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Characterization of the Volatilomic Fingerprint of Culinary Aromatic Herbs: A Comparative Study Based on Chemometric Analysis

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Abstract: Culinary aromatic herbs (CAHs), used worldwide for culinary and industrial purposes, are recognized for their wide range of beneficial health effects including antimicrobial, antioxidant, anti-hyperlipidemic, anti-inflammatory, anti-type 2 diabetes mellitus, antitumorigenic and anticarcinogenic, and anti-hypertensive properties, in addition to glucose- and cholesterol-lowering activities as well as properties that affect mental health and cognition via their phytochemical constituents, such as polyphenols (flavonoids and non-flavonoids), sulfur- and nitrogen-containing compounds, alkaloids, minerals, and vitamins. Moreover, the volatile organic metabolites (VOMs) found in CAHs offer unique analytical biosignatures linked to their sensory qualities and organoleptic characteristics. This study aimed to establish the volatilomic pattern of CAHs commonly used in Europe and in the Mediterranean region, oregano (*Origanum vulgare* L.) and two savory species: savory (*Satureja hortensis* L.) and lemon savory (*Satureja montana* L. var. *citriodora*). The volatilomic pattern of CAHs was established using headspace solid-phase microextraction (HS-SPME) followed by gas chromatography–mass spectrometry (GC-MS) determination. This is a powerful strategy to unravel the potential health benefits related to the most important VOMs identified in each aromatic herb. This comprehensive understanding will aid in establishing the authenticity of these herbs, while also safeguarding against possible fraudulent activities and adulterations. A total of 112 VOMs from different chemical families were identified. Terpenoids amounted to the major chemical family in the investigated aromatic herbs accounting for 96.0, 95.1, and 79.7% of the total volatile composition for savory, lemon savory, and oregano, respectively. Apart from contributing to flavor profiles, certain identified VOMs also possess bioactive properties, opening interesting avenues for potential application in the food, pharmaceutical, and cosmetic sectors. The volatilomic pattern combined with unsupervised principal component analysis facilitated the differentiation of the aromatic herbs under investigation, revealing the most related VOMs in each sample, which can be used as markers for the authentication of these valuable aromatic herbs, such as caryophyllene oxide (103), camphene (6), *p*-cymene (23), and borneol (74), among others. In addition, some VOMs have a high influence on the aromatic herb's bioactive potential, helping to prevent certain diseases including cancer, inflammatory-related diseases, diabetes, and cardiovascular diseases.

Keywords: aromatic herbs; volatile organic metabolites; volatilomic pattern; HS-SPME/GC-MS; chemometrics

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1. Introduction

The progression of lifestyles and advancements in scientific understanding regarding the interplay of food, nutrition, health, and well-being have sparked notable shifts in

dietary patterns over time. Present-day consumers are more knowledgeable, conscious, and inclined towards seeking out novel products that not only tantalize the tasty buds and appeal aesthetically but also offer health benefits and promote environmental sustainability. Moreover, while diets predominantly centered around animal-derived foods remain common, there is a growing inclination among consumers to pivot towards plant-based dietary choices, marking a significant departure from traditional norms. The antioxidant properties of herbs and spices are of particular interest because of the impact of oxidative modification of low-density lipoprotein cholesterol in the development of atherosclerosis.

In this context, throughout history, aromatic herbs and spices have held a prominent role in global cultures, serving diverse purposes and ingraining themselves in the human diet. From enhancing flavors and organoleptic properties and preserving foods and beverages naturally to being utilized in pharmaceuticals, cosmetics, and perfumes, these botanical treasures have played multifaceted roles. Additionally, they have been recognized for their potential health benefits, serving as preventive agents that contribute to human well-being [1–3].

Its composition encompasses various natural phytochemicals such as polyphenols, volatile organic metabolites (VOMs), terpenoids, carotenoids, phytosterols, alkaloids, vitamins, sulfur-containing compounds, and organic acids, among others [4–6]. These natural constituents, in conjunction with their synergistic effects on human health and their bioactive potential (e.g., antioxidant, antimicrobial, antiviral, anti-inflammatory, antidiabetic, anti-obesity, antipyretic, anti-hypertensive, and antidepressant properties, as well as their ability to induce cytochrome and other enzymes, inhibit cancer cell development, and provide cardio and neuroprotective effects), help elucidate the impact of aromatic herbs, spices, and other rich foods in bioactive constituents on human metabolism [7,8]. Furthermore, certain components found in plant-based foods, such as lycopene, curcumin, carvone, and limonene, have been linked to a decreased likelihood of developing cancer [2,7,8]. This remarkable potential has sparked growing interest within the scientific community regarding aromatic herbs, spices, and other plant-derived foods abundant in bioactive compounds. Additionally, the rising preference for flavors derived from natural sources highlights the significant potential of aromatic herbs and spices in this regard.

Unfortunately, the exorbitant market prices of many aromatic herbs and spices heighten the risk of adulteration of the genuine product, as is often the case with saffron and oregano [9–11]. Furthermore, given their nutritional value, widespread demand, and potential health benefits, a thorough understanding of the distinctive secondary metabolites responsible for their authenticity and quality is crucial. This knowledge serves as a potent tool for preventing and detecting potentially fraudulent activities, which represent a threat to public health.

