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# Volatile components as chemical markers of the botanical origin of Corsican honeys

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## Abstract

In accordance with the national Appellation d'Origine Contrôlée and the European Protected Designation of Origin labels, Corsican honeys can be classified into six ranges (spring, spring maquis, honeydew maquis, chestnut grove, summer maquis and autumn maquis). Toward proposing a new and faster method for performing honey quality assessments, an headspace-solid phase microextraction (HS-SPME)/Gas Chromatography (GC)/GC-Mass Spectrometry (MS) method with multivariate data analysis – principal component analysis (PCA), cluster analysis (CA), partial least square (PLS) – was developed using 269 Corsican samples, for which the volatile compositions were established *a priori*. Corsican honeydew and blossom honey could be differentiated by the richness of 3-furaldehyde in the category of “honeydew maquis”. This approach also allowed identification of chemical markers of the botanical origins of blossom honeys, including 2-aminoacetophenone, *p*-anisaldehyde, 4-*n*-propylanisole, isophorone, and isomers of lilac aldehyde. Therefore, characterization of the volatile fraction of Corsican honeys combined with chemometric analysis may be useful for detecting the nectar contribution of plant species in honeys with complex nectariferous origins.

## KEYWORDS

Corsican honey, HS-SPME/GC/GC-MS, PCA, PDO, PLS

## 1 | INTRODUCTION

With its rich melliferous plant species and endemic black honeybee, Corsica possesses a suitable natural environment for the development of a beekeeping sector. In accordance with the national Appellation d'Origine Contrôlée (AOC) and the European Protected Designation of Origin (PDO) labels,<sup>1</sup> Corsican honeys can be classified into six ranges (“spring”, “spring maquis”, “honeydew maquis”, “chestnut grove”, “summer maquis” and “autumn maquis”) depending on apiary location (main plants visited by honeybee), harvest period, melissopalynological data, and organoleptic properties of the honeys.<sup>2</sup> In addition, the “honeydew maquis” has been divided into two categories according to the honeydew origin of its raw material; typical Mediterranean honeydew is generally produced from rockrose (*Cistus* sp.) in littoral areas, oak (*Quercus* sp.), and/or chestnut (*Castanea sativa*) forests, while *Metcalfa* honeydew was obtained after the appearance of the insect

*Metcalfa pruinosa* in Corsica in 1995.<sup>3</sup> The typical Mediterranean and *Metcalfa* honeydews are distinct in terms of color (dark amber and very dark, respectively) and viscosity (weak and high, respectively). Currently, production of the Corsican honeys in the “honeydew maquis” range are essentially obtained from *M. pruinosa*.

Quality assessment of the two official designations PDO and AOC “*Miel de Corse - Mele di Corsica*” has been based on melissopalynological data considering the entire pollen spectrum via statistical analysis.<sup>4-6</sup> This method is associated with physico-chemical parameters (i.e., water content, coloration, and conductivity) that are still considered an official method for honey certification.<sup>1</sup> However, researchers have recently begun to identify new criteria for determining the botanical origin of honeys. Their work has frequently focused on the identification of chemical biomarkers such as amino acids, sugar, phenolic and/or volatile compounds.<sup>7-9</sup> These methods have been considered complementary because their procedures are usually not standardized and their analytic parameters are often adapted according to the botanical honey sample origin, targeted chemical compounds, and/or apparatus. However, these methods also offer new opportunities for defining the interactions between

the organoleptic properties of honeys and the melliferous plant resources. In terms of authentication, the development of interdisciplinary approaches (palynological, sensorial, and chemical analysis) is preferable for characterizing botanical and geographical origins.

Work on the volatile composition of honeys started in the early 1960s and to date, approximately 600 compounds belonging to various chemical families have been identified according to their botanical and/or geographical origins.<sup>9,10</sup> The extraction of volatile components from honeys has usually been performed using headspace-solid phase microextraction (HS-SPME), simultaneous steam distillation-solvent extraction, hydrodistillation or ultrasound-assisted extraction.<sup>9-11</sup> Most studies have focused on monofloral honeys, and constituents such as methyl anthranilate, methyl syringate and isophorone have been reported as chemical markers of the botanical origins of citrus, asphodel and strawberry tree honeys, respectively.<sup>11-13</sup> To our knowledge, no study to date has focused on the volatile composition of *Metcalfa* honeydew honeys, but various chemical markers of others honeydew honeys have been previously described; these have included oak-lactone (oak honeydew),<sup>14</sup> acetic acid,<sup>15</sup> 2,3-butanediol,<sup>16</sup> and borneol<sup>17</sup> (botanical raw material origin not specified).

The volatile fraction of Corsican honeys has been studied toward discriminating geographical origins (Corsican and non-Corsican honeys).<sup>18,19</sup> Moreover, the relationships between chemical variability, pollen diversity, and physico-chemical parameters of each range of Corsican honeys (except “honeydew maquis” honey) have been established using an interdisciplinary approach.<sup>20-24</sup> Based on these previous studies, the aim of the present work was to provide an overview of the volatile composition of Corsican honeys, including blossom and honeydew honeys (in all six PDO ranges), as well as blend honeys with mixed melliferous origins (presence of nectar and honeydew contributions). The objective of this research was to propose a new and faster approach for honey quality assessment utilizing an HS-SPME/GC/GC-MS-based method with multivariate data analysis (PCA, CA, PLS) to certify the botanical origin of 269 Corsican samples, for which the volatile compositions were established *a priori*.

