Investigation of Volatile Compounds in Combination with Multivariate Analysis for the Characterization of Monofloral Honeys

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Abstract: Lately there has been a growing demand for monofloral honeys with distinctive properties. Considering the limitations of pollen analysis, the volatile profile of honey has been proposed as a helpful supplementary tool for the confirmation of monoflorality; however, research remains regarding the volatile markers that may characterize the monofloral honey types. Therefore, in this study, we tried to expand the research by investigating the aroma profiles of five monofloral honey types (fir, pine, erica, thyme, cotton) and discriminate them through chemometric approach. A purge and trap–gas chromatograph–mass spectrometer system was used for the extraction, separation, and identification of volatile and semi-volatile compounds. Thyme honey had the richest quantitatively aroma profile, with 97 volatile compounds, whereas fir and cotton honeys had 65 and 60 volatile compounds, respectively. From a total of 124 compounds, the 38 were detected in all the studied honey types. Thyme honey was distinguished by the presence (or percentage participation) of benzeneacetaldehyde, benzealdehyde, and benzyl nitrile; erica honey of isophorone and furfural; cotton honey of 1-butanol, 2-methyl, 1-pentanol, and 4-methyl; and honeydew honeys of α-pinene, octane, and nonanal. The discriminant analysis confirmed that the percentage participation of volatile compounds may lead to the discrimination of the studied monofloral honey types.

Keywords: volatile compounds; volatile profile; monofloral honeys; discriminant analysis

1. Introduction

The aroma of honey is a distinguishable characteristic directly related to honey’s quality and, in turn, to consumer preferences [1]. This is also evidenced by the fact that more and more food industries are trying to find the ideal conditions for the honey collection and processing to maintain this characteristic unchanged. The aroma of honey consists of a complex mixture of volatile compounds, whose concentration depends on the source area, processing and storage conditions [2–4]. Studies report the presence of about 600 different volatile compounds in honey, in low concentrations, but including a variety of hydrocarbons, aldehydes, alcohols, ketones, acetates, benzenes and their derivatives, furan and pyran, norisopreoids, terpenes and their derivatives, sulfates, and cyclic compounds [5–9].

Some monofloral honeys have been found to possess richer aroma profiles compared with polyfloral honeys; thus, they present an increased marketing value [10]. The determination of the botanical origin of various honey species is usually based on pollen analysis [11,12], combined with physicochemical characteristics such as color, electrical conductivity, sugars, pH, mineral content [13–16], sensory evaluation [17], concentrations of flavonoids and phenolic acids [18,19], contents of nitrogenous components, such as proteins and amino acids [20], as well as the presence of specific organic [21], and inorganic acids [22]. However, with the development of gas chromatography (GC), and especially with the beginning of the use of mass spectrometry for detection, the interest of scientists...
turned to the study of volatile components of honey, in order to identify possible markers for botanical origin. The aromatic profile can be considered as a “fingerprint” of a monofloral honey types because it is directly related to the plant from which the bees collect the nectar or the honeydew [23–25].

Indeed, some honey types can be identified by a single characteristic compound, such as methyl anthranilate for citrus honey [26–29] and isophorone for arbutus [30] and Ericaceae honey [31]. Some volatile compounds were reported as potential honey indicators from certain geographic regions [1,32].

Although gas chromatography–mass spectrometry (GC–MS) is most commonly used [7,10,30], liquid chromatography (LC-MS), nuclear magnetic resonance (NMR), headspace gas chromatography–ion mobility spectrometry (HS-GCIMS), and electronic noses (sensors) have been also tested on the volatile fraction of honeys [33–35]. For the techniques which require the prior removal of sugar and water, both major components of honey [29], various isolation methods have been applied, including Likens–Nickerson simultaneous steam distillation extraction [36], dynamic headspace extraction (Purge and Trap, P&T) [1,10,30,32], ultrasound-assisted extraction [27], hydrodistillation [27], solvent extraction [2], and solid-phase microextraction [37]. Compared with the other extraction methods, in P&T, the volatiles are swept by a flow of inert gas and trapped on an adsorbent. Then, thermal desorption of this trap allows volatiles to enter the chromatographic system for separation. The main advantages of this technique include the reduction in or elimination of organic solvents, offering a green alternative to sample preparation, simultaneous multiclass compound extraction, and the reproducibility associated with a totally automated system [25].

The use of various methods of analysis in combination with the non-stability that volatile compounds present, due to different beekeeping treatments, soil and climate and storage conditions that were followed, lead to a substantial variation of aroma profiles of honey referred in the literature [38,39]. Thus, the further analysis of more monofloral honey types from different geographical origin would shed some light on the volatile markers for each type. Greece, thanks to its climate and diverse flora, offers the opportunity to produce various monofloral honey types with distinguishing sensory characteristics; however, few references exist about their volatile profiles or those which characterize them [27,32,40].

Thus, the aim of this study was to identify volatile components in monofloral honey types using GC–MS with a P&T extraction system, in order to highlight characteristic volatile chemical compounds for each kind, assisting with their authentication, quality control and, in turn, their market promotion, including the investigated honey types such as erica and cotton honeys, widely produced and consumed in Greece. Additionally, the creation of a prediction model would contribute to the possibility of categorizing among the different monofloral honey types, facilitating their authentication.

2. Materials and Methods

2.1. Sampling

The honey samples (~1 kg) were sourced by beekeepers all over Greece and harvested in 2019 and 2020 (Figure 1). The samples were fresh and unprocessed, coming directly from beekeepers in jars, under the guidance of applying the appropriate beekeeping practices in order to ensure the production of monofloral honey samples. Immediately after the harvest, the samples were put into ice boxes, sent through courier to the Laboratory of Apiculture-Sericulture, AUTH, and kept in a freezer until their analysis.

Their botanical origin was certified by pollen analysis (Von der Ohe et al., 2004) and sensory control. In total, 52 samples were selected and analyzed belonging to the fir (Abies sp.), pine (Pinus sp.), erica (Erica sp.), cotton (Gossypium sp.), and thyme (Thymus sp.) honey types.
2.2. Honey Extraction and Isolation of the Components

For the isolation of the volatile compounds, the trapping device system (Purge and Trap, OI Analytical, model 4560) was used, concentrated in a Tenax 07 column (OI Analytical). The method of Tananaki et al. [32] was applied, with some modifications. Specifically, 10 g (±0.001 g) of honey was diluted with 5 g ultrapure water (Millipore, model Simplicity 185) and 15 μL of internal standard (styrene, Merck, Belgium, >99%), and the solution was transferred in the purge vessels (25 mL). The vessels were stirred in vortex for 30–60 s and put in the Purge and Trap system for the extraction. A steel (No. 316) spiral component of 40 cm length was used to suppress the foam. The vessels were heated at 40 °C for 2 min without importing gas, to reduce the viscosity and facilitate the passage of helium gas from the mass of the solution during the extraction. Afterwards, the vessels were purged with the helium gas (40 mL min⁻¹) for 40 min, keeping the temperature of the samples at 40 °C. The volatile and semi-volatile compounds were collected on a Tenax™ TA trap (OI Analytical). The moisture was removed by heating at 100 °C for 2 min, and then the desorption was performed by raising the trap temperature at 180 °C for 6 min with simultaneous passing helium (40 mL min⁻¹) and the analytes were transferred through a thermostable transfer line (100 °C) to the gas chromatograph. The trap was cleaned each time by heating at 200 °C for 7 min.

2.3. Gas Chromatography–Mass Spectrometry (GC–MS) Conditions

An Agilent 6890 gas chromatograph, model, coupled with an Agilent 5973 mass detector, was used for separation of the extracted components, directly connected via a thermostatic transfer line to the extraction system. The gasified mixture was introduced via a split-splitless feeder, while the components were separated on an HP-5MS column (30 × 0.25 mm, df = 0.25 μm). The extraction gas as well as the carrier gas were He of high purity.
purity (99.999%), and before entering the analysis system, it was passed through a filter, in order to remove from it any small amounts of oxygen. The temperature program used for the separation was as follows: 40 °C for 5 min, increasing to 55 °C at 1 °C min⁻¹, to 120 °C at 3 °C min⁻¹, to 230 °C at 10 °C min⁻¹ and to 280 °C at 20 °C min⁻¹ (hold for 5 min). The operating conditions of the mass spectrometer were as follows: interface temperature, 280 °C; source temperature, 230 °C; quadrupole temperature, 150 °C; ionization, 70 eV. The chromatograms were processed and completed with the MSD ChemStation program, while the peaks were identified using the electronic libraries and tables of retention times and spectra that were kept in the Laboratory of Apiculture-Sericulture, AUTH [41]. The presence of volatile compounds was confirmed by using retention indices (RIs) based on the calculations using the standard mixture of alkanes (Sigma Aldrich, Darmstadt, Germany). Retention indices (RIs) are widely applied for the comparison of results with other studies, as well as to characterize stationary phases.