Viewing this matter through an analytical perspective, bioactive compounds, including VOMs, have emerged as valuable resources in examining food authenticity and detecting fraud. This is because the compositions or proportions of specific compounds often reflect the unique characteristics of a particular plant, and any deviation from the profile of authentic samples indicates potentially fraudulent activity [12–15].

In this context, gas chromatography–mass spectrometry (GC-MS) stands out as the gold standard instrumental methodology for analyzing VOMs across various samples. However, prior sample preparation is crucial to concentrate the VOMs and eliminate any interference, especially in complex samples like food matrices [16]. To address this, headspace solid-phase microextraction (HS-SPME) is a widely used technique that effectively characterizes the volatile profile of fruits and vegetables [17–19]. This technique offers quick extraction times and minimal sample manipulation, combining extraction and pre-concentration in a single step without the need for potentially harmful organic solvents, thus making it environmentally friendly. Furthermore, its combination with GC-MS coupled to a mass spectrometer equipped with a quadrupole inert mass selective detector (qMS) ensures high sensitivity, reproducibility, and robustness. Additionally, employing multivariate statistical analysis on chromatographic datasets proves to be a rapid and

powerful strategy for generating volatile fingerprints and distinguishing between different food matrices [17,18,20].

In this direction, the current work intends to establish the comprehensive volatilomic profile of three culinary aromatic herbs (CAHs) frequently consumed in the Mediterranean area, namely oregano and two different varieties of savory (savory and lemon savory), using HS-SPME/GC-qMS to examine the dominant VOMs and evaluate the diversity and similarity in the VOMs patterns. To the best of our knowledge, this is the first time that these three CAHs have been characterized in terms of their volatilomic fingerprint. By defining the volatilomic profile of each aromatic herb, we can enhance our understanding of its ability in authenticity determination and quality control. This enables the detection of potential adulterations that may alter the genuine volatile profile. Additionally, combining chromatographic data sets with multivariate statistical data analysis (MSDA) revealed a useful strategy for accessing valuable insights into the quality and authenticity of aromatic herbs. This method sheds light on the chemistry underlying the bioactive and flavor characteristics of these herbs, ultimately ensuring consumers receive food quality and safety assurances.

2. Materials and Methods

2.1. Chemical and Reagents

3-Octanol (internal standard, IS) and sodium chloride (NaCl, 99.5%) were purchased from Sigma-Aldrich (Madrid, Spain), while Air Liquide in Portugal provided the GC carrier gas, helium of purity 5.0. Ultrapure water (H_2O) was acquired from a Milli-Q® system (Millipore, Bedford, MA, USA). The SPME holder for manual sampling, the fiber DVB/CAR/PDMS (divinylbenzene/carboxen/polydimethylsiloxane), and the vials were supplied from Supelco (Bellefonte, PA, USA). The Kovats index (KI) was calculated using an alkane series, C8 to C20, with a concentration of 40 mg/L in *n*-hexane acquired from Fluka (Buchs, Switzerland).

2.2. Aromatic Herbs

Three aromatic herbs were freshly obtained from a local market in Funchal (Madeira Island, Portugal), namely savory (*Satureja hortensis* L.), lemon savory (*Satureja montana* L. var, *citriodora*), and oregano (*Origanum vulgare* L.). All samples were milled and homogenized using a grinder (A11 Basic analytical mill, IKA, Staufen, Germany) and stored at room temperature (25 ± 1 °C) until analysis. Images of the examined flowers are shown in Figure 1.

Figure 1. Types of aromatic herbs analyzed.

2.3. HS-SPME Procedure

HS-SPME procedure was performed according to the conditions reported by Izcara et al. [21], with minor alterations. Briefly, 1 g of aromatic herb, 0.3 g of NaCl, 5 µL of 3-octanol (102 µg/mL), and 6 mL of H_2O were placed into a 20 mL vial containing a magnetic stirring microbar. The vial was sealed with a PTFE-faced silicone septum and put in a thermostatic bath at 45 ± 1 °C with constant magnetic stirring (450 rpm). The DVB/CAR/PDMS fiber was exposed in the headspace of the glass vial for 50 min. After

that, the fiber was inserted into the holder needle, taken from the vial, and placed in the GC injector at 250 °C for 6 min to promote the thermal desorption of extracted VOMs. All assays were performed in triplicate (n = 3).

The SPME fiber was thermally conditioned in the GC injector agreeing to the manufacturer's recommendations before use, and it was conditioned daily for 10 min before the first extraction to ensure there was no carryover.