## 2 | EXPERIMENTAL

### 2.1 | Honey sampling

269 honeys samples were selected from the reference bank of the University of Corsica. These samples included the six ranges of Corsican honeys commercialized under AOC and PDO appellations: 50 “chestnut grove” (CH01-CH50), 45 “spring maquis” (MP01-MP45), 41 “spring” (PR01-PR41), 29 “summer maquis” (ME01-ME29), 30 “autumn maquis” (MA01-MA30), 48 “honeydew maquis” (MM01-MM48) and 26 blend honeys (MM49-MM74). Taking into account of the regional plant diversity and bioclimatic annual variations, the honey samples were provided from 74 beekeepers and various years of production between 2003 and 2013. After the harvest, these honeys were packaged directly in a sealed pot and stored at 14°C, which was the optimal condition for avoid the degradation of samples.<sup>25</sup> Before analysis, the selected honeys were examined by sensory analysis to ensure the conservation process.

### 2.2 | Melissopalynological and physico-chemical analysis

The melissopalynological and physico-chemical analysis of the 269 Corsican honeys was carried out using the methodology previously reported.<sup>20</sup> These results have enabled to establish the classification of samples under the varietal ranges of AOC/PDO appellation and the certification of geographical and botanical origins. The pollen spectrum (relative frequency of taxa and pollen density) and the physico-chemical parameters (coloration and electrical conductivity) of the blossom honey samples were also described in previous studies.<sup>20-24</sup> Pollen analysis allowed identification of 131 plant taxa in Corsican honeys. Their geographical origin was certified according to the Decree n°2013-1057<sup>1</sup> of Corsican AOC/PDO honey including the chorological and ecological analysis of pollen directory, the diversity of biogeographical origin of taxa, the presence of marker species (endemic and/or subendemic) and the absence of characteristic taxa of other Euro-Mediterranean honeys.<sup>1,2,5</sup>

### 2.3 | Volatile composition analysis

The volatile composition of samples was established using HS-SPME followed by GC-FID and GC-MS analyses. A divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 30 µm) SPME fiber was used to extract the volatile components from honey. Optimization of the SPME parameters was carried out using the methodology reported previously.<sup>20-24</sup>

GC-FID and GC-MS analyses were performed using a PerkinElmer (Waltham, MA, USA) AutoSystem XL GC apparatus equipped with a FID system or coupled to a PerkinElmer TurboMass detector (quadrupole). A fused-silica capillary column (30 m × 0.25 mm, film thickness 1 µm) coated with Rtx-1 (PDMS) was used. The oven temperature was programmed from 60 to 230°C at 2°C/min and then held isothermally at 230°C for 35 min. Other analytical parameters were described in our previous works as SPME inlet liner: 0.75 mm i.d. Supelco; injector temperature: 280°C; carrier gas: hydrogen and/or helium 1 ml/min; detector FID temperature: 280°C; MS source temperature: 150°C (ionization energy: 70 eV). Identification of the components was based on the comparison of their mass spectra and retention indices (relative to the retention times of a series of n-alkanes C<sub>5</sub> – C<sub>30</sub> [alkane standard mixture, Sigma-Aldrich]) with linear interpolation with those of authentic compounds, data of the laboratory's library or commercial libraries.<sup>26</sup> The relative concentrations of components were calculated from the GC peak areas obtain by GC-FID without using correction factors. The main goal of the study was to provide a differentiation of the honey varieties using composition of HS-SPME volatile fractions. The relative percentages obtained by GC-FID are used only for comparative purposes to get patterns of volatile profiles, and do not reflect the real amounts of compounds in honey samples, since these values are obtained by SPME without any internal standardization.

Optimization of the SPME parameters was carried out with seven honey samples (two for “spring” honey rang and one for each other category) and was based on the sum of the total peak areas measured using a gas chromatography-flame ionization detection (GC-FID) system. These samples were subjected to HS-SPME in a 20 ml vial. The

honey concentration in distilled water was optimized after six different experiments (0.5 g/ml, 1 g/ml, and 2 g/ml) with Na<sub>2</sub>SO<sub>4</sub> addition (1 g and 2 g). For each sample, the temperature (25°C, 50°C and 70°C), the equilibration time (30, 60 and 90 min) and the extraction time (15, 30 and 45 min) was also optimized in various experiments. For all honey samples, the extraction parameters were chosen as follows: 4 g of honey sample with 4 ml of water and 2 g of Na<sub>2</sub>SO<sub>4</sub> at a temperature between 70°C to 90°C, an equilibrium time of 90 min, and an extraction time between 30 min to 45 min.

