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Natural Extracts and Essential Oils as Ingredients in Cosmetics: Search for Potential Phytomarkers and Allergen Survey

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Abstract: The increasing use of natural ingredients such as essential oils (EOs) and natural extracts (NEs) in cosmetics is an analytical and legislative challenge due to their complex composition, which includes recognized allergenic compounds. In this work, 17 EOs and NEs have been characterized by gas chromatography coupled to mass spectrometry (GC-MS) of dilutions of the original samples. Additionally, solid phase microextraction (SPME) was applied for the analysis of volatile components. The results obtained allowed the identification of more than 90 compounds, including 20 allergens, in the analyzed samples and the study of potential phytomarkers of the addition of EOs and ENs in cosmetics.

Keywords: natural extract; essential oil; cosmetics; preservatives; allergens; phytomarker; solid phase microextraction; gas chromatography; mass spectrometry

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1. Introduction

The widespread use of cosmetic and personal care products has raised some social concerns about the harmful effects that some ingredients used in the formulations may have on the consumer's health. Current trends are focused both on natural products as "greener" or "safer" than conventional ones [1] and also on the avoidance of certain chemical compounds in products, commonly called "free-from" cosmetics. However, it is true that all cosmetic formulations are complex mixtures of multiple components with very different origins, chemical natures, and functions.

Most cosmetic products can be easily degraded by microorganisms, and microbial contamination represents a major health risk for consumers [2]. Preservatives play a crucial antimicrobial role since their addition is mainly aimed at inhibiting this deterioration due to microbial growth, thus ensuring the stability of cosmetic formulations over time. Different preservation strategies are available to ensure the microbiological safety of cosmetic products [3]. Over the last few decades, the most common way was to use synthetic preservatives. According to the predominant functional group in their molecular structure, they can be classified into alcohols and derivatives, halogenated, organic acids, esters, and salts, among others [4].

Although the benefits and positive protective effects of preservatives are undeniable, since the main modes of exposure are inhalation or absorption through the skin, possible negative health effects have also been described, as excessive exposure can lead to irritation, contact allergy, or skin dermatitis [5]. For this reason, the safety of these chemical ingredients has been questioned, which leads to further restrictions in the regulations of application. In the EU framework, there is a limited number of permitted preservatives listed in Annex V of Regulation 1223 [6], where limitations, requirements, label warnings, and maximum permitted concentrations in ready-to-use products are established. The

positive list of preservatives [7] includes more than 50 different substances or chemical families, and it is continuously undergoing legislative changes.

The negative public perception of traditional preservatives is prompting the cosmetic industry to search for alternative approaches to the preservation of cosmetic products, developing self-preserving cosmetics and even preservative-free products. In some of these formulations, traditional synthetic preservatives are replaced by antimicrobial substances, mainly of natural origin, which are generally considered multifunctional agents. Multifunctional additives are molecules providing more than one beneficial effect to the formulation or to the skin, e.g., glycols, glycerol ethers, essential oils, plant-based extracts, and fragrance ingredients. In this field, the demand for products containing natural extracts and mixtures of natural ingredients that are marketed with a preservative function is growing. So, by carefully selecting these ingredients, it is possible to reduce or eliminate the use of traditional preservatives. However, these multifunctional antimicrobial ingredients are not regulated for this function in Annex V. In this sense, a great number of natural extracts (NEs) and essential oils (EOs) are added to cosmetics with other traditional functions, e.g., as fragrance ingredients. In addition, due to their recognized antioxidant and antimicrobial properties [8–10], they can act in formulations in combination with chemical preservatives or alone as natural preservatives in preservative-free format cosmetics. Therefore, the use of these nature-based ingredients and their several functions in the production of cosmetics and related personal care products provides several advantages, such as improving the dermo-cosmetic and preservative properties, as well as the marketing image of the final product in view of current consumer demands. While synthetic preservatives are more affordable, the high prices of many NEs and EOs and their increasing demand make adulteration a frequent practice [11,12], meaning that there are other natural compounds and even other EOs that are cheaper and easier to acquire. Therefore, their authentication is crucially important for both consumers and companies.