2.4. Gas Chromatography–Mass Spectrometry Analysis

The separation and identification of VOMs from aromatic herbs were performed using an Agilent Technologies 6890N (Palo Alto, CA, USA) GC, equipped with a SUPELCOWAX® 10 capillary column (Sigma-Aldrich, Burlington, MA, USA) (60 m × 0.25 mm i.d. × 0.25 µm film thickness), and a mass spectrometer Agilent 5975. The carrier gas was helium (Helium N60, Air Liquid, Portugal) at a flow rate of 1 mL/min (column-head pressure: 13 psi). A splitless injector equipped with an insert of 0.75 mm i.d. and an injector temperature of 250 °C was used. Column temperature started at 40 °C for 1 min, then increased to 220 °C at 2.5 °C/min, and then held isothermally at 220 °C (kept 10 min). The Agilent quadrupolar mass spectrometer model 5975 had an electron impact (EI) of 70 eV, electron emission of 300 µA, transfer line temperature of 150 °C, and an ion source temperature of 230 °C. The mass acquisition was carried out in full scan mode in the mass range from 30 to 350 m/z. VOMs were identified by comparing their mass spectra with the National Institute of Standards and Technology (NIST) MS05 spectral database (Gaithersburg, MD, USA) and by comparing the KI calculated with the KI reported in the literature for similar column [22,23].

2.5. Multivariate Statistical Analysis

MetaboAnalyst 5.0, a web-based program, was used to perform the multivariate data analysis [24]. The raw GC-qMS data were preprocessed to eliminate VOMs with missing values before being normalized (data scaling by autoscaling). The data were submitted to a one-way analysis of variance (ANOVA), followed by Fisher's test for post hoc multiple comparisons of means from three aromatic herbs at p-value < 0.001, to discover significant differences. In addition, principal component analysis (PCA) and partial least squares-discriminant analysis (PLS-DA) were employed to give insights into the separations among the aromatic herbs under research and to find VOMs that may reveal variations across the sample sets, as PLS-DA may determine the set of VOMs that specifies the greatest separation among the aromatic herbs investigated by lowering the size of the data matrix by eliminating redundant variables. VOMs with a VIP score higher than 1.0 and differential expression in univariate analysis might be used to characterize aromatic herbs. The 10 most significant VOMs identified in aromatic herbs by ANOVA were used in hierarchical cluster analysis (HCA), which was generated using Ward's algorithm and Euclidean distance analysis, to identify clustering patterns that can help in the characterization of the aromatic herbs analyzed.

3. Results and Discussion

3.1. Volatilomic Profile of Aromatic Herbs

CAHs are significantly influenced by their volatile profile, which is determined by the chemical composition of the individual VOMs, their synergistic effects with other non-volatile compounds, odor thresholds, relative amounts, and growing conditions. The typical HS-SPME$_{DVB/CAR/PDMS}$/GC-qMS chromatograms of the aromatic herbs studied are shown in Figure S1.

A total of 112 VOMs were identified, including 47 terpenoids, 33 sesquiterpenoids, 15 esters, 10 carbonyl compounds, 5 alcohols, and 2 volatile phenols. Of the 112 VOMs identified, only 35 VOMs were common to all aromatic herbs analyzed. The detailed list of all VOMs identified in each of the aromatic herbs analyzed together with their KI, molecular formula (MF), chemical families, and relative peak area is given in Table S1.

Although savory (*Satureja hortensis* L.) and lemon savory (*Satureja montana* L. var. *citriodora*) belong to the genus *Satureja* and Lamiaceae family, they present a different volatilomic pattern, mainly in qualitative terms, as can be observed in Table S1.

Moreover, in qualitative terms, each aromatic herb has a unique VOM pattern that was not present in the other samples analyzed, e.g., hexyl butyrate, isobornyl acetate, terpinene-4-ol, and myrtenol were detected only in savory, while 3-nonanone, allocimene, α-cubebene, (+)-longifolene, γ-murolene, geranyl acetate, nerolidol are present in lemon savory. In addition, several VOMs that are unique to oregano were observed, namely ethyl acetate, p-mentha-1,8-diene, cosmene, β-ionone, and ylangene, among others.

Terpenoids, including monoterpenoids and sesquiterpenoids, denoted the majority, both in terms of the number of identified VOMs and detected amount, as can be observed in Figure 2. This chemical family in plants serves vital roles in both physiology and defense mechanisms. They contribute to physiological processes like photosynthesis and plant growth, while also acting as defense compounds against herbivores and pathogens, showcasing the intricate interplay between primary and secondary metabolism in plants [25]. The largest chemical family found in the investigated CAHs, with a total of 47 VOMs is represented by the monoterpenic compounds (MT) (C 10 compounds, derived from isoprene) (Table S1, Figure 2). These secondary metabolites, well-known for their floral, wood, and fruity notes, represent ca. 85.8% (savory), 57.7% (oregano), and 68.5% (lemon savory) of the total volatile composition expressed in GC peak areas, being thymol, *p*-cymene, γ-Terpinene, and carvacrol the ones that exhibited higher chromatographic areas in savory, geraniol, citral, β-Bisabolene, and nerol in lemon savory, while in oregano, the most dominant volatiles are carvacrol, β-terpineol, linalyl acetate, and caryophyllene. Several compounds from this chemical family can play an important role in the development of innovative functional foods, in addition to the formulation of pharmaceutical and cosmetic products, due to the wide range of bioactive properties including antitumoral and/or anticarcinogenic potential (D-limonene, β-pinene, β-myrcene, and α-muurolene), anti-inflammatory capacity (4-terpineol, β-pinene, D-limonene, caryophyllene, and menthol), antimicrobial activity (bornyl acetate, D-limonene, caryophyllene 4-terpineol, and sesquiphellandrene), and antioxidant properties (β-pinene, β-myrcene, 4-terpineol, and β-ocimene).

