presence of two components in the selected peak cluster. Finally, the peak clusters were resolved using MCR-ALS method. This method is performed with initial estimates of chromatographic profile obtained by EFA method. Constraints of non-negativity and unimodality are applied in ALS algorithm, these constraints would help to the MCR-ALS method to be more acuurate. Pure chromatographic profile and mass spectra for the selected peak cluster obtained using these techniques are shown in Figs.6 and 7, respectively. All of these tests showed that there are two components in this peak cluster. After chemometric analysis more information has been obtained from selected peak cluster and one other component except of α-Selinene was identified for selected peak cluster which was Eudesma-4(14),11-diene with MF of 944. After extracting each pure spectrum and the resolved chromatographic profiles for each component, the components can be identified by similarity searches using the NIST mass database and can be verified with their RIs. These steps were done for all of peak clusters. After resolving all the peak clusters to their pure chromatographic profiles and mass spectrum, a total of 82 components with a higher concentration than 0.01% were identified which they are presented in Tables 1. The use of curve resolution techniques leads to an improvement in the components identification obtained by the GC-MS data.

B. Quantitative analysis of black cardamom essential oil

To qualitative analysis of GC-MS data, peak area integration usually is used. The GC–MS two-dimensional data were resolved into pure chromatogram and mass spectrum for each component, after that the peak area integration at every m/z point for each component can be easily calculated. Its sum is called the overall volume integration (OVI) [34, 35], which is directly proportional to the concentration of the components. The advantages of this technique is that all mass spectral points are taken into account. The results demonstrate that 82 components with concentration higher than 0.01% exist in the black cardamom essential oil. The most important components are 1,8-Cineole (36.66%), β-Pinene (8.55%), α-Terpineol (8.44%), 1R-α-Pinene (5.10%) ,and Limonene (4.51%).

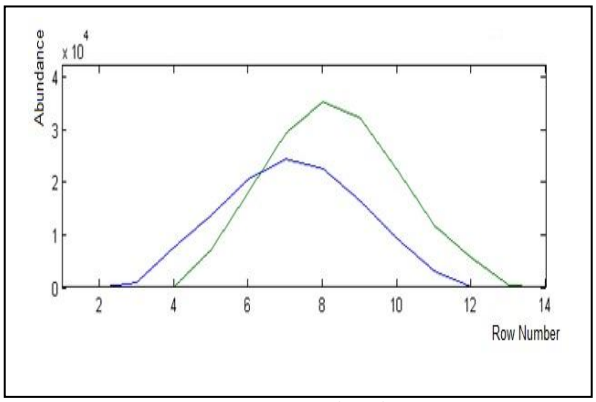

Fig.6 . Resolved chromatogram profile of the selected peak cluster

V. CONCLUSION

The identification in GC-MS analysis is performed by direct similarity searches in MS database. However, in complex samples such as black cardamom essential oil, overlapped and embedded peaks can lead wrong similarity match in the MS library. By the use of chemometrics and curve resolution methods a complete analysis of the black cardamom essential oil becomes possible. After resolving all peak clusters into their chromatographic profile and mass spectra using MCR approaches, eighty two components with concentration higher than 0.01% were identified.

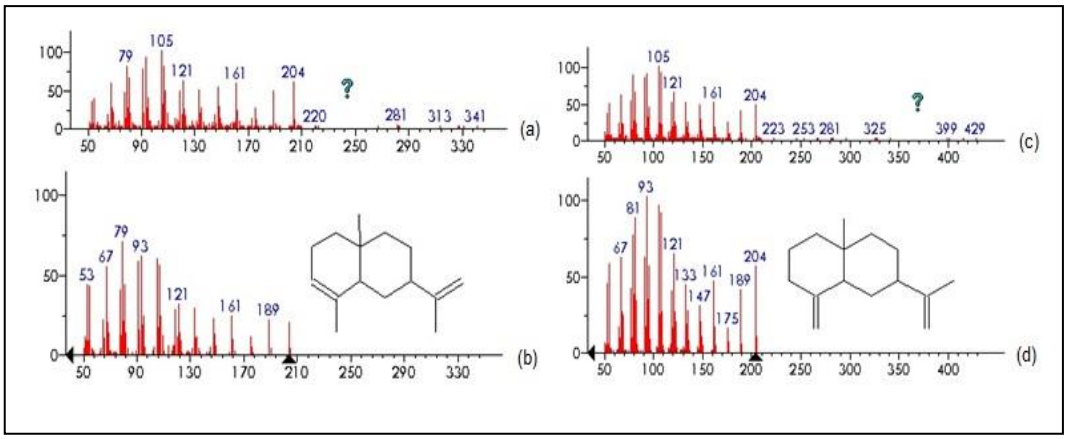

Fig.7 (a) standard and (b) resolved mass spectra of α-Selinene,
(c) standard and (d) resolved mass spectra of Eudesma-4(14),11-diene