Both NEs and EOs are complex mixtures of chemical substances whose major components are allergenic fragrances, and therefore, require analytical control. For many years, the Scientific Committee for Consumer Safety (SCCS) [13] has cataloged a total of 82 substances, including natural extracts and oils, as established human contact allergens. While only 26 allergenic fragrances in cosmetics were regulated by the EU [6], the new regulation [14] has extended the list of 26 regulated ingredients by a further 56 new allergens, making it mandatory to label a total of 82 substances identified as allergens in the coming years. The list comprises 28 natural extracts (NE_{28}) and 54 individual chemical (IC_{54}) compounds, making their analysis difficult in complex matrices such as cosmetics.

For now, cosmetics manufacturers are obliged to label only the presence of the 26 allergens in the finished product when their concentration is higher than 0.001% for leave-on cosmetics or higher than 0.01% in rinse-off products [6]. However, they often only consider for this calculation the allergens contributed by fragrance substances, as they have traditionally been the main and sometimes the only source of allergens in cosmetics. With the new trend towards the use of these multifunctional antimicrobial ingredients, this labeling will probably have to be revised upwards.

Over the last few years, a considerable number of articles have significantly contributed to improving the challenge of the analysis of traditional preservatives in cosmetics. New trends in the preparation and extraction procedures for cosmetic ingredients in general [15] have been sought in recent years, with inclinations towards simple, sustainable, and environmentally friendly methodologies. For preservatives, this includes procedures based on solid phase extraction (SPE), matrix solid phase dispersion (MSPD) [16], and additionally advanced microextraction techniques such as solid phase microextraction (SPME) and liquid–liquid microextraction (LLME), among others, combined with chromatographic techniques. Regarding the alternative options, different techniques have been applied for the analysis of essential oils and natural extracts, some of which are easy to handle, such as the measurement of physicochemical parameters. But considering that adulteration occurs at low concentration levels to avoid detection by common methods and the need to

analyze their constituents, other analytical methods need to be improved to achieve these objectives. In this sense, adequate methodology for the analysis of these complex mixtures will allow the characterization of the new natural preservatives and the determination of the total allergen content. Gas chromatography coupled to mass spectrometry is the most commonly used analytical method for the analysis of allergenic fragrances, while liquid chromatography is used less frequently. Some published studies have been conducted for the analysis of certain individual chemical compounds listed [17–20]. Analytical techniques are crucial for the quality control of an ingredient or product, especially when the factors surrounding the natural raw materials, as in the case of essential oils and natural extracts, can affect their composition. In addition, cosmetics manufacturers must also guarantee their compliance with current regulations and ensure the absence of fraud among their products. Cosmetic companies have a significant challenge regarding analytical techniques to identify and quantify fragrances in the final cosmetic products. However, no analytical tools have been described to assess the NE_{28} and, consequently, the extended list of fragrance allergens. Thus, the aim of this work is to search for selective phytomarkers to determine the presence of NE_{28} in cosmetic formulations. In addition, an estimation of the real allergen levels in cosmetic products containing Nes and Eos would be possible by a prior assessment of the allergen content in those NE and EO pure original products, establishing groups based on the expected affinities due to a close botanical origin. To characterize the composition of the selected pure samples of Eos and Nes, direct injection of sample dilutions and solid-phase microextraction (SPME) were applied, followed by gas chromatography coupled to mass spectrometry (GC-MS) analysis. After the identification of allergens, potential phytomarker compounds were examined. The results obtained are useful to prevent and regulate fraud and thus contribute to improving the safety of users of cosmetics that include NEs and EOs in their formulation.

2. Materials and Methods

2.1. Chemicals, Reagents, and Materials

Ethyl acetate was supplied by Scharlab (Barcelona, Spain) and was of analytical grade. The SPME manual holders and fibers were supplied by Supelco (Bellefonte, PA, USA). The commercial fiber coating used throughout the present work was 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB). Prior to first use, the fiber was conditioned as recommended by the manufacturer, inserting in the GC injector under helium flow at 250 °C for 30 min.