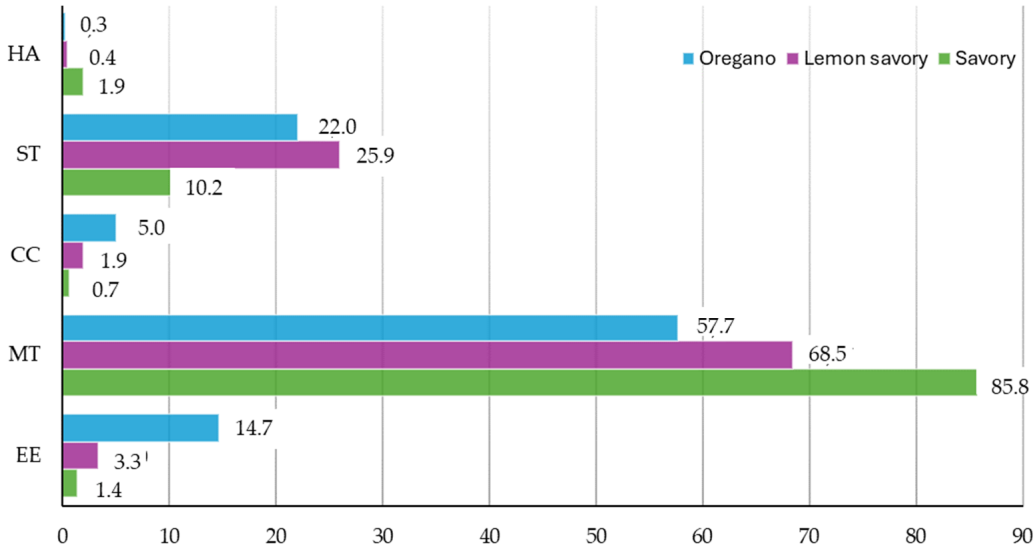

Figure 2. Distribution in relative percentage (%) of chemical families found in the investigated herbs—oregano, savory, and lemon savory. EE: esters; MT: monoterpenic; CC: carbonyl compound ST: sesquiterpenic; HA: higher alcohols.

On average, sesquiterpenic compounds (C 15, 3 isoprene units) constitute the second most abundant chemical family in the investigated herbs. They correspond to a total of 33 volatile compounds that represent ca. 10.2% (savory), 22.0% (oregano), and 25.9% (lemon

savory) of the total GC peak areas (Table S1, Figure 2). Sesquiterpenoids are well-known for their odors with cloves, woody, and turpentine notes, when present at levels higher than their odor threshold values, and also for their biological effects related mainly to anti-inflammatory and antimicrobial properties.

Esters (EEs) are the third major chemical family of oregano and lemon savory, accounting for 14.7% and 3.3% of the total volatile profile. It was possible to observe that esters' contribution to the total volatile profile was almost 6 and 10 times higher in oregano than in lemon savory and savory, respectively. On the other hand, higher alcohols (HAs) represent the third major chemical family, accounting for 1.94% of the total volatile profile of savory, with 1-octen-3-ol representing 91.9% of the total alcohol fraction. The contribution of this chemical family to the total volatile profile was 5 and 7 times higher in savory than in lemon savory and oregano, respectively.

A new Debiased Sparse Partial Correlation algorithm (DSPC) for estimating partial correlation networks that can differentiate between direct and indirect associations and provide insights into the dependence structure between VOMs was developed (Figure 3). A key assumption underlying this modeling strategy is that the number of true connections among the VOMs is much smaller than the available sample size, i.e., the true network of partial correlations among the VOMs is sparse.