## 2.4 | Chemometric analysis

### 2.4.1 | Unsupervised pattern recognition

Principal Component Analysis (PCA) is unsupervised pattern recognition and it is often the first step of exploratory data analysis to detect groups in the measured data. PCA models the directions of maximum variations in a data set by projecting as a swarm of points in a space defined by principal components (PCs). PCs describe, in decreasing order, the higher variations among the objects, and because they are calculated to be orthogonal to another one, each PC can be interpreted independently. That permits an overview of the data structure by revealing relationships between the objects as well as the detection of deviating objects. To find these sources of variations, the original data matrix is decomposed into the object space, the variable space, and the error matrix. The error matrix represents the variations not explained by the previously extracted PCs and is dependent on the problem definition.<sup>27</sup> The PCA algorithm is used with mean centered data.

### 2.4.2 | Partial least square regression

This technique can be adapted for classification<sup>28,29</sup> as well as for quantitative analysis. The model was built by the full cross validation method during the calibration developments. The evaluation of the errors in the calibration was carried out by computing the standard error of calibration (SEC) after comparing the real concentration with the computed one for each component. The formula for the standard error of calibration is:

$$SEC = \sqrt{\left(\frac{\sum_{i=1}^N (C_i - C'_i)^2}{N-1-p}\right)} \quad (1)$$

where  $C'_i$  is the known value,  $C_i$  is the value calculated by the calibration equation,  $N$  is the number of samples, and  $p$  is the number of independent variables in the regression optimized by cross-validation.

The standard error of prediction (SEP) gives an estimation of the prediction performance during the step of validation of the calibration equation:

$$SEP = \sqrt{\left(\frac{\sum_{i=1}^M (C_i - C'_i)^2}{M}\right)} \quad (2)$$

where  $M$  is the number of samples in the prediction set.

PLS-discriminant analysis (DA) method: PLS-DA is carried out using an exclusive binary coding scheme with one bit per class. Therefore, for each sample, the origin may be represented by a multidimensional output vector with 1 at the position corresponding to varietal origin and 0 at the other positions. During the calibration process, the PLS-DA method is trained to compute the "membership values," one for each class; the sample is then assigned to the class showing the highest membership value.<sup>30</sup> Six models were computed, one for each origin. Two data sets were using the calibration one and the prediction one. The data set were randomized, 50% ( $n = 138$ ) of the samples were used for the calibration set and 50% ( $n = 134$ ) were used on the prediction one. The performance of the calibration models was estimated from the percentage of correctly classified samples (%CC). The %CC was estimated by the formula:

$$\%CC = N_c / (N_c + N_{ic}) \cdot 100$$

where  $N_c$  is the number of correctly classified samples and  $N_{ic}$  is the number of incorrectly classified samples.<sup>31</sup>

The chemometric applications are performed by the UNSCRAMBLER software version X10.3 from CAMO (Computer Aided Modeling, Trondheim, Norway).

## 2.5 | Cluster analysis

The chemical data was also subjected to cluster analysis (CA) by performing R software (R Foundation-Institute for Statistics and Mathematics, Melbourne, Austria). The CA produced a dendrogram (tree) using Ward's method of hierarchical clustering, which is based on the Euclidean distance between pairs of honey samples.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Melissopalynological characteristics of Corsican honeys

Melissopalynological analysis allows identification of the main nectariferous species and/or characteristic plant associations for each blossom honey. The pollen profiles of two honey ranges are distinguished by "over" represented taxa of *C. sativa* (associated essentially with *Rubus* sp.) and "normal" represented taxa of *Erica arborea* (combined with other characteristic spring nectariferous species such as *Genista* sp., *Salix* sp., *Lavandula stoechas*, *Prunus* sp., *Viburnum tinus* and *Crataegus monogyna*) for "chestnut grove" (CH01-CH50) and "spring maquis" samples (MP01-MP45), respectively. The pollen spectrum of "autumn maquis" honey (MA01-MA30) exhibited "under" represented taxa of *Arbutus unedo*, associated with typical autumnal species as *Hedera helix*, *Smilax aspera* and *Rosmarinus officinalis*. The botanical origins of "spring" are more complex with "under" represented taxa in pollen spectrum. Two groups were distinguished from the "spring" range: "spring clementine" honeys (PR01-PR18), which were characterized by the association of cultivated plants, especially *Citrus* sp., *Actinidia sinensis* and *Prunus* sp., and "non-clementine" honeys (PR19-PR41), which were dominated by spontaneous herbaceous or shrub species such as *Asphodelus ramosus*, *Trifolium* sp., *Echium*

sp., *Pistacia lentiscus* and *Phillyrea* sp. The pollen profile of “summer maquis” honeys (ME01–ME29) could be differentiated by the combination of *Anthyllis hermanniae*, *Rubus* sp., and endemic high altitude subshrub species such as *Thymus herba-barona*, *Teucrium* sp. and *Genista* sp.