2.2. Samples

In the choice of samples, the 28 ENs highlighted as contact allergens by the SCCS of the European Commission [13] are used as references. Samples from two different origin groups were selected, allowing the search for frequently occurring substances exclusive to each group that act as markers. Fifteen pure EOs and two NEs (Jasmine Absolute and Rose Absolute) were commercially acquired, comprising eight obtained from flowers and nine from trees.

Table 1 lists the 17 samples divided into groups, indicating their CAS numbers and the solubility indicated by the safety data sheets (SDS).

The constituent substances of these complex samples of EOs and NEs include recognized allergens, which in turn have specific functions and properties that are transferred to the final product. Table 2 lists the individual allergenic substances included in the SDS of the purchased samples and details their use and function as ingredients in cosmetics [21,22]. The chemical formulas and structures of these compounds are included in Supplementary Table S1.

Table 1. Characteristics of the analyzed samples: sample code, CAS numbers and solubility indicated by the safety data sheets.

Code	CAS	Solubility [a]
Flowers		
Jasmine absolute	84776-64-7	H_2O (I), EtOH (S)
Rose absolute	90106-38-0	EtOH (S)
Geranium Egypt	90082-51-2	EtOH (S)
Lavender	90063-37-9	EtOH (S)
Lavandin super	91722-69-9	EtOH (S)
Verbena oil	Aromatic substances mixture	H_2O (I), EtOH (S)
Ylang Ylang Extra	83863-30-3	H_2O (I), EtOH (PS)
Ylang Ylang II	83863-30-3	H_2O (I), EtOH (PS) alcohol (PS)
Trees		
Cinnamon leaves	84649-98-9	H_2O (I), EtOH (S)
Cassia	84961-46-6	H_2O (I), EtOH (S)
Atlas cedar	92201-55-3	EtOH (S)
Cedar super	85085-41-2	H_2O (I), EtOH (S)
Clove buds	84961-50-2	EtOH (S)
Eucalyptus	84625-32-1	EtOH (S)
Laurel leaves	84603-73-6	H_2O (I), EtOH (S)
Perú oil super	8007-00-9	H_2O (I), EtOH (S)
Indian Sandalwood	84787-70-2	H_2O (I), EtOH (S)

[a] I: insoluble; S: soluble; PS: partially soluble.

Table 2. Compounds declared as allergens [13]: CAS numbers, their function or use in cosmetics, and samples in which their presence is detailed in the safety data sheets.

Compound	CAS	Cosmetic Function/Use	Declared in
Benzyl alcohol	100-51-6	Preservative/solvent	Jasmine absolute, rose absolute, Perú oil
Benzyl benzoate	120-51-4	Solvent	Jasmine absolute, cinnamon leaves, Perú oil, Ylang ylang II, Ylang ylang extra
Benzyl cinnamate	103-41-3	Masking agent	Perú oil
Benzyl salicylate	118-58-1	UV absorber	Ylang ylang II, Ylang ylang extra
Camphor	464-49-3	Denaturant/plasticiser	Lavandin super
Cinnamaldehyde	104-55-2	Denaturant	Cassia, cinnamon leaves
Cinnamyl alcohol	104-54-1	Masking agent	Cassia
Citral	5392-40-5	Masking agent	Jasmine absolute, rose absolute, geranium Egypt
Citronellol	106-22-9	Masking agent	Rose absolute, geranium Egypt, verbena oil
Coumarin	91-64-5	Masking agent	Cassia, lavandin super
Eugenol	97-53-0	Denaturant/tonic	Jasmine absolute, rose absolute, clove buds, laurel leaves, cinnamon leaves, Ylang ylang II, Ylang ylang extra
Farnesol	4602-84-0	Soothing/solvent/deodorant	Rose absolute, Ylang ylang II, Ylang ylang extra
Geraniol	106-24-1	Tonic	Rose absolute, geranium Egypt, lavender, lavandin super, Ylang ylang II, Ylang ylang extra, verbena oil
Isoeugenol	97-54-1	Masking agent	Ylang ylang II, Ylang ylang extra
Limonene	138-86-3	Solvent	Geranium Egypt, lavender, lavandin super, laurel leaves, eucalyptus, cinnamon leaves, verbena oil