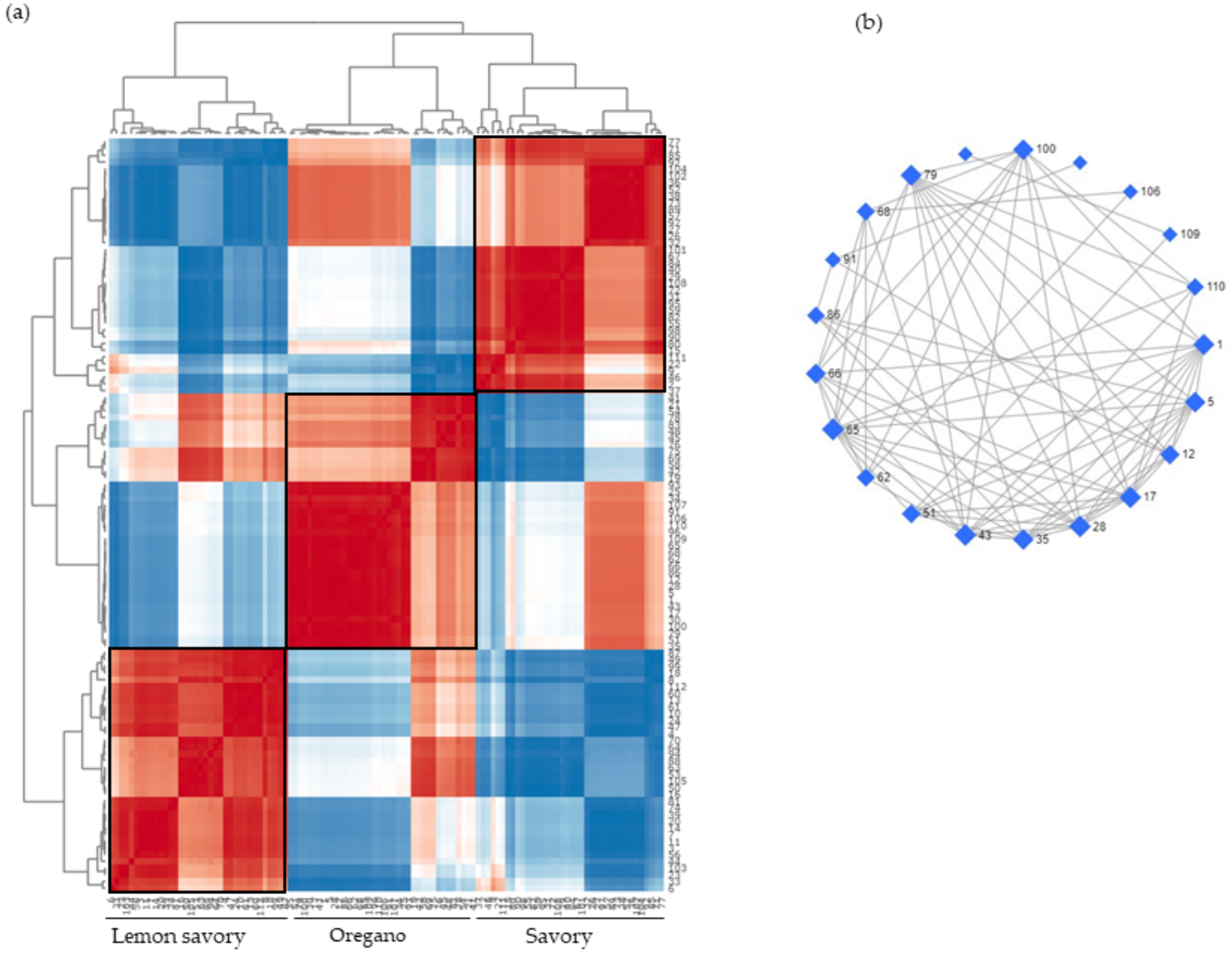

Figure 3. (**a**) Correlation analysis after data normalization and Pearson's correlation analysis; and (**b**) DPSC network using a subset of data selected by setting a Pearson's correlation coefficient (attribution of the peak numbers is shown in Table S1).

In this context, DSPC reconstructs a graphical model and provides partial correlation coefficients and *p*-values for every pair of VOM features in the dataset, which allows for discovering connectivity among large numbers of volatiles using fewer samples. The results can be visualized as weighted networks, where nodes represent metabolites and edges represent partial correlation coefficients or the associated *p*-values (Figure 3b).

The VOMs identified in CAHs can be used to determine their authenticity and detect adulteration since each analyzed CAH has a unique volatile profile, which consists of specific compounds in particular ratios. This comprehensive understanding can be very useful for detecting potential adulterations of the original product comparing any deviations from the authentic sample. In this context, the presence of unexpected VOMs can reveal the presence of adulterants. In addition, the variation in relative amounts of certain volatiles, for instance, a significant reduction in the concentration of key volatiles, can also indicate potential adulteration.

3.2. Bioactive Potential of Volatile Organic Metabolites Identified in Aromatic Herbs

Many VOMs have been identified in foods, but their biological actions and roles are still partially understood. Nevertheless, these VOMs are effective in the prevention and treatment of a variety of disorders, including cancer [26], cardiovascular disease [27], diabetes [28], and inflammatory diseases [29]. As stated above, terpenoids are the most abundant chemical identified in aromatic herbs, and they are linked to diverse biological properties, such as anti-inflammatory, anti-hyperglycemic, antiviral, and antifungal, among others, which can help to preserve human health [29–31]. Some potential applications of the investigated CAHs are summarized in Figure 4.

Figure 4. Potential applications of investigated CAHs.

Thymol, the most representative terpenoid of savory, exhibits diverse biological potentials, including antimicrobial, antioxidant, anti-inflammatory, antispasmodic, and anti-

cancer activities. Studies suggest its efficacy in combating bacterial and fungal infections, attributed to its ability to disrupt bacterial cell membranes and inhibit microbial growth, making it effective in extending the shelf life of food products. This terpenoid is commonly utilized in food preservation applications, such as in meat products, dairy items, and beverages, to inhibit the growth of bacteria, fungi, and other microorganisms, thereby enhancing food safety and maintaining product quality [32–35]. On the other hand, the most representative terpenoid in lemon savory is geraniol. This monoterpene alcohol can be used as a natural preservative in food due to its antioxidant and antimicrobial properties, as a fragrance ingredient in cosmetics, and as a therapeutic agent in cancer treatment and wound healing [36,37]. Carvacrol, a phenolic monoterpene present in oregano, exhibits notable biological properties, including antimicrobial, antioxidant, anti-inflammatory, and anticancer activities.