The pollen spectrum of honeydew honey was characterized by the absence of dominant nectariferous taxon and the presence of various microorganisms such as spores, fungi, or microscopic algae, which were referred to as “honeydew indicators”. Two types of honeydew honeys were reported: the “*Metcalfa* honeydew” (MM01–MM43), which was characterized by numerous “honeydew indicators” associated with typical plant genus (*Chenopodiaceae/Amaranthaceae*, *Artemisia* sp., *Myrtus* sp., *Eucalyptus* sp., *Plantago* sp. and *Asparagus* sp.), and “Mediterranean traditional honeydew” (MM44–MM48), which was rich in polleniferous species, especially *Cistus* sp. from maquis or *Quercus* sp. from mixed forests and exhibited fewer “honeydew indicators” than “*Metcalfa* honeydew”.

Finally, the pollen spectrum of blend honeys was marked by the presence of “honeydew indicators” and complex nectariferous origins (proportion and taxa association) according to harvest period, such as “chestnut grove” and/or “spring maquis” honey (contributions of *C. sativa* and/or *E. arborea*, respectively).

### 3.2 | Volatile composition of Corsican honeys

HS-SPME, GC, and GC/MS analysis of the volatile fraction of 269 Corsican honeys allowed identification of 102 compounds (Table 1). Among these, only three components were reported in all honey samples, which exhibited a high quantitative variability according to honey range: 3-furaldehyde **C10** (0.1–40.1%), benzaldehyde **C21** (0.3–28.0%), and phenylacetaldehyde **C29** (0.1–57.8%). Although these compounds were detected in 269 honey samples, they could not be considered markers of geographic origin because they are also present in the honeys of other geographic origins in France, Italy, and Germany.<sup>32</sup>

The volatile composition of Corsican honeys was dominated by oxygenated compounds, which accounted for 68.7–96.5%. In the 195 blossom honeys, the major oxygenated compound class was aromatics (32.9–56.4%), except for “autumn maquis” honeys, which had isophorone derivatives (42.5%) as the major class of components. The volatile fraction of “chestnut grove”, “spring”, and “summer maquis” honeys also exhibited relatively high amounts of linear constituents (30.2%, 21.8%, and 25.4%, respectively), followed by furan components (11.9%, 15.2%, and 7.7%, respectively), while the “spring maquis” honey possessed only 10.3% and 9.1% of the furan and linear compounds. Conversely, the honeydew honeys were rich in furan (29.2%) and aromatic components (21.3%), while the blend honeys were characterized by aromatic (47.7%) and furan constituents (17.9%). Finally, the volatile composition of Corsican honeys was also characterized by a low concentration of terpenes (0–6.7%). Therefore, it is noteworthy that the volatile composition of Corsican honeys differed according to their botanical origins.

### 3.3 | Chemometric analysis of Corsican honeys

In order to synthesize the chemical variability of Corsican honeys, PCA was performed on volatile data from 269 honeys. As shown in Figure 1

a, the first and second axes (PC1/PC2) explained 27% of the total variance. The honeydew and blend honeys were differentiated from blossom honeys based on the first Principal Component (PC1). Indeed, honeydew and blend honeys exhibited some common chemical characteristics, particularly a higher content of 3-furaldehyde **C10** (24.6% and 13.9%, respectively) than blossom honeys (4.1%). The second Principal Component (PC2) allowed discrimination of three blossom honey groups: “chestnut grove”, “spring” associated with “summer maquis”, and “spring maquis” linked to “autumn maquis”.

The origins of these samples were also determined using PLS-DA regression. Tables 2 and 3 show these results. The six varieties were discriminated and well predicted with a percent of correct classification between 99–100%, as shown in Table 2. Classification was 100% correct for the “chestnut grove”, “spring maquis”, “autumn maquis” and “honeydew” honeys, and 99% for “summer maquis” and “spring” ranges, with one false sample in each category. The results for prediction of honey origin were excellent. Indeed, of the 131 samples used in the prediction set, only two were not well predicted.

### 3.4 | Data analysis of blossom honeys

To improve discrimination between blossom honey ranges, PCA was performed on the honeydew and blend honey samples separately. As shown in Figure 1b, PCA obtained with the first and third axes (PC1/PC3) explained 36% of the total variance of volatile fractions from 195 blossom honeys. Thus, six groups were distinguished by the PC1 axis; the “chestnut grove” and “summer maquis” honeys were positively projected. The “chestnut grove” honey was characterized by high content of acetophenone **C33** (7.0%), 2-aminoacetophenone **C79** (11.4%), and some linear acids such as octanoic acid **C63** (5.0%) and nonanoic acid **C77** (5.9%). According to the literature, acetophenone and its derivatives (aminoacetophenones) are considered the chemical markers of chestnut honey.<sup>33,34</sup> The “summer maquis” honeys were characterized by high amounts of phenylacetaldehyde **C29** (33.6%) and the presence of linear acids such as butanoic acid **C7** and 3-methyl butanoic acid **C13**, which were absent in the other honey samples. Eleven “summer maquis” samples (ME19–ME29) exhibited a significant content of 2-aminoacetophenone **C79** (7.2%), which is considered an indicator of *C. sativa* nectar contribution.