2.4. Statistical Analysis

For statistical processing of the results, the SPSS 19.0 statistical package software for Windows was used. The level of significance was set at $\alpha = 0.05$. Specifically, a multivariate analysis of variance (MANOVA) was applied for the compounds that were detected in 100% honey samples of each category, to determine the significant volatile compounds that could affect their classification and for those compounds, a linear discriminant analysis (LDA) was followed, in order to determine whether the studied honey types could be further discriminated. Considering the large number of predictors that arose from the LDA, the stepwise method was further applied to select the variables that fit better to the prediction model. Then, samples (test set) were analyzed on their volatile compounds and the possibility of their inclusion to a certain monofloral honey type was examined, to test the accuracy of the prediction model.

3. Results and Discussion

In total, 124 chemical compounds were found. Peaks with a low correlation of their mass spectra were not identified, but were rendered “unknown” and their respective fragments were described, whereas 7 compounds were identified as isomers. The percentage participation (%) of compounds (average and standard deviation), their retention time (R.T.), retention indices (RIs), and mass fractions (m/z) (the underlined fractions are the main for each compound) are given in Table 1, whereas the representative chromatogram for each kind is presented in Figure 2.

The percentage participation of different categories of organic compounds is shown in Figure 3, where the presence of hydrocarbons, aldehydes, and alcohols is highlighted. Indeed, the group of hydrocarbons stood out (40.3%), followed by ketones, alcohols, and aldehydes with 15.3%, 14.5%, and 12.9%, respectively. To a lesser extent, esters (2.4%) and sulfur compounds (1.7%) were found, whereas a small percentage of organic compounds was not identified, named as “unknown” (5.6%). Another group, which accounted for 7.3%, included volatile compounds such as heterocyclics, which were rarely detectable in honey samples, without justifying their grouping into a separate class of compounds.
Table 1. Percentage participation (%) of volatile compounds found in Greek monofloral honey types (retention time, R.T.; retention indices, RIs; m/z, mass fractions, average and standard deviation).

| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.I.exp * | R.I.lit * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|-----------|-----------------------------------|-----------|-----------|------------------------------------------------------------|
| C1  | 3.25      | Methyl butanal (isomer) (58, 71, 86) | 643       | 632 [42]  | 5.32 ± 1.48 ab** 6.39 ± 3.78 a 2.90 ± 0.86 bc 2.27 ± 1.08 c 4.38 ± 0.78 abc |
| C2  | 3.56      | Cyclopentane, 1,3-dimethyl-(isomer) (58, 70, 83, 98) | 680       | 682 [43]  | 1.62 ± 1.43 b 1.52 ± 0.56 b 0.94 ± 0.86 bc 0.66 ± 0.49 3.21 ± 1.20 a |
| C3  | 3.73      | Heptane (57, 71, 100)               | 700       | 700 [44]  | 2.83 ± 0.41 a 2.71 ± 0.88 a 2.70 ± 0.69 a 1.69 ± 0.89 b 2.89 ± 0.52 a |
| C4  | 3.91      | Furan, 2,5-dimethyl-(57, 81, 96)   | 706       | 696 [45]  | 0.95 ± 0.55 a 1.00 ± 0.61 a 0.50 ± 0.59 ab 0.02 ± 0.0 b nd *** |
| C5  | 4.25      | Cyclohexane, methyl (55, 89, 98)   | 718       | 720 [46]  | 3.41 ± 1.19 a 4.07 ± 2.08 a 2.50 ± 1.18 a 2.95 ± 3.76 a 3.58 ± 0.80 a |
| C6  | 4.44      | 3-Buten-1-ol, 2-methyl (56, 68, 83, 86, 98) | 724       | 716 [47]  | 1.92 ± 1.38 a 0.63 ± 0.56 a 0.35 ± 0.37 a 1.14 ± 3.37 a 1.87 ± 1.05 a |
| C7  | 4.55      | 1-Pentanol (55, 70)                | 728       | 735 [48]  | 1.24 ± 1.69 b 2.60 ± 1.99 b 1.15 ± 1.02 b 5.15 ± 3.67 a 0.76 ± 0.70 b |
| C8  | 4.6       | 1-Butanol, 2-methyl (57, 70, 85, 100) | 730       | 726 [47]  | 1.52 ± 2.37 nd nd nd 1.04 ± 2.85 5.87 ± 6.08 |
| C9  | 4.62      | unknown (55, 64, 68, 82)           | 731       | nd        | nd nd nd 4.49 ± 5.87 nd |
| C10 | 4.64      | 1-Butanol, 3-methyl (56, 68, 73, 86, 98) | 731       | 718 [49]  | nd nd nd 0.89 ± 2.51 nd |
| C11 | 4.68      | Methyl isobutyl ketone (58, 70, 85, 100) | 733       | 729 [46]  | 3.23 ± 0.83 ab 4.86 ± 2.06 a 3.22 ± 1.67 ab 1.85 ± 0.85 b 2.28 ± 3.31 b |
| C12 | 4.77      | Disulfide, dimethyl (64, 79, 94)   | 736       | 723 [50]  | 2.84 ± 1.76 a 2.22 ± 1.51 ab 1.32 ± 1.16 bc 1.30 ± 1.05 bc 0.80 ± 0.28 c |
| C13 | 4.8       | 2-Butenal, 2-methyl (55, 79, 84, 94, 100) | 737       | 730 [51]  | nd 0.29 ± 0.63 0.24 ± 0.71 0.58 ± 0.80 3.12 ± 3.78 |
| C14 | 4.9       | 3-Pentanone, 2-methyl (57, 71, 100) | 740       | 722 [52]  | 0.35 ± 0.33 0.19 ± 0.46 0.26 ± 0.39 nd nd |
Table 1. Cont.

| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.L.exp * | R.I.lit * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|-----------|-----------------------------------|-----------|-----------|------------------------------------------------------------|
|     |           | Fir (n = 6) | Pine (n = 19) | Erica (n = 9) | Thyme (n = 13) | Cotton (n = 5) |
| C15 | 5.1       | unknown (58, 73, 86, 94, 101, 115) | 747        | nd        | 0.52 ± 0.84 | 0.13 ± 0.29 | 0.16 ± 0.32 | 2.66 ± 1.79 |
| C16 | 5.41      | Toluene (65, 91) | 758        | 755 [46] | 16.31 ± 2.49 ab | 14.25 ± 5.69 b | 12.69 ± 3.34 ab | 10.26 ± 4.17 b | 14.64 ± 1.97 ab |
| C17 | 5.75      | 2-Buten-1-ol, methyl-(isomer) (55, 71, 86, 97, 112) | 769        | 766 [53] | nd        | 0.55 ± 1.78 ab | 0.83 ± 1.32 ab | 0.04 ± 0.09 b | 1.41 ± 0.50 a |
| C18 | 5.82      | unknown (55, 71, 77, 86, 97, 112) | 772        | nd        | 0.15 ± 0.23 | 0.17 ± 0.45 | 0.15 ± 0.22 | 0.06 ± 0.08 | nd |
| C19 | 6.08      | 2-Buten-1-ol, methyl-(55, 84) | 781        | 769 [54] | 0.26 ± 0.49 b | 0.13 ± 0.18 b | 0.08 ± 0.12 b | 0.12 ± 0.19 b | 0.95 ± 0.88 a |
| C20 | 6.25      | 1-Octene (55, 70, 83, 97, 112) | 787        | 782 [43] | 2.53 ± 0.92 a | 1.45 ± 0.76 b | 0.72 ± 0.43 c | 0.32 ± 0.19 c | 0.66 ± 0.2 ac |
| C21 | 6.61      | Octane (57, 71, 85, 114) | 799        | 800 [44] | 20.91 ± 4.49 a | 21.64 ± 11.28 a | 7.16 ± 4.49 b | 5.35 ± 1.85 b | 10.78 ± 3.62 b |
| C22 | 8.22      | Furfural (67, 96) | 826        | 831 [55] | 8.85 ± 2.75 b | 3.66 ± 3.23 b | 21.72 ± 13.95 a | 5.62 ± 3.73 b | 6.60 ± 3.31 b |
| C23 | 8.6       | 1-Pentanol, 4-methyl-(56, 69, 84, 96) | 832        | 851 [56] | nd        | 0.04 ± 0.18 b | nd        | nd        | nd        | 2.18 ± 1.40 a |
| C24 | 9.6       | 2-Cyclopenten-1-one, 3,5,5-trimethyl-(60, 96, 109, 124) | 848        | nd        | 0.05 ± 0.06 | 0.51 ± 1.51 | nd        | nd        | nd        | 1.80 ± 2.22 |
| C25 | 9.66      | 3-Hexen-1-ol (55, 67, 82, 91) | 849        | 838 [57] | nd        | nd        | nd        | 0.02 ± 0.03 | 1.80 ± 2.22 |
| C26 | 9.77      | Ethylbenzene (60, 67, 82, 91, 106) | 851        | 850 [46] | 0.10 ± 0.08 a | 0.04 ± 0.09 a | 0.07 ± 0.09 a | 0.03 ± 0.05 a | 0.08 ± 0.11 a |
| C27 | 9.91      | 3-Penten-1-ol, methyl-(isomer) (56, 69, 84, 96, 100) | 854        | 845 [55] | nd        | nd        | nd        | nd        | 0.82 ± 0.57 |
| C28 | 10.27     | p-Xylene (91, 106) | 859        | 855 [42] | 0.48 ± 0.21 ab | 0.57 ± 0.31 a | 0.29 ± 0.15 bc | 0.22 ± 0.13 c | 0.48 ± 0.06 ab |
| C29 | 10.64     | Hexanol (56, 69, 84, 95) | 865        | 852 [49] | nd        | 0.04 ± 0.11 | 0.01 ± 0.02 | 0.02 ± 0.04 | 0.04 ± 0.08 |
Table 1. Cont.

| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.Lexp * | R.Lit * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|------------|------------------------------------|----------|---------|-------------------------------------------------------------|
|     |            |                                    |          |         | Fir (n = 6) | Pine (n = 19) | Erica (n = 9) | Thyme (n = 13) | Cotton (n = 5) |
| C30 | 11.4       | Bicyclo [2.2.1]hept-2-ene, 2,3-dimethyl- | 878      | 876 [58] | 1.25 ± 1.80 | nd           | nd           | nd           | nd           |
|     |            | [Santene] (79, 94, 122)             |          |         |               |              |              |              |              |
| C31 | 11.97      | 1-Nonene (56, 69, 84, 91, 97, 109, 126) | 887      | 895 [59] | 0.07 ± 0.11 | 0.01 ± 0.02 | 0.09 ± 0.10 | nd           | 0.03 ± 0.07 |
| C32 | 12.07      | 2-Heptanone (58, 71, 99, 114)       | 889      | 871 [60] | 0.08 ± 0.03^a| 0.12 ± 0.20^a| nd           | 0.03 ± 0.04^a| nd           |
|     |            | Furan, 2,5-diethyltetrahydro-       | 893      | 884 [61] | nd           | 1.04 ± 2.15^b| 0.30 ± 0.38^b| 6.09 ± 2.22^a| nd           |
|     |            | (55, 70, 88, 99, 104)               |          |         |               |              |              |              |              |
| C34 | 12.62      | Nonane (57, 71, 85, 128)            | 898      | 900 [44] | 1.95 ± 0.42^a| 1.47 ± 0.43^b| 0.99 ± 0.23^c| 1.25 ± 0.53^bc| 2.49 ± 0.64^c |
| C35 | 12.84      | Heptanal (55, 70, 81, 96)           | 901      | 882 [60] | 0.13 ± 0.16  | 0.03 ± 0.08  | 0.27 ± 0.18  | 0.02 ± 0.06  | nd           |
| C36 | 13.58      | Ethanone, 1-(2-furanyl)-            | 909      | 887 [48] | 0.13 ± 0.20^b| 0.29 ± 0.24^b| 2.87 ± 0.80^a| 0.18 ± 0.15^b| 0.35 ± 0.25^b |
|     |            | (51, 67, 95, 110)                   |          |         |               |              |              |              |              |
| C37 | 14.67      | Cyclopentanone, 2,4,4-trimethyl-    | 920      | nd       | nd           | nd           | nd           | nd           | nd           |
|     |            | (56, 69, 83, 111, 126)              |          |         |               |              |              |              |              |
| C38 | 15.16      | alpha-Pinene (53, 77, 93, 105, 121, 136) | 925      | 931 [62] | 1.43 ± 2.02^ab| 3.78 ± 3.71^a| 0.43 ± 0.18^b| 0.14 ± 0.22^b| 0.18 ± 0.26^b |
| C39 | 16.35      | Camphene (58, 67, 79, 93, 107, 121, 136) | 938      | 943 [62] | nd           | 0.04 ± 0.12  | nd           | nd           | nd           |
| C40 | 17.66      | Benzaldehyde (51, 77, 106)          | 952      | 937 [54] | 0.91 ± 1.00^c| 4.09 ± 3.99^bc| 1.96 ± 1.38^bc| 11.01 ± 4.86^a| 5.08 ± 2.51^b |
| C41 | 18.16      | Dimethyl trisulfide (56, 64, 79, 93, 126) | 957      | 943 [50] | 0.07 ± 0.18  | nd           | nd           | 0.03 ± 0.09  | nd           |
| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.L.exp * | R.I.exp * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|-----------|-----------------------------------|-----------|-----------|------------------------------------------------------------|
|     |           |                                   |           |           | Fir (n = 6) | Pine (n = 19) | Erica (n = 9) | Thyme (n = 13) | Cotton (n = 5) |
| C42 | 18.46     | 2-Furancarboxaldehyde, 5-methyl-(53, 81, 110) | 960       | 926 [63] | nd | nd | 0.09 ± 0.12 | 0.04 ± 0.09 | nd |
| C43 | 18.54     | Benzene, 1-ethyl-4-methyl-(105, 120) | 961       | 954 [46] | 0.14 ± 0.19 | 0.02 ± 0.06 | 0.04 ± 0.12 | 0.01 ± 0.03 | 0.06 ± 0.13 |
| C44 | 19.06     | .beta.-Pinene (53, 69, 77, 93, 106, 121) | 967       | 970 [62] | nd | 0.30 ± 0.40 | nd | nd | nd |
| C45 | 19.56     | Benzene, 1,2,3-trimethyl-(91, 105, 120) | 972       | 1005 [54] | 0.03 ± 0.05 | 0.04 ± 0.08 | 0.02 ± 0.05 | nd | 0.09 ± 0.05 |
| C46 | 20.16     | Benzonitrile (55, 70, 76, 103) | 978       | 958 [55] | nd | nd | nd | 0.31 ± 0.80 | nd |
| C47 | 20.23     | 1-Octen-3-ol (57, 67, 72, 85, 100) | 979       | 963 [57] | nd | 0.04 ± 0.10 a | 0.03 ± 0.10 b | 0.08 ± 0.21 b | 0.49 ± 0.47 a |
| C48 | 20.91     | Benzene, 1,3,5-trimethyl-(91, 105, 120) | 986       | 1020 [55] | 1.55 ± 1.92 a | 0.79 ± 0.36 ab | 1.24 ± 0.23 b | 0.60 ± 0.28 b | 0.90 ± 0.12 ab |
| C49 | 21.12     | unknown (55, 67, 82, 96, 110, 137) | 988       | nd | 0.39 ± 0.50 | nd | nd | nd | nd |
| C50 | 21.18     | Furan, 2-pentyl-(53, 69, 81, 93, 105, 138) | 989       | 977 [54] | nd | 0.09 ± 0.32 | 0.06 ± 0.09 | 1.17 ± 0.64 | 0.15 ± 0.23 |
| C51 | 22.05     | Decane (57, 71, 91, 105, 117, 142) | 998       | 1000 [44] | 0.11 ± 0.11 | 0.06 ± 0.14 | nd | 0.19 ± 0.13 | 0.23 ± 0.26 |
| C52 | 22.1      | 2,6-Dimethyl-1,3,5,7-octatetraene, E,E-(57, 77, 91, 105, 119, 134) | 999       | 966 [55] | 0.07 ± 0.18 | 0.10 ± 0.16 | 0.05 ± 0.11 | 0.03 ± 0.10 | 0.09 ± 0.19 |
| C53 | 22.36     | 0°CTanal (57, 69, 84, 100, 110) | 1002      | 1005 [55] | 1.36 ± 1.61 a | 0.61 ± 0.67 b | 0.42 ± 0.22 b | 0.46 ± 0.18 b | 0.47 ± 0.28 b |
| C54 | 22.4      | unknown (55, 69, 84, 95, 109, 137, 152) | 1003      | nd | 0.19 ± 0.83 | nd | nd | nd | 0.17 ± 0.37 |
Table 1. Cont.

| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.L.exp * | R.L.it * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|-----------|-----------------------------------|---------|---------|------------------------------------------------------------|
|     |           |                                   |         |         | Fir \( n = 6 \) | Pine \( n = 19 \) | Erica \( n = 9 \) | Thyme \( n = 13 \) | Cotton \( n = 5 \) |
| C55 | 22.56     | unknown (55, 67, 82, 96, 110, 137) | 1005    |         | 0.51 ± 0.69 | nd | 0.01 ± 0.02 | 0.07 ± 0.16 | nd |
| C56 | 22.58     | 2,4-Hexadiene, 2,5-dimethyl-(55, 70, 82, 95, 110) | 1006    |         | nd | nd | 0.20 ± 0.27 | 0.01 ± 0.03 | nd |
| C57 | 23.05     | 2-Cyclohexen-1-one (68, 81, 124) | 1011    |         | nd | nd | 0.38 ± 0.23 | nd | nd |
| C58 | 23.14     | 3-Carene (77, 93, 105, 121, 136) | 1012    | 1015 [62] | nd | 0.85 ± 1.42 | 0.11 ± 0.32 | 0.20 ± 0.63 | 0.30 ± 0.64 |
| C59 | 23.47     | Benzene, 1,2,4-trimethyl-(68, 77, 91, 105, 120) | 1017    | 1020 [55] | 0.34 ± 0.13 b | 0.11 ± 0.13 b | 0.96 ± 0.61 a | 0.22 ± 0.10 b | 0.32 ± 0.10 b |
| C61 | 23.86     | Benzene, 1-methyl-4-(1-methyllethyl)-[p-Cymene] (77, 91, 119, 134) | 1022    | 1011 [62] | 0.28 ± 0.17 b | 0.62 ± 0.56 b | 0.24 ± 0.15 b | 1.46 ± 0.37 a | 0.51 ± 0.53 b |
| C62 | 24.15     | D-Limonene (53, 68, 93, 107, 121, 136) | 1026    | 1020 [62] | 0.29 ± 0.30 a | 3.87 ± 7.34 a | 0.04 ± 0.08 a | 0.28 ± 0.22 a | 2.64 ± 4.01 a |
| C63 | 25.3      | 3-Cyclohexen-1-one, 3,5,5-trimethyl-[b-isophorone] (55, 67, 81, 96, 123, 138) | 1041    | 1044 [64] | nd | nd | 0.08 ± 0.13 | nd | nd |
| C64 | 25.58     | Benzenecetaldehyde (65, 91, 120) | 1044    | 1048 [65] | 0.14 ± 0.20 b | 0.34 ± 0.55 b | 1.53 ± 1.34 b | 12.18 ± 9.38 a | 1.09 ± 0.78 b |
| C65 | 26.02     | Benzene, 1-methyl-3-propyl-(65, 91, 105, 120, 134) | 1050    | 1042 [46] | nd | 0.05 ± 0.09 | 0.08 ± 0.12 | nd | 0.01 ± 0.02 |
| C66 | 26.5      | 2-Cyclohexen-1-one, 3,5,5-trimethyl-[a-isophorone] (54, 82, 91, 138) | 1056    | 1086 [48] | nd | nd | 0.13 ± 0.20 | 0.02 ± 0.07 | nd |
Table 1. Cont.

| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.L.exp * | R.L.it * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|------------|------------------------------------|-----------|----------|------------------------------------------------------------|
|     |            |                                    |           |          | Fir (n = 6) | Pine (n = 19) | Erica (n = 9) | Thyme (n = 13) | Cotton (n = 5) |
| C67 | 26.57      | Benzene, 1-ethyl-2,3-dimethyl-(91, 119, 134) | 1057      | 1085 [66] | 0.12 ± 0.14 ab | 0.06 ± 0.15 b | 0.25 ± 0.16 a | 0.11 ± 0.12 ab | 0.21 ± 0.18 ab |
| C68 | 26.61      | 1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-[γ-terpinene] (77, 93, 105, 119, 136) | 1058      | 1047 [62] | nd          | 0.10 ± 0.18  | nd          | 0.11 ± 0.22  | nd          |
| C69 | 26.96      | Octane, 1-chloro (55, 69, 83, 94, 105) | 1063      | 1051 [67] | 0.30 ± 0.27 a | 0.22 ± 0.25 ab | 0.12 ± 0.14 ab | 0.03 ± 0.07 b | 0.23 ± 0.08 ab |
| C70 | 27.06      | Acetophenone (51, 77, 105, 120) | 1064      | 1052 [49] | nd          | nd          | nd          | 0.03 ± 0.07  | nd          |
| C71 | 27.52      | Cycloheptanemethanol (55, 67, 77, 82, 97, 108) | 1070      | 1143 [55] | nd          | 0.08 ± 0.13  | nd          | 0.02 ± 0.05  | 0.02 ± 0.04 |
| C72 | 27.53      | Beta.Farnesene (55, 69, 79, 93, 119, 137, 152) | 1071      |          | 0.07 ± 0.18 | nd          | nd          | 0.05 ± 0.09  | nd          |
| C73 | 27.7       | 2-Furanmethanol,5-ethenylethyltetrahydro-α,α,α,α-terpinolene (55, 67, 79, 93, 105, 121, 136) | 1072      | 1064 [68] | 0.05 ± 0.09 b | 0.13 ± 0.27 b | 0.06 ± 0.13 b | 0.30 ± 0.56 b | 1.54 ± 1.16 a |
| C74 | 28.4       | Benzene, 2-ethyl-1,4-dimethyl-(91, 105, 119, 134, 207) | 1081      | 1068 [46] | 0.07 ± 0.07 | 0.02 ± 0.07  | 0.09 ± 0.09  | 0.05 ± 0.05  | 0.03 ± 0.05 |
| C75 | 28.68      | Benzene, 1-methyl-4-(1-methylethynyl)-(91, 117, 132) | 1083      | 1081 [68] | 0.17 ± 0.20 b | 0.53 ± 1.36 b | 0.13 ± 0.10 b | 0.93 ± 0.31 ab | 1.90 ± 2.86 a |
| C76 | 28.7       | Cyclohexene, 1-methyl-4-(1-methylethyldiene)-α-Terpinolene (55, 67, 79, 93, 105, 121, 136) | 1085      | 1078 [62] | nd          | 0.04 ± 0.13  | 0.01 ± 0.01  | nd          | nd          |
| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.L.exp * | R.L.it * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|-----------|-----------------------------------|-----------|---------|-------------------------------------------------------------|
|     |           | Fir (n = 6) | Pine (n = 19) | Erica (n = 9) | Thyme (n = 13) | Cotton (n = 5) |
| C77 | 29.28     | 2-Nonanone (53, 58, 67, 71, 95, 142) | 1093      | 1074 [60] | 0.18 ± 0.06 a | 0.11 ± 0.17 ab | nd                  | 0.03 ± 0.09 b | 0.02 ± 0.03 b |
| C78 | 29.73     | 1,6-Octadien-3-ol, 3,7-dimethyl-(55, 67, 71, 80, 93, 121) | 1095      | 1081 [62] | nd | nd | nd | 0.10 ± 0.27 | nd |
| C79 | 29.75     | Undecane (57, 71, 85, 93, 119) | 1099      | 1100 [44] | 0.81 ± 0.42 ab | 0.031 ± 0.22 cd | 0.16 ± 0.06 d | 0.51 ± 0.37 bc | 0.99 ± 0.62 a |
| C80 | 30.01     | Nonanal (57, 70, 82, 98, 114) | 1103      | 1104 [55] | 8.49 ± 5.83 a | 7.97 ± 6.23 a | 3.03 ± 1.26 b | 2.73 ± 1.15 b | 3.43 ± 2.24 b |
| C81 | 30.82     | 2-Cyclohexen-1-one, 3,5,5-trimethyl-[isophorone] (54, 82, 138) | 1117      | 1097 [55] | nd | nd | 10.62 ± 13.79 | 0.03 ± 0.08 | nd |
| C82 | 30.85     | Phenylethyl Alcohol (65, 91, 122) | 1119      | 1136 [55] | nd | nd | nd | 0.36 ± 0.66 | nd |
| C83 | 31.97     | 1,4,8-p-Menthatriene (77, 91, 119, 134) | 1136      | nd | nd | nd | 0.03 ± 0.07 | 0.01 ± 0.04 | nd | 0.05 ± 0.11 | 0.20 ± 0.22 |
| C84 | 32.2      | Benzyl nitrile (51, 67, 90, 109, 117, 137) | 1140      | 1138 [55] | nd | 0.03 ± 0.15 | nd | 2.20 ± 2.98 | nd |
| C85 | 32.26     | 2,6,6-Trimethyl-2-cyclohexene-1,4-dione (4-Ketoisophorone) (68, 96, 152) | 1141      | 1115 [54] | nd | nd | 0.85 ± 0.64 | nd | nd |
| C86 | 32.28     | Lilac aldehyde (isomer I) (55, 67, 81, 93, 111, 121, 153) | 1144      | 1153 [69] | 0.15 ± 0.37 | nd | nd | 0.06 ± 0.20 | nd |
| C87 | 32.56     | Ethaneone, 1-(1,4-dimethyl-3-cyclohexene-1-yl)-(67, 77, 90, 109, 117, 137, 152) | 1146      | 1145 [70] | nd | nd | nd | 0.05 ± 0.13 | 0.08 ± 0.12 |
| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.L.exp * | R.L.lit * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|-----------|-------------------------------------|-----------|-----------|---------------------------------------------------------------|
|     |           |                                     |           |           | Fir \( (n = 6) \)    Pine \( (n = 19) \)    Erica \( (n = 9) \)    Thyme \( (n = 13) \)    Cotton \( (n = 5) \) |
| C88 | 32.59     | 2-Hydroxy-3,5,5-trimethyl-cyclohex-2-enone (2-Hydroxyisophorone) \( (55, 70, 83, 96, 112, 139, 154) \) | 1147      | nd        | nd                  | 0.19 ± 0.37  | nd                  | nd                  |
| C89 | 32.6      | Tetramethylbenzene (isomer) \( (91, 119, 134) \) | 1148      | 1145 [46] | nd                  | nd                  | nd                  | nd                  |
| C90 | 32.77     | Lilac aldehyde (isomer II) \( (55, 67, 81, 93, 111, 125, 153) \) | 1150      | 1148 [71] | 0.16 ± 0.40         | 0.01 ± 0.06  | nd                  | 0.11 ± 0.27  |
| C91 | 33        | 2H-Pyran,3,6-dihydro-4-methyl-2-(2-methyl-1-propenyl)-(55, 68, 83, 91, 109, 119, 134) | 1154      | 1137 [72] | 0.02 ± 0.06         | nd                  | nd                  | 0.07 ± 0.14  | 0.02 ± 0.04 |
| C92 | 33.48     | Borneol \( (55, 69, 79, 95, 110, 139) \) | 1162      | 1148 [62] | nd                  | 0.01 ± 0.03  | 0.03 ± 0.06  | nd                  |
| C93 | 33.81     | unknown \( (55, 73, 91, 105, 121, 131, 149, 207) \) | 1167      | nd        | nd                  | 0.13 ± 0.20  | nd                  | nd                  |
| C94 | 34.18     | Benzoic acid, ethyl ester \( (51, 77, 105, 122, 150) \) | 1173      | 1160 [55] | nd                  | nd                  | 0.14 ± 0.43  | nd                  |
| C95 | 34.2      | 3-Cyclohexen-1-ol,4-methyl-1-(1-methylethyl)-(71, 93, 111, 119, 128, 136) | 1174      | 1161 [62] | nd                  | 0.01 ± 0.04  | nd                  | 0.06 ± 0.09  |
| C96 | 34.22     | Naphthalene \( (63, 102, 128) \) | 1175      | 1170 [73] | nd                  | 0.01 ± 0.04  | 0.43 ± 0.79  | 0.03 ± 0.06  |
| C97 | 34.62     | 3,6-Dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran-(55, 69, 91, 109, 137, 152) | 1179      | 1178 [74] | 0.10 ± 0.18         | nd                  | nd                  | 0.01 ± 0.04  |
| C98 | 34.65     | 1-Nonanol \( (56, 70, 83, 98, 128) \) | 1181      | 1169 [55] | nd                  | 0.02 ± 0.09  | nd                  | nd                  |
| C99 | 34.97     | 4-Carene \( (77, 93, 105, 121, 136) \) | 1187      | nd        | nd                  | nd                  | nd                  | 0.09 ± 0.16  | nd                  |
| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.L.exp * | R.L.it * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|-----------|------------------------------------|------------|----------|----------------------------------------------------------|
|     |           |                                    |            |          | Fir (n = 6) | Pine (n = 19) | Erica (n = 9) | Thyme (n = 13) | Cotton (n = 5) |
| C100 | 35.2      | Methyl salicylate (92, 120, 152)   | 1190       | 1176 [49]| nd         | nd            | 0.38 ± 0.49 a | 0.06 ± 0.13 b | nd               |
| C101 | 35.46     | 1,3-Cyclohexadiene-1-carboxaldehyde, 2,6,6-trimethyl-(77, 91, 107, 121, 150) (Safranal) | 1195       | 1186 [55]| nd         | 0.02 ± 0.07 b | 1.63 ± 0.72 a | 0.19 ± 0.31 b | nd               |
| C102 | 35.61     | Octanoic acid, ethyl ester (57, 70, 73, 88, 107, 121, 127, 150) | 1197       | 1183 [55]| nd         | nd            | 0.20 ± 0.54 | nd         | nd               |
| C103 | 35.93     | Naphthalene,1,2,3,4-tetrahydro-1,6-trimethyl-(77, 91, 117, 131, 144, 159, 174) | 1203       | 1235 [75]| nd         | nd            | nd           | 0.29 ± 0.70 | nd               |
| C104 | 35.95     | Decanal (57, 70, 82, 95, 112, 128) | 1204       | 1204 [55]| 2.17 ± 1.65 abc | 0.92 ± 0.6 c | 3.41 ± 2.25 a | 1.79 ± 0.99 bc | 2.95 ± 0.74 ab |
| C105 | 36.27     | 3-Cyclohexene-1-acetaldehyde, alpha, 4-dimethyl-[1-p-menthen-9-al] (55, 67, 79, 94) | 1210       | 1232 [76]| 0.63 ± 1.55 | nd            | nd           | 0.02 ± 0.08 | nd               |
| C106 | 36.55     | Furan, 3-phenyl-(115, 144)         | 1216       | 1216 [55]| nd         | 0.06 ± 0.26 b | 0.01 ± 0.02 b | 1.34 ± 0.75 a | nd               |
| C107 | 37.3      | Bicyclo [3.3.0]octan-2-one, 4,7,7-trimethyl-(54, 82, 91, 110, 131, 146, 151, 166) | 1231       | nd         | nd         | 0.18 ± 0.28 | 0.02 ± 0.06 | nd               |
| C108 | 37.56     | Benzaldehyde, 4-(1-methylethyl)-(Cuminal) (51, 77, 91, 105, 119, 133, 148) | 1236       | 1230 [55]| nd         | nd            | nd           | 0.11 ± 0.13 | nd               |
Table 1. Cont.