Recent studies have explored its potential as a natural antimicrobial agent in food preservation and its therapeutic effects in various diseases (e.g., cancer) [34,38,39]. In addition, research related to anticancer properties of carvacrol and thymol suggests its potential to inhibit the growth and proliferation of cancer cells through various mechanisms (e.g., apoptosis induction, cell cycle arrest, inhibition of angiogenesis, and metastasis) against a diversity of cancer types, like as breast, cervical, colon, prostate, and lung cancers [40–42]. However, more research is needed to fully elucidate its anticancer mechanisms and evaluate its efficacy in clinical settings. Linalyl acetate, an ester representative of the total volatile fraction of oregano, can be used as a flavoring agent in a diversity of food and beverage products. Its pleasant floral and sweet odors make it a common choice for enhancing the taste of confectionery items, desserts, and beverages, among others [43].

However, it would be emphasized that although several bioactive compounds have been detected, the quantity of aromatic herbs consumed by humans throughout the day is low. This can bring us to another dimension related to the encapsulation of these compounds with formulations containing the bioactive from CAHs at levels that can exert in the organism the targeted biological effects.

3.3. Statistical and Multivariate Data Analysis: Characterization of Aromatic Herbs

To assess the effectiveness of HS-SPME/GC-qMS in describing CAHs in terms of volatilomic pattern, a statistical analysis of the data matrix (9 samples × 112 VOMs) was performed using the MetaboAnalyst 5.0 web-based program [24], where PCA and PLS-DA were applied as multivariate analysis, as defined in Section 2.5. One-way ANOVA followed by Fisher's test for post hoc multiple comparisons of means from three aromatic herbs at p-value < 0.001 was carried out to select the VOMs that statistically significantly differed among the studied aromatic herbs. Only 6 VOMs from 112 VOMs were not significantly different among the aromatic herbs, namely 3-carene (9), perillene (32), 6-methyl-5-hepten-2-ol (36), α-cubebene (38), copaene (44), and nerolidol (102). The statistically different VOMs were submitted to PCA analysis to attain the earliest overview of differences/similarities among aromatic herbs. To further recognize the differences among CAHs, a PLS-DA model was performed (Figure 5, and a total variance of 98.2% was obtained by the PC1 vs. PC2. From the data matrix used, 10 VOMs were identified with VIP scores higher than 1.0, namely α-pinene (3), camphene (6), β-pinene (7), limonene (14), *p*-cymene (23), (-)-β-elemene (56), borneol (74), δ-cadinene (81), geraniol (92), and caryophyllene oxide (103) (Figure 5b).