The “spring maquis” and “autumn maquis” were negatively projected. The “spring maquis” honey were characterized by 4-propylanisol **C75** (14.7%) and *p*-anisaldehyde **C70** (11.7%). This latter compound was considered a marker of *E. arborea* honeys because of its absence in honeys of other botanical origins.<sup>35</sup> The “autumn maquis” honeys were distinguished by their high content of isophorone derivatives (42.5%) such as isophorone **C46** (34.8%) and 4-oxo-isophorone **C47** (3.6%). These results were in accordance with the volatile composition of *A. unedo* honeys previously described;<sup>12,36</sup> thus, it could be considered a chemical marker of strawberry tree nectar. The trimethylphenol isomers (31.7%) such as 2,3,4-trimethylphenol **C73** (4.6%) and 3,4,5-trimethylphenol **C83** (27.1%) were reported only in Corsican *A. unedo* honey.

The “spring” honeys were differentiated into two subgroups called “spring clementine” and “spring non-clementine” honeys. The “spring clementine” honeys were characterized by lilac aldehyde isomers (**C48**,

**TABLE 1** Volatile composition of 269 Corsican honeys

N <sup>o</sup> a	Compounds	RI (lit) <sup>b</sup>	RF <sup>c</sup>	Chestnut grove <sup>d</sup> (CH01 - CH50)		Spring maquis (MP01 - MP45)		Autumn maquis (MA01 - MA30)		Spring (PR01 - PR41)		Summer maquis (ME01 - ME29)		Honeydew maquis (MM01 - MM48)		Blend honey (MM49 - MM74)						
				Mean <sup>d</sup>	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	
C1	3-methyl-3-butanol	711	704	1.9 ± 1.4	0.3	6.5	-	-	-	2.3 ± 2.0	0.3	11.3	1.3 ± 1.0	0.2	5.0	-	-	-	-			
C2	2,5-Dimethylfuran	715	710	-	-	-	-	1.2 ± 0.9	0.1	3.5	-	-	-	-	-	-	-	-	-			
C3	2-methyl butanol	728	727	1.6 ± 0.9	0.1	3.5	-	-	-	-	-	-	-	-	-	-	-	-	-			
C4	(E)-pent-2-enal	725	728	-	-	1.4 ± 1.7	0.1	9.0	-	-	-	-	-	-	-	-	-	-	-			
C5	Toluene	745	741	-	-	-	-	-	-	6.1 ± 4.0	1.5	17.3	4.2 ± 2.4	0.7	8.3	-	-	-	-			
C6	3-methyl-2-butanol	755	750	-	-	-	-	-	-	-	-	0.6 ± 1.1	0.1	5.2	-	-	-	-	-			
C7	Butanoic acid	779	771	-	-	-	-	-	-	-	-	1.7 ± 1.9	0.1	5.3	-	-	-	-	-			
C8	Hexanal	777	773	1.2 ± 1.4	0.1	6.4	-	-	-	1.4 ± 1.1	0.1	6.3	1.2 ± 1.1	0.1	3.7	-	-	-	-			
C9	Octane	800	800	2.6 ± 1.5	0.1	8.5	0.3 ± 0.4	0.1	2.2	1.9 ± 1.4	0.3	5.6	0.6 ± 0.5	0.1	1.8	1.2 ± 0.7	0.1	3.5	0.8 ± 0.9	0.1	3.8	
C10	3-Furaldehyde	799	804	4.9 ± 2.6	0.8	11.0	5.6 ± 2.2	2.4	11.0	3.6 ± 2.9	0.6	18.5	4.5 ± 2.7	0.7	10.4	24.6 ± 8.3	10.0	40.4	13.9 ± 6.8	3.9	29.2	
C11	2-Furanmethanol	825	834	-	-	-	-	-	-	-	-	-	-	-	-	0.9 ± 0.5	0.1	2.5	0.5 ± 0.5	0.1	1.7	
C12	Furfural	836	835	2.1 ± 1.8	0.2	8.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