|   | R.T. (min) | Volatile Compound (Mass Fractions) | R.I.exp * | R.I.lit * | Percentage Participation (%) (Average ± Standard Deviation) |
|---|------------|------------------------------------|-----------|-----------|-------------------------------------------------------------|
|   |            |                                    |           |           | Fir ($n = 6$) | Pine ($n = 19$) | Erica ($n = 9$) | Thyme ($n = 13$) | Cotton ($n = 5$) |
| C109 | 38.1       | Naphthalene,1,2,3,4-tetrahydro-2,5,8-trimethyl- (77, 91, 105, 115, 131, 144, 159, 174) | 1247      | 1289 [55] | nd | 0.01 ± 0.03 | nd | 0.11 ± 0.24 | 0.04 ± 0.06 |
| C110 | 38.11      | Benzofuran,2,3-dihydro-2,2,5,6-tetramethyl (91, 105, 133, 144, 161, 176) | 1249      | nd | nd | 0.04 ± 0.09 | nd | nd | nd |
| C111 | 38.27      | 1-Naphthalenol, 2-methyl-(91, 115, 129, 158) | 1251      | nd | nd | nd | 0.04 ± 0.08 | nd |
| C112 | 38.43      | 2H-1-Benzopyran,3,5,6,8a-tetrahydro-2,5,5,8a-tetramethyl-, cis[Edulan II] (77, 91, 133, 177) | 1254      | 1247 [77] | nd | 0.01 ± 0.03 | 0.02 ± 0.05 | 0.02 ± 0.07 | nd |
| C113 | 39.38      | 1-Butanone, 3-methyl-1-phenyl-(51, 77, 91, 105, 115, 146, 162) | 1273      | 1273 [78] | nd | nd | nd | 0.15 ± 0.25 | nd |
| C114 | 40         | Naphthalene, 2-methyl-(115, 142) | 1286      | 1277 [79] | nd | nd | 0.35 ± 0.92 | nd | nd |
| C115 | 40.67      | Tridecane (57, 71, 85, 99, 112) | 1299      | 1300 [44] | 0.18 ± 0.04 | 0.05 ± 0.06 | 0.01 ± 0.03 | 0.05 ± 0.06 | 0.16 ± 0.05 |
| C116 | 41.24      | 2H-1-Benzopyran,3,5,6,8a-tetrahydro-2,5,5,8a-tetramethyl-, trans[Edulan I] (77, 91, 133, 177, 192) | 1315      | 1315 [80] | nd | 0.01 ± 0.05 | 0.21 ± 0.20 | 0.10 ± 0.27 | nd |
| C117 | 42.78      | Naphthalene,1,2-dihydro-1,1,6-trimethyl-(115, 128, 142, 157, 172) | 1357      | 1136 [81] | nd | 0.34 ± 0.85 a | 2.86 ± 1.90 a | 3.48 ± 6.43 a | 0.33 ± 0.15 a |
| C118 | 43.14      | 4,7-Dihydroxy-5-methylcumarin (122, 149, 164, 192) | 1367      | nd | nd | 0.55 ± 0.63 | 0.01 ± 0.04 | nd |
Table 1. Cont.

| a/a | R.T. (min) | Volatile Compound (Mass Fractions) | R.Lexp * | R.I.lit * | Percentage Participation (%) (Average ± Standard Deviation) |
|-----|-----------|----------------------------------|----------|-----------|-------------------------------------------------------------|
|     |           |                                  |          |           | Fir (n = 6) | Pine (n = 19) | Erica (n = 9) | Thyme (n = 13) | Cotton (n = 5) |
| C119 | 43.92     | 2-Buten-1-one, 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-(E) [Damascenone, trans-] (69, 77, 91, 105, 121, 147, 175, 190, 207) | 1388     | 1362 [72] | nd          | 0.01 ± 0.03 b | 0.45 ± 0.22 a | 0.24 ± 0.48 ab | 0.05 ± 0.08 b |
| C120 | 44.78     | Caryophyllene (55, 69, 79, 93, 105, 119, 133, 147, 161, 175) | 1420     | 1424 [62] | 0.08 ± 0.08 | 0.06 ± 0.09 | nd          | 0.10 ± 0.12 | 0.03 ± 0.08 |
| C121 | 45.08     | 1H-Cycloprop[a]naphthalene, 1a,2,3,5,6,7a,7b-octahydro-1,1,7a-tetramethyl-[1aR(1a.alpha.,7.alpha.7a.alpha.,7b.alpha.)]- (Calarene) (79, 91, 105, 119, 133, 147, 161, 189, 204) | 1434     | 1427 [82] | nd          | 0.08 ± 0.18 | 0.01 ± 0.02 | nd          | nd          |
| C122 | 45.75     | n-H/C (57, 71, 85, 99, 113, 119) | 1465     |           | 0.02 ± 0.06 | 0.02 ± 0.06 | 0.01 ± 0.04 | 0.58 ± 0.39 | 0.10 ± 0.06 |
| C123 | 46.48     | Pentadecane (57, 71, 85) | 1499     | 1500 [44] | 0.08 ± 0.07 b | 0.05 ± 0.06 ab | 0.01 ± 0.02 s | 0.07 ± 0.04 b | 0.10 ± 0.09 a |
| C124 | 46.95     | Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylthyl)-, (1S-cis)-[b-Cadinene] (81, 91, 105, 119, 134, 161, 189, 204) | 1528     | 1508 [83] | 0.01 ± 0.01 | 0.01 ± 0.02 | nd          | nd          | nd          |

* R.Lexp: Retention index values based on the calculations using the standard mixture of alkanes, using the formula $I_x = 100 \times n + 100 \times (t_x - t_n)/(t_{n+1} - t_n)$. R.I.lit: Retention index values found in the literature. ** Different letters in the same row show significant differences among the honey types, based on Duncan’s multiple range test (α = 0.05), after applying the MANOVA in the compounds that were found in 100% of honey samples of each honey type. *** nd: not detected.
Figure 2. Representative chromatogram for each studied monofloral honey type.

Figure 3. Grouping of the organic volatile compounds found in the examined honey samples.

Thyme honey quantitatively had the richest aroma profile compared with the other studied honey types: in total, 97 volatile compounds were detected, followed by erica with 83, and pine with 81 compounds. Cotton and fir honeys had the fewest volatile compounds detected, with 65 and 63, respectively (Table 1). The rich volatile fraction of thyme honey...
has been discussed in the literature [31,84,85], whereas for erica and cotton honey, the references are inadequate [86].

In thyme honey samples, the compounds benzeneacetaldehyde (C64), benzaldehyde (C40), toluene (C16), furan, 2,5-diethyltetrahydro-(C33), and furfural (C22) were found in the largest percentages (12.18%, 11.01%, 10.26%, 6.09%, and 5.62%, respectively). From those, benzeneacetaldehyde (C64), benzaldehyde (C40), and furan, 2,5-diethyltetrahydro (C33) are common honey constituents; however, they were found in significantly higher percentages in thyme honey compared with the other examined monofloral honey types. Benzeneacetaldehyde (C64) and benzaldehyde (C40) were also abundant in thyme honey samples analyzed in other studies [6,87,88]. The compounds methyl butanal isomer (C1), cyclopentane, 1,3-dimethyl-isomer (C2), heptane (C3), methyl isobutyl ketone (C11), disulfide, dimethyl (C12), toluene (C16), 1-octene (C20), octane (C21), furfural (C22), p-xylene (C28), furan, 2,5-diethyltetrahydro-(C33), nonane (C34), benzaldehyde (C40), benzene, 1,3,5-trimethyl-(C48), octanal (C53), benzene, 1-methyl-4-(1-methylethyl)-[p-Cymene] (C61), benzeneacetaldehyde (C64), benzene, 1-methyl-4-(1-methylethenyl)-(C75), nonanal (C80), decanal (C104), furan, 3-phenyl-(C106), and naphthalene, 1,2-dihydro-1,1,6-trimethyl-(C117) were found in all the examined thyme honey samples, i.e., in 100%. The concentration of p-cymene (C61) was three times higher in thyme honey than in the other analyzed honey types, in contrast to the study of Castro-Vázquez et al. [6], who did not detect the compound in thyme, but did in eucalyptus honeys. Additionally, benzyl nitrile (C84) and furan, 3-phenyl-(C106) seemed to be characteristic for thyme honey, because in the other honey types, they were not detected or found in percentages below 0.2%.