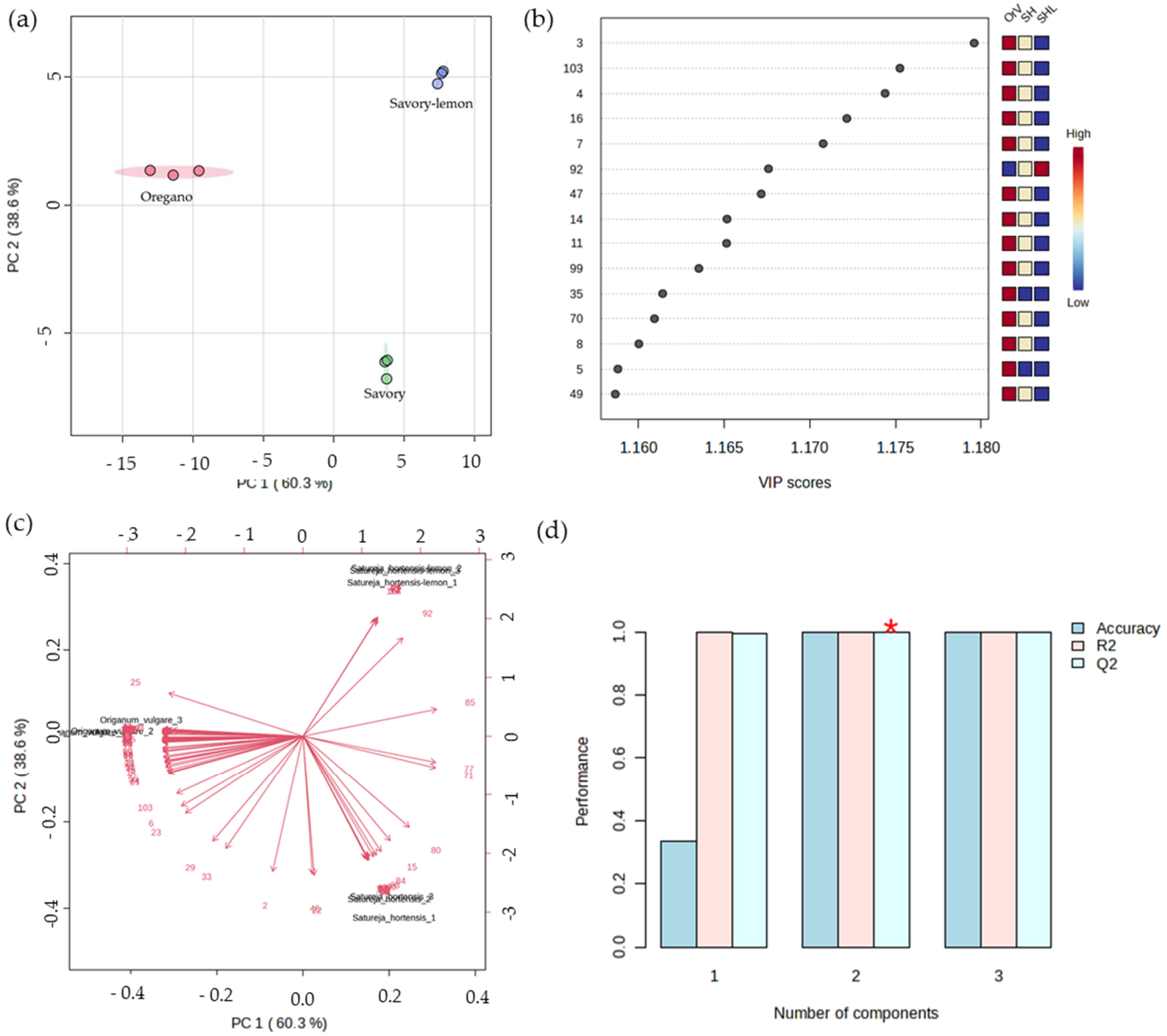

Figure 5. PLS-DA of the volatilomic pattern of aromatic herbs (n = 3 for each data point): (**a**) score scatter plot; (**b**) VIP scores; (**c**) biplots of all analyte targets identified in CAHs; and (**d**) select an optimal number of components for classification (attribution of the peak numbers is shown in Table S1). * Indicates the best estimate value of the predictive ability of the model, and is calculated via cross-validation (CV).

Figure 5c shows the biplot of the two first principal components (PC1 vs. PC2) for aromatic herbs, which explains 75.7 and 22.5% of the total variability of the data set, letting an appropriate differentiation of the aromatic herbs. The optimal number of components for classification is presented in Figure 5d. The predictive ability of the model is represented by Q2 and is calculated via cross-validation (CV). Good predictions will have a low predicted residual sum of squares (PRESS) or high Q2. Furthermore, HCA was carried out utilizing the significant VOMs identified in aromatic herbs by ANOVA. The resulting heatmap using Euclidean distance and Ward's clustering approaches (Figure 6) and the top 25 VOMs showed an instinctive visualization of the data matrix and, in conjunction with the previous statistical analysis, allowed for better identification of the inherent clustering patterns between each aromatic herb. A color scale is used to show the relative amount of each component (from yellow-green to violet, representing the minimum and maximum values).