Table 2. *Cont.*

Compound	CAS	Cosmetic Function/Use	Declared in
Linalool	78-70-6	Deodorant	Jasmine absolute, lavender, lavandin super, laurel leaves, cinnamon leaves, Ylang ylang II, Ylang ylang extra, verbena oil
Linalyl acetate	115-95-7	Masking agent	Lavender, lavandin super
Terpinen-4-ol	562-74-3	Denaturant/solvent	Lavender, laurel leaves
Terpinolene	586-62-9	Fragrance	Cinnamon leaves
α-Pinene	80-56-8	Antifoaming	Geranium Egypt, laurel leaves, eucalyptus, cinnamon leaves
α-Terpineol	98-55-5	Denaturant/solvent	Lavender, lavandin super
β-Caryophyllene	87-44-5	Skin continioning	Clove buds, geranium Egypt, lavender, lavandin super, Ylang ylang II, Ylang ylang extra, cinnamon leaves
β-Pinene	127-91-3	Perfuming	Geranium Egypt, laurel leaves, eucalyptus, cinnamon leaves

2.3. Sample Preparation

First, sample preparation was kept as simple as possible, including simple dilution. After preliminary tests, pure samples were diluted 1:100 in ethyl acetate for direct injection in the GC-MS.

For SPME, 10 µL of the sample was placed in a 10 mL vial. After sealing with an aluminum cap furnished with PTFE-faced septa, samples were left to equilibrate for 30 min, and then the SPME fiber (PDMS/DVB) was exposed to the headspace (HS-SPME) for 15 min at 25 °C. Once the exposure period had finished, the fiber was retracted into the needle of the holder syringe and immediately inserted into the GC injection port. The desorption time was set at 5 min, and the desorption temperature was kept at 260 °C. To avoid potential contamination and memory effects on the fiber, blanks were periodically run. Two replicates of each sample were processed for analysis.

2.4. GC-MS Analysis

The GC-MS analysis was performed using an Agilent 7890A chromatograph coupled to an Agilent 5975C inert mass spectra detector (MSD) with a triple-axis detector and an Agilent 7693 autosampler from Agilent Technologies (Palo Alto, CA, USA). Two chromatographic columns were used. The first column was a low-polarity ZB-Semivolatiles (30 m × 0.25 mm i.d., 0.25 µm film thickness) from Phenomenex (Torrance, CA, USA), operated with an oven temperature program that applies 50 °C (held 3 min) to 200 °C at 4 °C min^{-1}, and a final ramp to 290 °C at 20 °C min^{-1} (held 3 min) (total run time: 50 min); the second column was a polar J&W Scientific DB-WAX 128-7052 (50 m × 0.20 mm i.d., 0.2 µm film thickness) from Agilent Technologies, applying an oven program from 50 °C (held 3 min) to 240 °C at 4 °C min^{-1} (held 5.5 min), with a total run time of 56 min. Helium (purity 99.999%) was employed as carrier gas at a constant flow of 1.0 mL min^{-1} (first column) and 0.8 mL min^{-1} (second column), and the injection temperature was 270 °C and 240 °C, respectively. The injection volume was 1 µL for direct injection. The mass spectrometer detector (MSD) was operated in the electron impact (EI) ionization positive mode (+70 eV). The ion source temperature was 150 °C. The temperature of the transfer line was set at 290 °C and 240 °C for the first and second columns, respectively.

Full Scan (FS) acquisition mode was employed, monitoring mass/charge (m/z) fragments between 30 and 800. The tentative identification of the compounds was performed by comparison of the experimental MS spectra and those provided by the spectral library database (NIST MS Search 2.0).

3. Results and Discussion

The analysis of the diluted samples using the two columns, shows a large number of compounds present in each sample. The overall data were examined by comparing

the identified compounds using both columns, evaluating their concordance with the information contained in the SDS, and, as a final objective, seeking to identify group phytomarkers (trees and flowers). All this, considering the extended list of 82 substances in the Cosmetics EU regulation and highlighted as contact allergens by SCCS [13].