C13	3-methyl butanoic acid	830	831	-	-	-	-	-	-	-	-	1.8 ± 1.8	0.1	6.2	-	-	-	-	-	-	-	-
C14	2-methyl butanoic acid	860	858	-	-	-	-	-	-	2.2 ± 3.5	0.1	20.4	1.3 ± 0.9	0.1	3.8	-	-	0.4	0.4	-	-	-
C15	2-methyl octane	868	873	-	-	-	-	-	-	0.6 ± 0.4	0.1	1.7	0.3 ± 0.2	0.1	0.7	-	-	-	-	-	-	-
C16	Styrene	873	874	0.6 ± 0.3	0.2	1.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C17	Heptanal	884	876	-	-	-	-	-	-	-	-	-	-	-	-	0.5 ± 0.5	0.1	1.1	-	-	-	-
C18	2-Acetyl-furane	878	879	-	-	0.5 ± 0.2	0.2	1.0	0.2 ± 0.2	0.1	0.9	-	-	-	-	0.6 ± 0.3	0.1	1.4	0.4 ± 0.2	0.1	0.8	0.8
C19	Nonane	900	899	0.5 ± 0.6	0.2	4.3	-	-	-	1.2 ± 0.9	0.2	3.8	1.2 ± 0.9	0.2	3.4	0.3 ± 0.2	0.1	0.4	-	-	-	-
C20	Anisol	913	910	-	-	-	-	-	-	-	-	-	-	-	-	0.4 ± 0.2	0.1	0.9	0.4 ± 0.3	0.1	1.1	1.1
C21	Benzaldehyde	929	930	10.8 ± 6.2	2.5	28.0	8.4 ± 3.5	3.1	20.2	7.5 ± 4.5	2.4	18.4	9.1 ± 3.3	4.4	18.2	4.4 ± 2.5	0.3	14.3	3.9 ± 1.5	1.5	6.8	6.8
C22	Heptanol	957	952	-	-	-	-	-	-	-	-	-	-	-	-	0.2 ± 0.3	0.1	1.4	0.2 ± 0.2	0.1	0.4	0.4
C23	Octen-3-ol	962	959	-	-	0.4 ± 0.2	0.1	1.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C24	Hexanoic acid	973	970	2.1 ± 2.0	0.1	10.1	-	-	-	1.1 ± 0.8	0.3	3.9	2.1 ± 1.7	0.4	7.7	1.2 ± 1.0	0.2	4.8	0.8 ± 0.6	0.2	2.1	2.1
C25	Octan-4-ol	973	975	0.9 ± 1.2	0.1	7.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C26	Octanal	981	980	1.4 ± 1.6	0.1	11.4	0.5 ± 0.3	0.1	1.8	1.2 ± 1.0	0.2	6.6	0.9 ± 0.9	0.1	5.2	0.9 ± 0.8	0.1	4.5	0.3 ± 0.2	0.1	0.7	0.7
C27	p-Methylanisol	1004	995	-	-	-	-	-	-	0.9 ± 1.2	0.1	6.1	0.4 ± 0.5	0.2	1.7	0.5 ± 0.5	0.1	2.4	2.7 ± 2.0	0.2	7.7	7.7
C28	Benzyl alcohol	1006	1009	-	-	-	-	-	-	-	-	-	-	-	-	1.6 ± 1.4	0.2	7.6	2.1 ± 2.3	0.1	7.0	7.0
C29	Phenylacetaldehyde	1012	1010	1.8 ± 2.2	0.2	9.9	2.8 ± 1.8	0.5	9.8	15.8 ± 1	0.8	39.1	33.6 ± 12	12	57.8	3.9 ± 2.2	0.2	11.2	4.9 ± 3.5	0.9	16.2	16.2
C30	p-cymene	1015	1012	4.6 ± 3.4	0.6	19.1	0.4 ± 0.3	0.1	1.9	-	-	0.7 ± 0.3	0.1	1.2	-	-	-	-	-	-	-	-
C31	Limonene	1025	1021	0.7 ± 0.8	0.1	4.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C32	β-Isophorone	1027	1026	-	-	-	-	-	0.7 ± 1.1	0.1	4.2	-	-	-	-	-	-	-	-	-	-	-
C33	Acetophenone	1036	1035	7.0 ± 2.6	0.7	13.8	0.2 ± 0.1	0.1	0.9	0.2 ± 0.1	0.1	0.5	2.1 ± 1.5	0.2	4.8	0.5 ± 0.6	0.1	3.1	0.9 ± 0.7	0.1	3.0	3.0
C34	Phenylethanol	1037	1046	-	-	-	-	-	-	-	-	-	-	-	-	0.4 ± 0.3	0.1	1.1	0.5 ± 0.3	0.1	1.0	1.0
C35	(E)-2-Oct-2-en-1-ol	1052	1050	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.6	0.6	-	-	-
C36	trans-Furanoid-linalol oxide	1058	1058	0.9 ± 0.4	0.4	2.2	0.7 ± 0.3	0.1	1.8	1.9 ± 1.1	0.5	6.3	1.2 ± 0.9	0.1	4.1	1.3 ± 0.7	0.4	3.6	0.9 ± 0.6	0.1	2.6	2.6
C37	Methyl benzoate	1072	1059	-	-	0.2 ± 0.2	0.1	1.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-

(Continues)