In case of erica honey, the compounds at the greatest concentrations were furfural (C22), toluene (C16), isophorone (C81), octane (C21), and decanal (C104) (21.72%, 12.69%, 10.62%, 7.16%, and 3.41%, respectively), whereas isophorone (C81) and furfural (C22) seemed to stand out in erica honeys, compared with the other studied honey types. The significant content of isophorone is also reported by Radovic et al. [1], and that of furfural by Gyuot et al. [31]. The compounds methyl butanal (isomer) (C1), cyclopentane, 1,3-dimethyl-(isomer) (C2), heptane (C3), 1-pentanol (C7), methyl isobutyl ketone (C11), disulfide dimethyl (C12), toluene (C16), 1-octene (C20), octane (C21), furfural (C22), p-xylene (C28), nonane (C34), ethanone, 1-(2-furanyl)-(C36), alpha.-pinene (C38), benzaldehyde (C40), benzene, 1,3,5-trimethyl-(C48), benzene, 1,2,4-trimethyl-(C59), benzeneacetaldehyde (C64), benzene, 1-ethyl-2,3-dimethyl-(C67), nonanal (C80), 4-ketoisophorone (C85), methyl salicylate (C100), safranal (C101), decanal (C104), naphthalene, 1,2-dihydro-1,1,6-trimethyl-(C117), and damascenone, trans-(C119) were found in 100% of all the examined erica honey samples, with 4-ketoisophorone (C85) found only in erica honey. Ethanone, 1-(2-furanyl)-(C36), safranal (C101) and decanal (C104) were detected in significantly higher percentages in erica honey compared with the other studied monofloral honey types. Tan et al. [89] suggested the presence of degraded carotenoids (3,5,5-trimethyl-cyclohex-2-enederivatives) as characteristic of heather honey (Ericaceae family), compounds also found in the present study, in contrast to Radovic et al. [1], who identified an absence of these compounds from erica honey. Probably, the different geographical origin contributes to the variations of erica volatile profile, indicating the need for further research regarding the Ericaceae honey.

Furthermore, the compounds 1-octene (C20), octane (C21), toluene (C16), nonanal (C80), and alpha.-pinene (C38) were detected in higher concentrations in honeydew honeys (pine, fir) compared with blossom honeys, in percentages 21.54%, 14.25%, 7.97%, and 3.78%, respectively, for pine honeys, and in percentages 20.91%, 16.31%, 8.49%, and 1.43%, respectively, for fir honeys. In the case of pine honey, the compounds methyl butanal (isomer) (C1), cyclopentane, 1,3-dimethyl-(isomer) (C2), heptane (C3), furan, 2,5-diethyltetrahydro-(C4), cyclohexane, methyl-(C5), 1-pentanol (C7), methyl isobutyl ketone (C11), disulfide dimethyl (C12), toluene (C16), 1-octene (C20), octane (C21), furfural (C22), p-xylene (C28), nonane (C34), alpha.-pinene (C38), benzaldehyde (C40), and benzene, 1,3,5-trimethyl-(C48) were detected in 100% of the examined pine honey samples. Tananaki et al. [32], analyzing 44 honey samples for the discrimination between Greek and Turkish pine honey, found the
compounds octane (C21), p-xylene (C28), alpha-pinene (C38), benzaldehyde (C40), nonane (C34), furfural (C22), and 1-octene (C20) in 100% of Greek honey samples. Additionally, beta-pinene (C44), which was found only in some pine honey samples in our study, was used by Tananaki et al. [32], among other compounds, for the separation of Turkish and Greek honey classification.

As for fir honeys, the compounds methyl butanal (isomer) (C1), cyclopentane, 1,3-dimethyl-(isomer) (C2), heptane (C3), furan, 2,5-dimethyl-(C4), cyclohexane, methyl-(C5), 3-buten-1-ol, 2-methyl-(C6), methyl isobutyl ketone (C11), disulfide dimethyl (C12), toluene (C16), 1-octene (C20), octane (C21), ethylbenzene (C26), p-xylene (C28), santene (C30), 2-heptanone (C32), nonane (C34), alpha-pinene (C38), benzaldehyde (C40), benzene, 1,3,5-trimethyl-(C48), octan (C53), benzene, 1,2,4-trimethyl-(C59), p-cymene (C61), 2-nonanone (C77), undecane (C79), nonanal (C80), decanal (C104), and tridecane (C115) were detected in 100% of the examined fir samples. Karabagias et al. [40] also noted high concentrations of 1-octene and octane in honeydew honeys and nonanal in fir honeys. Santene (C30) was detected only in fir honeys, which is in agreement with the results of Tananaki et al. [41], who found this compound in 100% of the analyzed fir honey samples (n = 33).

Lastly, in cotton honeys, the compounds toluene (C16), octane (C21), furfural (C22), and benzaldehyde (C40) were identified in the greatest percentages (14.64%, 10.78%, 6.60%, and 5.08%, respectively). Additionally, the compounds methyl butanal (isomer) (C1), cyclopentane, 1,3-dimethyl-(isomer) (C2), heptane (C3), cyclohexane, methyl-(C5), 3-buten-1-ol, 2-methyl-(C6), disulfide dimethyl (C12), toluene (C16), 2-buten-1-ol, methyl-(isomer) (C17), 2-butenal, 3-methyl-(C19), 1-octene (C20), octane (C21), furfural (C22), 1-pentanol, 4-methyl-(C23), 3-penten-1-ol, methyl-(isomer) (C27), p-xylene (C28), nonane (C34), ethanal, 1-(2-furanyl)-(C36), benzaldehyde (C40), 1-octen-3-ol (C47), benzene, 1,3,5-trimethyl-(C48), benzene, 1,2,4-trimethyl-(C59), D-limonene (C62), benzenecacataldehyde (C64), benzene, 1-ethyl-2,3-dimethyl-(C67), octane, 1-chloro (C69), 2-furanmethanol, 5-ethylenetetrahydro-alpha,alpha,alpha,5-trimethyl-cis-(C73), benzene, 1-methyl-4-(1-methylethenyl)-(C75), undecane (C79), nonanal (C80), decanal (C104), tridecane (C115), naphthalene, 1,2-dihydro-1,1,6-trimethyl-(C117), and pentadecane (C123) were found in 100% of cotton honey samples, whereas the compounds, 1-butanol, 2-methyl-(C8), 2-butenal, 3-methyl-(C19), 1-pentanol, 4-methyl-(C23), 3-penten-1-ol, methyl-(isomer) (C27), 1-octen-3-ol (C47), 2-furanmethanol, 5-ethylenetetrahydro-alpha,alpha,alpha,5-trimethyl-cis-(C73), and benzene, 1-methyl-4-(1-methylethenyl)-(C75) were found in higher percentages in cotton honey, compared with the other studied honey types. The compound 2-furanmethanol, 5-ethylenetetrahydro-alpha,alpha,alpha,5-trimethyl-cis-(C73) was also reported in high concentrations in the study by Odeh et al. [48] and 3-penten-1-ol, methyl-(isomer) (C27) in the study of Alissandrakis et al. [27]. Nonanal (80) and benzenecacataldehyde (C64) are also referred in cotton honeys from other countries, such as Turkey and Palestine [90,91].

The use of P&T linked to GC–MS is widely used for the identification of volatile compounds in food science [92,93]. The high-resolution power and sensitivity of gas chromatography (GC), together with the structural information provided by mass spectrometry (MS), has made the coupling GC–MS the technique of choice for the qualitative and quantitative analysis of food volatiles [93,94]. However, the preliminary steps of fractionation from major non-volatile components of the honey matrix (sugars and water) and preconcentration are still necessary for the chromatographic separation of honey volatiles. In the purge-and-trap (P&T) technique, volatiles swept by a flow of inert gas are trapped on an adsorbent, while further thermal/solvent desorption of the trap allows volatiles to enter the chromatographic system for separation. Furthermore, in P&T, the reduction in or elimination of organic solvents is achieved, offering a green alternative to sample preparation, combined with simultaneous multiclass compound extraction and reproducibility associated with a totally automated system [25].