Despite the widespread use of low-polarity columns in the analysis by GC-MS of EOs/NEs, the higher-polarity column allowed a better separation of sample components.

A minimum of 28 compounds in the clove buds and Indian sandalwood EOs and a maximum of 85 compounds in the laurel leaf EO were identified. The group of flower EOs is characterized by sharing more than 50 components common to all of them, while the group of tree EOs presents a more differentiated composition according to their origin.

The allergenic content among the EOs and NEs varies notably, ranging from apparently innocuous essential oils such as cedar super (with zero allergens present, Figure 1) to others such as Ylang ylang extra, which contains 14 allergens. The number of allergens varies according to the sample and is independent of the flower or tree origin. In this way, although more allergens were found in the flower EOs, some EOs from trees contained a large number of allergenic substances, as was the case for the cinnamon leaf EO (Figure 2).

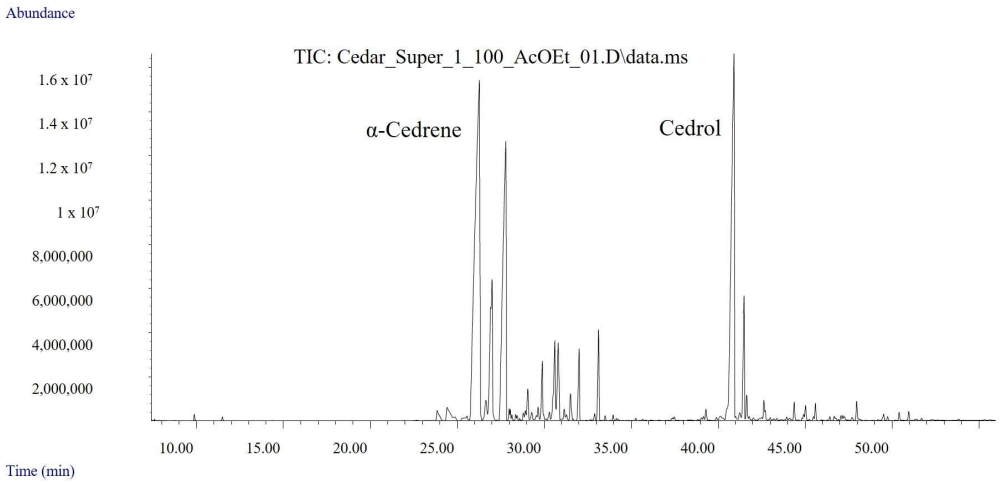

Figure 1. Example of a polar column chromatogram for the cedar super sample, indicating two major compounds.

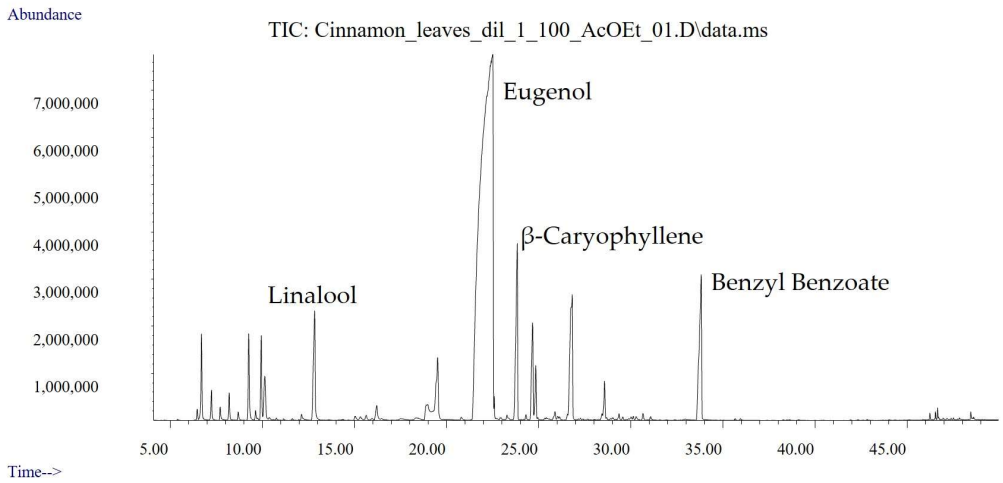

Figure 2. Example of a non-polar column chromatogram for the cinnamon leaves sample, indicating some fragrance allergens.