**TABLE 1** (Continued)

N <sup>o</sup>	Compounds	RI (lit) <sup>b</sup>	RI <sup>c</sup>	Chestnut grove <sup>d</sup> (CH01 - CH50)			Spring maquis (MP01 - MP45)			Autumn maquis (MA01 - MA30)			Spring (PR01 - PR41)			Summer maquis (ME01 - ME29)			Honeydew maquis (MM01 - MM48)			Blend honey (MM49 - MM74)		
				Mean <sup>d</sup>	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
C38	Octanol	1063	1065	0.5 ± 0.3	0.1	1.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C39	cis-Furanoid-linalool oxide	1072	1073	1.4 ± 0.5	0.3	2.6	0.6 ± 0.3	0.2	1.7	-	-	-	1.1 ± 0.3	0.5	2.0	1.1 ± 0.4	0.4	2.2	1.2 ± 0.6	0.2	2.9	1.2 ± 0.5	0.2	2.4
C40	p-Cymene	1075	1075	-	-	-	0.7 ± 0.7	0.1	3.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C41	β-Phenylethanol	1085	1077	-	-	-	-	-	-	-	-	-	3.7 ± 1.6	1.6	5.8	2.8 ± 2.0	0.9	6.7	4.2 ± 3.2	0.4	19.2	2.8 ± 2.4	0.2	9.4
C42	Nonanal	1076	1082	2.8 ± 1.5	0.7	7.8	1.7 ± 1.5	0.2	9.4	-	-	-	2.7 ± 1.8	0.4	7.6	3.5 ± 2.6	0.7	10.0	1.1 ± 1.8	0.2	10.3	1.0 ± 1.3	0.1	5.3
C43	Linalool	1086	1084	-	-	-	1.8 ± 1.4	0.4	7.1	-	-	-	7.3 ± 9.0	0.2	32.3	-	-	-	-	-	-	-	-	-
C44	3-acetyl-2,5-dimethylfuran	1084	1085	-	-	-	-	-	-	0.2 ± 0.1	0.1	0.4	-	-	-	-	-	-	-	-	-	-	-	-
C45	Hotrienol	1083	1085	2.3 ± 1.7	0.1	8.0	2.6 ± 4.2	0.1	24.2	-	-	-	5.2 ± 4.5	0.7	10.5	-	-	-	-	-	-	-	-	-
C46	Isophorone	1100	1092	1.3 ± 0.5	0.1	3.0	0.9 ± 0.5	0.3	2.8	3.48 ± 5	20.0	42.0	6.0 ± 7.3	0.1	29.3	0.8 ± 1.2	0.1	4.6	3.3 ± 2.6	0.4	13.5	2.1 ± 3.1	0.1	15.1
C47	4-Oxo-isophorone	1122	1123	0.6 ± 0.3	0.1	1.9	0.8 ± 0.9	0.1	5.6	3.6 ± 1.4	2.0	8.3	1.6 ± 1.4	0.3	6.4	0.4 ± 0.3	0.2	0.9	0.7 ± 0.8	0.2	4.9	0.8 ± 0.6	0.1	2.3
C48	Lilac aldehyde (stereoisomer 1)	1124	1123	-	-	-	1.9 ± 2.0	0.4	11.8	-	-	-	5.2 ± 2.4	1.3	8.9	0.4 ± 0.5	0.2	2.6	0.4 ± 0.2	0.1	0.7	0.6 ± 0.5	0.1	2.1
C49	Citronellal	1129	1125	-	-	-	0.6 ± 0.3	0.1	1.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C50	Dihydrolinalool	1118	1125	-	-	-	-	-	-	-	-	-	1.2 ± 0.6	0.5	3.0	-	-	-	0.5 ± 0.3	0.2	1.4	0.6 ± 0.4	0.2	1.7
C51	4-Vinylanisol	1130	1126	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.7 ± 0.3	0.2	1.1	1.1 ± 1.1	0.2	4.0
C52	2,2-dimethyl-4-oxocyclohexane-1-carbaldehyde	1132	1130	-	-	-	-	-	-	2.9 ± 0.9	1.1	5.2	-	-	-	-	-	-	-	-	-	-	-	-
C53	Lilac aldehyde (stereoisomer 2)	1133	1138	-	-	-	0.8 ± 0.9	0.1	5.3	-	-	-	10.1 ± 4	2.4	16.5	0.4 ± 1.0	0.4	5.1	0.7 ± 0.6	0.1	1.8	0.5 ± 0.6	0.1	1.8
C54	Ethyl benzoate	1150	1144	-	-	-	0.2 ± 0.1	0.1	0.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C55	trans-Pyranoide-linalo-ol oxide	1144	1144	0.5 ± 0.4	0.1	1.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C56	Lilac aldehyde (stereoisomer 3)	1146	1147	-	-	-	0.3 ± 0.1	0.1	0.9	-	-	-	4.6 ± 1.9	1.1	8.1	0.1 ± 0.4	0.7	2.2	0.4 ± 0.3	0.1	1.0	0.4 ± 0.3	0.1	1.4
C57	Nonanol	1149	1150	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.8 ± 2.3	0.5	9.7	1.0 ± 0.9	0.1	3.2
C58	cis-Pyranoide-linalool oxide	1148	1151	0.8 ± 0.4	0.3	2.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C59	Menthofuran	1150	1152	1.1 ± 1.0	0.2	6.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C60	Benzoic acid	1163	1160	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3 ± 0.2	0.1	0.6
C61	Methyl salicylate	1171	1165	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5 ± 0.3	0.1	1.1	-	0.4	0.4
C62	α-Terpineol	1176	1170	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.7 ± 0.3	0.1	1.5	0.5 ± 0.4	0.1	1.5
C63	Octanoic acid	1167	1172	5.0 ± 2.2	0.4	11.5	-	-	-	0.3 ± 0.2	0.1	0.8	1.7 ± 1.2	0.3	6.0	2.9 ± 1.4	0.5	7.0	1.9 ± 1.7	0.2	7.7	1.3 ± 1.1	0.1	4.2
C64	5-Hydroxymethylfurfural	1176	1173	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2 ± 0.1	0.1	0.8	0.2 ± 0.1	0.1	0.5
C65	Decanal	1180	1184	0.9 ± 0.8	0.1	3.7	0.9 ± 0.5	0.1	3.2	0.5 ± 0.2	0.1	1.1	1.3 ± 0.6	0.2	2.8	1.0 ± 0.7	0.3	3.0	0.9 ± 1.0	0.2	5.4	0.8 ± 0.8	0.1	4.4
C66	Octylacetate	1188	1184	0.7 ± 0.7	0.1	3.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C67	p-Menthen-9-al (isomer 1)	1188	1189	-	-	-	0.5 ± 0.4	0.1	1.9	-	-	-	1.9 ± 0.4	1.2	2.7	-	-	-	-	-	-	-	-	-
C68	p-Menthen-9-al (isomer 2)	1190	1191	-	-	-	0.4 ± 0.4	0.1	2.2	-	-	-	1.7 ± 0.4	0.5	2.5	-	-	-	-	-	-	-	-	-
C69	m-Anisaldehyde	1194	1195	0.2 ± 0.1	0.1	0.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C70	p-Anisaldehyde	1218	1215	0.6 ± 0.9	0.1	5.3	11.7 ± 4.0	0.7	21.3	-	-	-	0.7 ± 0.9	0.1	4.6	0.2 ± 0.5	0.2	1.9	1.8 ± 1.3	0.2	3.3	7.0 ± 5.3	0.9	17.9
C71	(Z)-Cinnamaldehyde	1219	1222	0.6 ± 0.6	0.1	2.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C72	(E)-Cinnamaldehyde	1234	1231	0.7 ± 0.6	0.1	2.2	0.6 ± 0.4	0.1	1.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C73	2,3,5-Trimethylphenol	1260	1251	-	-	-	0.8 ± 0.1	0.1	5.0	4.6 ± 2.5	1.3	13.2	0.6 ± 0.6	0.1	2.0	0.1 ± 0.2	0.2	0.6	0.2 ± 0.3	0.1	1.5	1.0 ± 2.1	0.1	9.8