The MANOVA that was applied for the compounds found in 100% of honey samples of each honey type showed significant differences among the honeys for some characteristic compounds, such as 1-octene (C20), benzaldehyde (C40), and nonanal (C80) (Table 1). In turn, a linear discriminant analysis through the stepwise method (SLDA) was used in order
to determine whether the significant volatile compounds could discriminate the examined monofloral honey types. The first canonical variable corresponded to 58.9%, whereas the second corresponded to 25.5% of variation (Table 2).

Table 2. Eigenvalues, variation (%), cumulative variation and functions at group centroids exported by SLDA.

| Botanical Origin | Function 1 | Function 2 | Function 3 | Function 4 |
|------------------|------------|------------|------------|------------|
| Fir              | −10.623    | −5.151     | −11.559    | 2.967      |
| Pine             | −2.250     | 4.176      | −0.549     | −3.841     |
| Erica            | 21.424     | −8.579     | 0.103      | 0.008      |
| Thyme            | 0.918      | 7.740      | 2.879      | 4.136      |
| Cotton           | −19.655    | −14.369    | 8.287      | 0.265      |

Additionally, regarding the group centroids of the first function, fir honeys had a mean of −10.623, pine honeys a mean of −2.250, erica honeys a mean of 21.424, thyme honeys a mean of 0.918, and cotton honeys a mean of −19.655. All the monofloral honey types were discriminated, and this was more obvious for erica and cotton honeys because they were located in the most distant places (Figure 4), which was also confirmed by the different chromatograms that these two honey types presented, compared with the other studied monofloral honey types (Figure 2). Samples of the same honey type were located at the same quadrant, concentrated around the centroid of the respective honey type, showing the large correlation inside the same group (Figure 4).

Additionally, the stepwise method was applied to determine the compounds that will be used in the prediction model. The original group cases were correctly classified at a 94.2% rate, whereas the cross-validated group cases were correctly classified at a 92.3% rate (Table 3).

Five F scores were calculated (Table 4) and used for the classification in the group membership of five samples (test set) whose botanical origin was known ("reference samples") for verification of the predictive model. The samples were assigned to the group for which the classification function had the largest F score (Table 4). For all the reference samples, the prediction was correct.

The combination of chemometric approaches, such as principal component analysis (PCA), cluster analysis (CA), or discriminant analysis (DA), with the analysis of volatile compounds for the characterization of other monofloral honey types studied by other authors had also led to promising results for the correct classification of honey samples [32,95,96]. However, due to the complexity of volatile compounds’ structure that makes them unstable along with the various methods of analysis used for their determination, a larger number of honey samples could optimize the prediction model, and thus, the honey authentication.
Discrimination of monofloral honey types based on their volatile compound participation, after applying discriminant analysis. The stepwise method was applied to determine the compounds that will be used in the prediction model. The original group cases were correctly classified at a 94.2% rate, whereas the cross-validated group cases were correctly classified at a 92.3% rate (Table 3).

### Table 3. Classification results (original and cross-validated) extracted from the prediction model after applying SLDA analysis.

| Botanical Origin | Predicted Group Membership |
|------------------|----------------------------|
|                  | Fir | Pine | Erica | Thyme | Cotton | Total |
| **Original (%)** |     |      |       |       |        |       |
| Fir              | 100.0 | 0 | 0 | 0 | 0 | 100.0 |
| Pine            | 10.5 | 84.2 | 0 | 0 | 0 | 100.0 |
| Erica           | 0 | 0 | 100.0 | 0 | 0 | 100.0 |
| Thyme           | 0 | 0 | 0 | 100.0 | 0 | 100.0 |
| Cotton          | 0 | 0 | 0 | 0 | 100.0 | 100.0 |
| **Cross-validated (%)** |     |      |       |       |        |       |
| Fir              | 83.3 | 16.7 | 0 | 0 | 0 | 100.0 |
| Pine            | 10.5 | 84.2 | 0 | 5.3 | 0 | 100.0 |
| Erica           | 0 | 0 | 100.0 | 0 | 0 | 100.0 |
| Thyme           | 0 | 0 | 0 | 100.0 | 0 | 100.0 |
| Cotton          | 0 | 0 | 0 | 0 | 100.0 | 100.0 |

**Figure 4.** Discrimination of monofloral honey types based on their volatile compound participation, after applying discriminant analysis.

**Table 3.** Classification results (original and cross-validated) extracted from the prediction model after applying SLDA analysis.
Table 4. Fisher’s linear discriminant functions exported for the 5 monofloral honey types (test set) and assignment of probable botanical origin for five samples (references Xn).

| Honey Type | Function | Assigned Honey Type | Correct Honey Type |
|------------|----------|---------------------|--------------------|
| Fir        | $-21.793 + 3.485 \times C_{19} + 9.247 \times C_{20} + 1.916 \times C_{24} + 0.548 \times C_{34} - 2.373 \times C_{38} - 4.593 \times C_{49} - 1.776 \times C_{62} - 0.166 \times C_{68} + 95.518 \times C_{121} - 0.369 \times C_{124}$ | Thyme | Thyme |
| Pine       | $-7.115 + 2.145 \times C_{19} + 4.959 \times C_{20} - 0.139 \times C_{24} + 0.187 \times C_{34} + 0.236 \times C_{38} + 0.777 \times C_{49} + 4.041 \times C_{62} + 0.063 \times C_{68} + 14.959 \times C_{121} + 0.020 \times C_{124}$ | Thyme | Thyme |
| Erica      | $-37.589 + 1.069 \times C_{19} - 1.149 \times C_{20} - 8.629 \times C_{24} - 1.562 \times C_{34} + 23.255 \times C_{38} - 29.924 \times C_{49} + 6.489 \times C_{62} + 0.033 \times C_{68} - 11.829 \times C_{121} + 13.108 \times C_{124}$ | Thyme | Thyme |
| Thyme      | $-17.553 + 1.509 \times C_{19} + 2.871 \times C_{20} - 3.605 \times C_{24} - 1.289 \times C_{34} + 1.240 \times C_{38} + 2.005 \times C_{49} + 9.706 \times C_{62} - 0.728 \times C_{68} - 23.198 \times C_{121} + 5.044 \times C_{124}$ | Thyme | Thyme |
| Cotton     | $-109.333 + 29.508 \times C_{19} + 2.678 \times C_{20} + 59.756 \times C_{24} + 2.982 \times C_{34} - 2.621 \times C_{38} + 108.549 \times C_{49} - 17.208 \times C_{62} - 0.037 \times C_{68} + 87.765 \times C_{121} - 46.286 \times C_{124}$ | Thyme | Thyme |

| $X_1$ | $X_2$ | $X_3$ | $X_4$ | $X_5$ |
|-------|-------|-------|-------|-------|
| 26.05 | 38.70 | 2.62  | 19.43 | 13.58 |

4. Conclusions

A Purge and Trap GC–MS system was used for the extraction, separation, and identification of characteristic volatile and semi-volatile compounds of five distinguished monofloral honey types—thyme, pine, fir, erica, and cotton—with the latter two remaining less well explored regarding their aroma profile. In total, 124 compounds were found. Thyme honey, whose profile, regarding the presence of volatiles, was the richest compared with the other honey types of this study, was characterized by the presence of benzeneacetaldehyde, benzaldehyde, and benzyl nitrile. Isophorone and furfural seem to characterize erica honey, 1-butanol, 2-methyl-, and 1-pentanol, 4-methyl- the cotton honey and alpha.-pinene, octane and nonanal the honeydew honeys. The application of multivariate statistical analysis to P&T GC–MS data showed that the use of volatile profiles could lead to discrimination among the different monofloral honey types. Further analysis of more monofloral honey types could be a helpful tool for the confirmation of honey authentication through volatile profile analysis.

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