The use of phytomarkers for the presence of a certain EO can greatly facilitate the quality control of cosmetic products containing this EO in their ingredients. Some compounds were identified in a single sample and could therefore be used as unique markers for the

presence of a certain EO in a cosmetic product with a label indicating the content of that EO in its composition, facilitating the detection of fraud in the case of its absence. Other compounds could act as origin group markers if they are present only in EOs extracted from trees or flowers.

A higher proportion of compounds unique to the species have been identified in samples from the flower group, so they are not useful as markers for the flower group. In addition, most of these compounds are not recognized allergens and therefore do not require follow-up monitoring. Therefore, it seems more interesting to look for group phytomarkers among the compounds whose control is necessary because they are recognized allergens [13]. Figure 3 depicts the occurrence of several allergens according to their origin (flowers or trees).

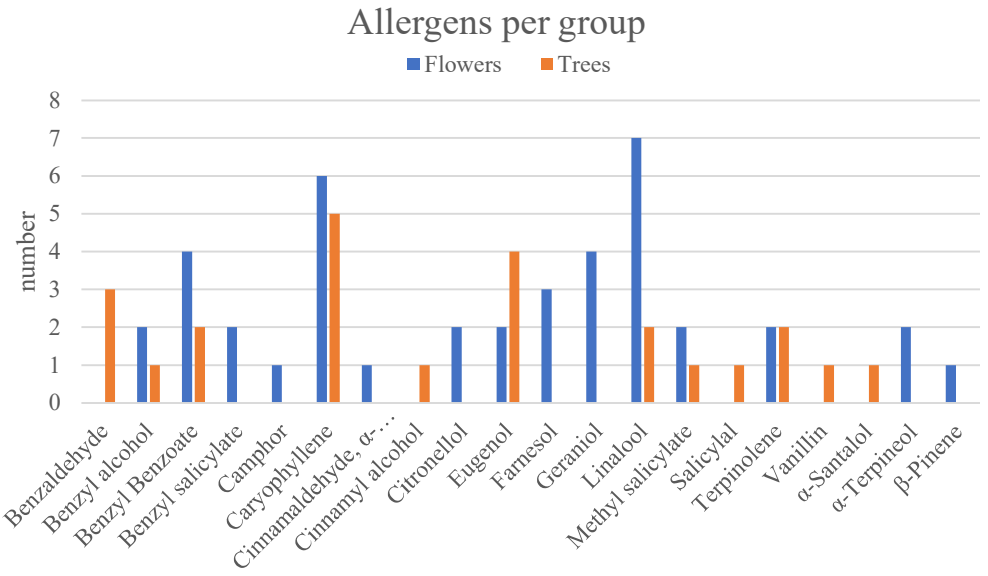

Figure 3. Distribution of allergens by the group of origin: flowers (blue) and trees (orange).

The figure shows the abundance of allergens in the analyzed EOs/NEs and also shows that most of the allergens found are ubiquitous substances that do not allow differentiation between the origin groups. The most common allergens are caryophyllene (appearing five times in the tree group and seven times in the flower group), while others are present only once (camphor and cinnamaldehyde in flowers; vanillin and α-santalol in trees). This fact, in addition to supporting the need to characterize the allergenic composition and regulate the use of EOs as natural preservatives due to their possible adverse effects, identifies those allergens with greater validity as sample or group markers.

Allergens found exclusively in the flower group were β-pinene, α-terpineol, geraniol, farnesol, citronellol, α-hexyl-cinnamaldehyde, benzyl salycilate, and camphor, while those exclusive to the tree group were α-santalol, vanillin, salycilal, cinnamyl alcohol, and benzaldehyde. Allergen markers found for specific NEs/EOs were salicylal and cinnamaldehyde in cassia oil, vanillin in Perú oil, α-santalol in Indian sandalwood, levomenthol in geranium Egypt oil, α-hexyl-cinnamaldehyde in jasmine absolute, and citral in rose absolute.