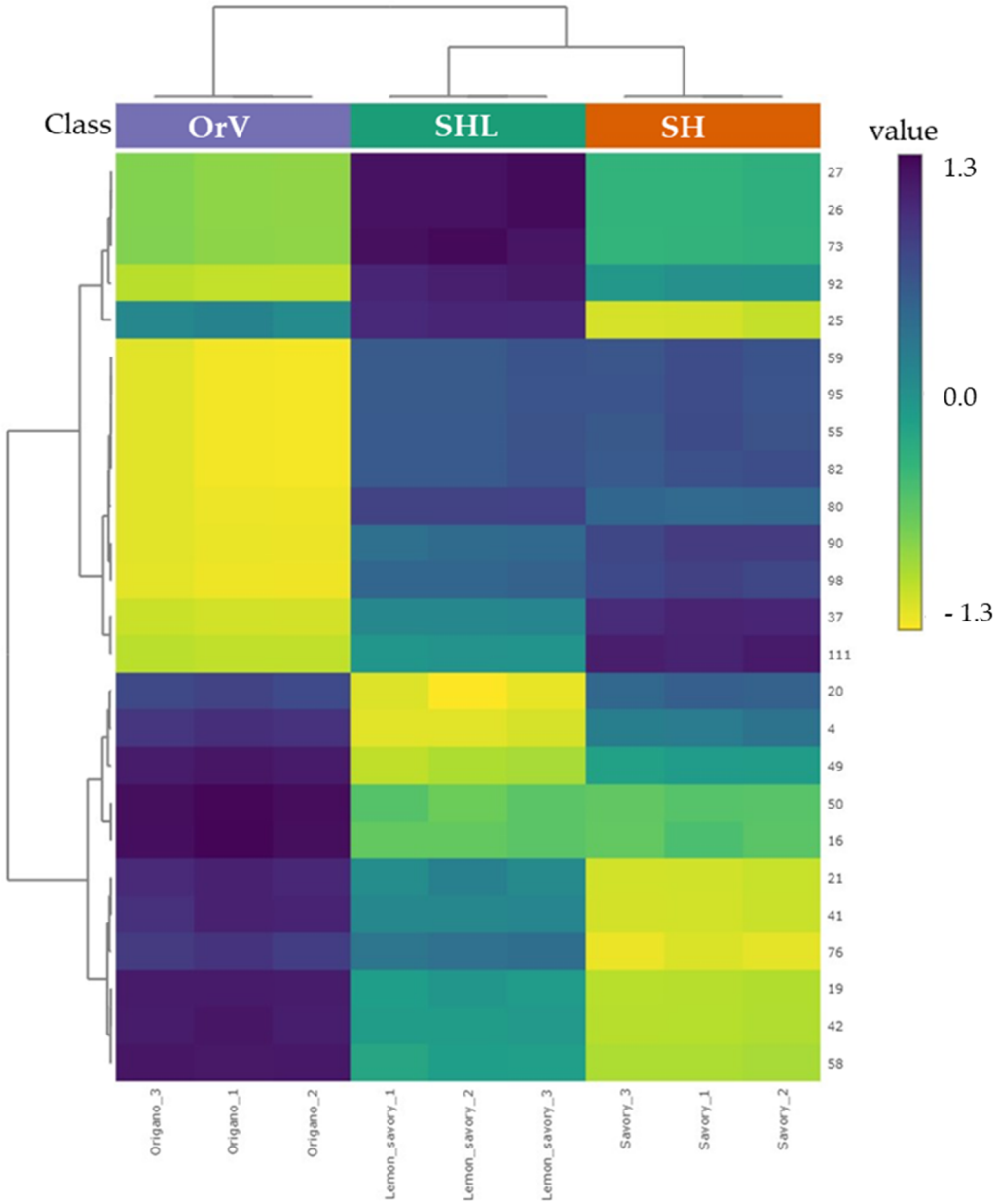

Figure 6. The dendrogram and heatmap representing the 112 VOMs released from oregano (OrV), savory (SH), and lemon savory (SHL) considering the GC-MS peak areas after autoscaling, generated by Euclidean distance and Ward's clustering (attribution of the peak numbers is shown in Table S1). The relative content of each volatile is illustrated through a chromatic scale (from yellow-green to violet, the minimum and the maximum, respectively).

4. Conclusions

The obtained results revealed that in semi-quantitative terms, monoterpenoids and sesquiterpenoids are the most abundant chemical families in all aromatic herbs, accounting for 96.0, 95.1, and 79.7% of the total volatile composition of savory, lemon savory, and oregano, respectively. The data obtained showed that a combination of volatilomic patterns and statistical analysis is a suitable tool to discriminate aromatic herbs investigated. α-Pinene, camphene, β-pinene, limonene, *p*-cymene, (-)-β-elemene, borneol, δ-cadinene, geraniol, and caryophyllene oxide were the VOMs responsible for discriminating CAHs, based on PLS-DA model.

Taken together, our findings showed that certain VOMs found in aromatic herbs have biological effects on human health and, consequently, may help in the prevention of several

illnesses, including cancer, inflammatory disorders, diabetes, and cardiovascular diseases. In addition, the sensory properties associated with VOMs lower olfactory thresholds, allowing the VOMs identified in aromatic herbs (e.g., linalyl acetate) to serve as flavoring agents in the food and cosmetic industries. The results thus point to the potentially beneficial effects of incorporating CAHs into the human diet. As several metabolic diseases and age-related degenerative disorders are closely linked to oxidative processes in the body, the use of herbs and spices as a source of antioxidants to combat oxidation warrants further attention. Immediate studies should focus on validating the antioxidant capacity of herbs and spices after harvesting and testing their effects on markers of oxidation. The establishment and knowledge of the volatile pattern is a powerful approach for evaluating adulteration. It relies on identifying and quantifying specific volatile compounds and comparing them to known authentic profiles to detect deviations that suggest adulteration.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/separations11060181/s1, Figure S1. Chromatogram of the volatile fraction of the aromatic herbs obtained by HS-SPME$_{DVB/CAR/PDMS}$/GC-qMS. Numbers above the peaks indicate the volatile organic metabolites (VOMs) identified in Table S1; Table S1. Relative area of volatile organic metabolites (VOMs) identified in aromatic herbs using HS-SPME$_{DVB/CAR/PDMS}$/GC-qMS.

Author Contributions: Conceptualization, S.I., R.P., I.S. and J.S.C.; methodology, S.I., R.P. and J.S.C.; software, S.I. and R.P.; validation, S.I., R.P. and J.S.C.; formal analysis, S.I. and R.P.; investigation, S.I. and R.P.; resources, J.S.C.; data curation, S.I., R.P. and J.S.C.; writing—original draft preparation, S.I. and R.P.; writing—review and editing, S.M.-Z., I.S. and J.S.C.; visualization, S.M.-Z.; supervision, I.S. and J.S.C.; project administration, J.S.C.; funding acquisition, J.S.C. and I.S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All the data in this research are presented in the manuscript and Supplementary Materials.

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

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