Table 1. The volatile chemical components of black cardamom essential oil

No.	Compound	Percentage % GC-MS	Percentage % MCRC	Retention Time	Retention Index
1	α-Thujene	0.38	0.42	9.88	899
2	1R-α-Pinene	4.83	5.10	11.47	932
3	Camphene	0.11	0.14	12.10	945
4	Sabinen	0.99	1.07	13.18	967
5	β-Pinene	7.70	8.55	13.47	973
6	β-Myrcene	-	0.86	13.86	981
7	2,3-Dehydro-1,8-cineole	0.12	0.13	14.55	995
8	α-Phellandrene	0.04	0.07	14.84	1001
9	α-Terpinen	0.45	0.51	15.50	1014
10	Limonene	-	4.51	16.01	1024
11	D-Limonene	-	0.94	16.31	1030
12	1,8-Cineole	37.36	36.66	16.67	1037
13	γ-Terpinen	0.85	1.00	17.33	1050
14	Terpinolen	0.24	0.35	18.09	1065
15	Linalool	0.14	0.21	19.21	1087
16	Terpineol, cis-β-	0.10	0.18	19.82	1099
17	2-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)-, cis-	0.07	0.09	20.66	1116
18	(1R)-endo-(+)-Fenchyl alcohol	-	0.08	21.30	1129
19	2-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)-, trans-	0.14	0.53	21.60	1135
20	α-Campholenal	0.05	0.12	21.89	1141
21	cis-p-Menth-2,8-dienol	-	0.06	22.29	1149
22	trans-Pinocarveol	0.30	0.05	22.78	1159
23	Isopinocarveol	-	0.18	23.02	1164
24	Bicyclo[2.2.1]heptan-2-ol, 7,7-dimethyl-, acetate	0.04	0.09	23.23	1168
25	Borneol	-	0.31	23.76	1179
26	L-4-terpineol	4.01	4.39	24.16	1187
27	p-Cymen-8-ol	0.06	0.11	24.60	1196
28	p-menth-1-en-8-ol	-	0.54	24.85	1201
29	α-Terpineol	12.50	8.44	25.08	1206
30	Myrtenol	0.24	0.32	25.36	1212
31	Benihinal	0.12	0.19	25.69	1219
32	cis-Piperitol	0.06	0.11	25.97	1225
33	cis-Carveol	0.18	0.29	26.29	1232
34	Cyclopentan-1-al, 4-isopropylidene-2-methyl-	0.04	0.10	26.36	1234
35	Neral	0.13	0.02	26.66	1240
36	2,6-Octadien-1-ol, 2,7-dimethyl-	-	0.01	26.85	1244
37	Carvol	-	0.02	27.13	1250
38	p-Ethylguaiacol	0.06	0.02	27.50	1258
39	Carvacrol	0.05	0.10	28.30	1275
40	Thymol	0.05	0.10	28.81	1286
41	Cyclohexasiloxane, dodecamethyl-	0.09	0.14	29.04	1291
42	Terpinyl formate	-	0.10	29.86	1309

43	Cyclohexene, 4-isopropeny-l-methoxymethoxymethyl-	-	0.08	30.08	1314
44	Acetaldehyde, (3,3-dimethylcyclohexylidene)-, (E)-	0.15	0.20	30.92	1333
45	α-Terpinyl acetate	1.63	1.80	31.31	1342
46	Geraniol formate	-	0.07	31.58	1348
47	Copaene	-	0.05	32.33	1365
48	β-Elemen	-	0.06	33.39	1389
49	Toluene, 3,4,5-trimethoxy-	-	0.12	33.99	1403
50	Caryophyllene	0.04	0.08	34.45	1414
51	Varidiflorene	-	0.12	36.61	1466
52	cis-α-Bisabolene	-	0.09	36.90	1473
53	Patchoulene	-	0.08	37.40	1485
54	Cycloheptasiloxane, tetradecamethyl-	0.10	0.15	37.77	1494
55	β-Guaiene	-	0.04	38.18	1504
56	γ-Cadinene	0.12	0.01	38.41	1510
57	β-Cubebene	0.12	0.23	38.61	1515
58	α-Selinene	0.22	0.07	38.89	1522
59	Eudesma-4(14),11-diene	-	0.09	39.20	1530
60	γ-Gurjunene	0.12	0.02	39.71	1543
61	Patchoulene	-	0.02	39.83	1546
62	(-)-β-Cadinene	0.08	0.04	40.22	1556
63	δ-Cadinene	-	0.02	40.42	1561
64	unkown	-	0.01	40.54	1564
65	±-trans-Nerolidol	1.57	1.74	40.77	1570
66	Spiro[4.5]decan-7-one, 1,8-dimethyl-8,9-epoxy-4-isopropyl-	-	0.07	40.89	1573
67	Spiro[4.5]dec-6-en-8-one, 1,7-dimethyl-4-(1-methylethyl)-	-	0.07	41.08	1578
68	(-)-Spathulenol	0.77	0.88	41.24	1582
69	Isoaromadendrene epoxide	-	0.22	41.44	1587
70	Viridiflorol	0.04	0.10	41.64	1592
71	Tricyclo[5.2.2.0(1,6)]undecan-3-ol, 2-methylene-6,8,8-trimethyl-	0.14	0.04	41.91	1599
72	unkown	-	0.01	42.06	1603
73	Caryophyllene oxide	0.14	0.01	42.29	1609
74	Cubenol	-	0.19	42.44	1413
75	2-Methyl-4-(2,6,6-trimethylcyclohex-1-enyl)but-2-en-1-ol	0.48	0.65	42.77	1622
76	(-)-δ-Cadinol	-	0.22	43.07	1630
77	unkown	-	0.02	43.27	1635
78	α-Cadinol	0.12	0.05	43.78	1649
79	tau.-Muurolol	-	0.02	44.04	1656
80	Juniper camphor	0.04	0.11	45.13	1685
81	Longifolenaldehyde	0.08	0.16	45.89	1706
82	7R,8R-8-Hydroxy-4-isopropylidene-7-methylbicyclo[5.3.1]undec-1-ene	-	0.16	47.82	1760

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