Table 3 shows the allergen composition of the samples and its agreement with the sample SDS. It is important to highlight the discordance between the SDS composition and the results found experimentally.

The fact that natural ingredients are complex mixtures of many chemical constituents, the precise nature of which is often unknown, presents problems regarding their allergic behavior [23]. As a result, their allergenic potency is also unclear. Several natural substances have caused contact allergies [24,25], and most contact fragrance allergens have been classified as moderate skin sensitizers [26]. The mechanisms of action of these substances include skin penetration and autoxidation (prehaptenes). For example, in the case of contact

allergy caused by the fragrance terpenes limonene and linalool (identified in the samples considered in this work), both are prehaptenes, which means that pure fragrance chemicals with a low sensitizing power are modified outside the skin by air oxidation, resulting in a higher allergenic potential [27]. For both linalool and limonene, specific compounds formed during their oxidation have been identified as the main causes of sensitization.

Table 3. Allergens identified in the samples. Italics indicate agreement with the safety data sheets.

Compound	Identification by GC-MS Analysis
α-Terpineol	*Lavender, lavandin super,* laurel leaves, eucalyptus, cinnamon leaves, Perú oil, Ylan ylang extra, verbena oil
β-Caryophyllene	*Clove buds, geranium Egypt, lavender, lavandin super, Ylang ylang II, Ylang ylang extra, cinnamon leaves,* cassia, laurel leaves, eucalyptus, rose absolute, verbena oil
β-Pinene	*Cinnamon leaves,* lavender, lavandin super, Ylang ylang II, Ylang ylang extra, verbena oil
Benzyl alcohol	*Jasmine absolute, rose absolute, Perú oil,* Ylang ylang II, Ylang ylang extra
Benzyl benzoate	*Jasmine absolute, cinnamon leaves, Perú oil, Ylang ylang II, Ylang ylang extra,* verbena oil
Benzyl cinnamate	*Perú oil*, Ylang ylang extra
Benzyl salicylate	*Ylang ylang II, Ylang ylang extra,* jasmine absolute
Camphor	Lavender, *lavandin super*
Cinnamaldehyde	*Cassia*
Cinnamyl alcohol	*Cassia*, cinnamon leaves, Ylang ylang extra
Citral	*Rose absolute*
Citronellol	*Rose absolute, geranium Egypt*, eucalyptus
Eugenol	*Jasmine absolute, rose absolute, clove buds, laurel leaves, cinnamon leaves, Ylang ylang extra,* cassia, Perú oil
Farnesol	*Rose absolute, Ylang ylang II, Ylang ylang extra*
Geraniol	*Rose absolute, geranium Egypt, lavender, lavandin super, Ylang ylang II, Ylang ylang extra, verbena oil*, eucalyptus
Limonene	Atlas cedar, cassia
Linalool	*Jasmine absolute, lavender, lavandin super, laurel leaves, cinnamon leaves, Ylang ylang II, Ylang ylang extra, verbena oil,* clove buds, eucalyptus, geranium Egypt, rose absolute
Terpinen-4-ol	Eucalyptus, Perú oil, rose absolute
Terpinolene	*Cinnamon leaves,* laurel leaves, eucalyptus, lavender, lavandin super, Ylang ylang extra, geranium Egypt, verbena oil

Depending on the quality of the starting plant material and the extraction method used, the composition of these volatile natural complex mixtures can be different. These factors will determine their allergenic potential and are also important to ensure their safe use in personal care products. However, other papers listed specific substances studied in the present work as compounds identified in certain essential oils, such as linalool, α-terpineol, and camphor in lavender essential oil [28] or as citronellol, geraniol, citral, and farnesol in rose essential oil [29]. Regarding individual fragrances, eugenol is the main component in clove essential oil; geraniol also occurs naturally in geranium essential oil in lower concentrations, and linalool in cinnamon oil [29]. For cinnamon species, cinnamyl alcohol is commonly found [30].

As can be seen in Figure 4, samples generally contain more allergens than declared. The most pronounced difference in allergenic compounds identified experimentally compared

to those reported in the SDS is found in the samples, namely Ylang ylang extra and verbena oil, with a difference of six and five, respectively. In other cases, the difference is smaller, as is the case with cinnamon leaves, laurel leaves, and lavender, in which one less compound is reported. In addition, there are some examples, like EOs of Atlas cedar or Indian sandalwood, whose data sheets do not mention any allergens and in whose samples L-α-terpineol and limonene, and α-santalol, respectively, were identified.

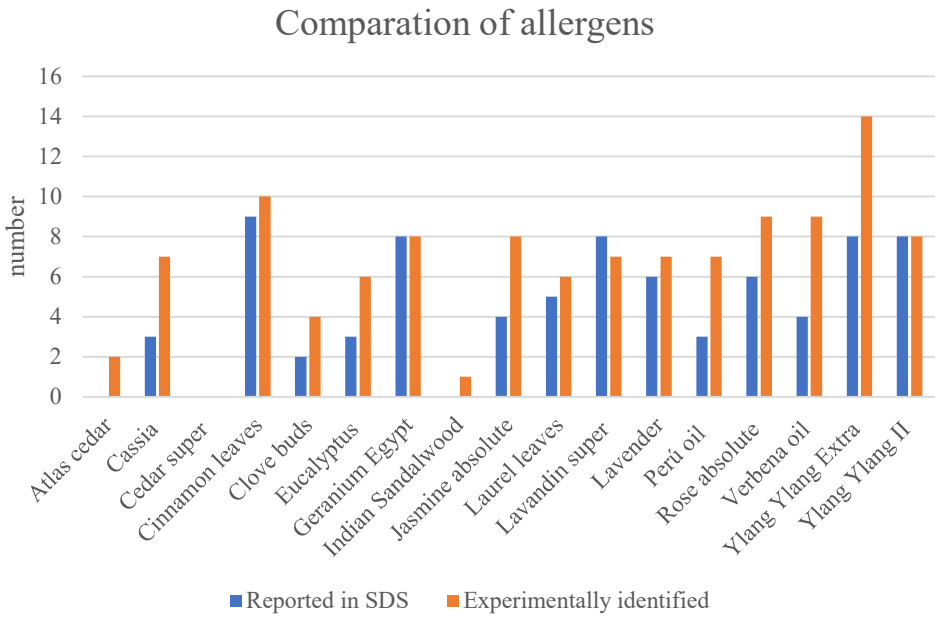

Figure 4. Number of allergens reported in the Eos/Nes corresponding SDS (blue) and identified in this work (orange).

On the contrary, four allergens (linalyl acetate, α-pinene, coumarin, and isoeugenol) are listed in the SDS, but their presence was not detected in the samples. In some cases, this may be because the CAS indicated by the SDS may actually correspond to a racemic mixture, but in others, it was not found in the sample's analysis.

Fewer compounds were identified using HS-SPME-GC-MS than by direct injection of the diluted samples, but still more compounds were identified than those listed in the SDS for each sample. In terms of the volatile allergenic substances present, cinnamon leaf EO stands out with 14 substances.

Regardless, as demonstrated throughout this study, individual samples of both essential oils and natural extracts contain numerous contact allergens. This poses an added problem, since research has previously demonstrated that exposure to a combination of two contact fragrance allergens has a synergistic effect compared to the expected response by testing with each substance alone [31]. Furthermore, a mixture of contact fragrance allergens has a higher potency with respect to the risk of sensitization compared to exposure to individual sensitizing fragrance substances [32]. Hence the importance of quality control of these innovative natural ingredients in order to ensure the safety of cosmetic and personal care products that incorporate such ingredients.

4. Conclusions

This work provides the basis for the identification of AEs and NEs in cosmetic products, applicable both to the quality control of raw materials and to the detection of possible fraud in procurement and/or labeling. The identification of the allergenic content of 17 samples of AEs and NEs revealed that all samples contained more allergenic substances than those declared in the corresponding safety data sheet. Although the list of samples to be considered could be extended, the results obtained support the creation of a list of specific plant markers for samples obtained from trees or flowers.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cosmetics11030084/s1, Table S1: Compounds declared as allergens [13]: chemical formulas and structures.

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

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

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