(Continues)

**TABLE 1** (Continued)

N <sup>ca</sup>	Compounds	RI (lit) <sup>b</sup>	RI <sup>c</sup>	Chestnut grove <sup>d</sup> (CH01 - CH50)		Spring maquis (MP01 - MP45)		Autumn maquis (MA01 - MA30)		Spring (PR01 - PR41)		Summer maquis (ME01 - ME29)		Honeydew maquis (MM01 - MM48)		Blend honey (MM49 - MM74)							
				Mean <sup>d</sup>	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max					
C74	4-Ethylguaiaicol	1257	1251	-	-	-	-	-	-	-	-	-	-	1.4 ± 1.0	0.3	4.1	1.2 ± 1.9	0.1	9.3				
C75	4-Propylanisol	1254	1257	-	-	14.7 ± 5	3.0	29.4	-	-	2.1 ± 1.8	0.2	6.3	2.0 ± 1.2	1.0	3.3	10.8 ± 7.7	1.8	31.0				
C76	4-Hydroxy-2-methylacetophenone	1254	1257	-	-	-	-	-	-	-	-	-	-	-	1.9	1.9	-	-	-				
C77	Nonanoic acid	1263	1260	5.9 ± 2.4	1.5	13.5	-	-	0.7 ± 0.7	0.1	2.5	2.9 ± 1.3	0.5	6.4	5.1 ± 2.4	0.3	10.6	6.8 ± 3.3	0.5	13.8	2.5 ± 2.3	0.2	9.0
C78	Decanol	1264	1265	-	-	-	-	-	-	-	-	-	-	1.1 ± 0.7	0.3	2.1	0.6 ± 0.3	0.2	1.2				
C79	2-Aminoacetophenone	1261	1266	11.4 ± 5.4	2.7	26.5	-	-	-	-	-	-	3.6 ± 3.9	3.2 ± 2.4	0.2	13.4	9.9 ± 9.1	0.5	38.3				
C80	Thymol	1267	1272	1.5 ± 2.6	0.1	9.6	-	-	-	-	-	-	-	-	-	-	-	-	-				
C81	Carvacrol	1278	1280	0.2 ± 0.2	0.1	1.0	-	-	-	-	-	-	-	-	-	-	-	-	-				
C82	Undecanal	1287	1286	-	-	-	-	-	0.8 ± 0.4	0.1	1.6	-	-	-	-	-	-	-	-				
C83	3,4,5-Trimethylphenol	-	1290	-	-	2.6 ± 3.8	0.1	22.1	27.1 ± 7	13.7	43.9	1.5 ± 2.3	0.1	9.4	0.2 ± 0.3	0.3	1.6	1.1 ± 1.9	0.2	8.1	4.3 ± 8.8	0.2	38.6
C84	Methyl anthranilate	1308	1300	-	-	-	-	-	-	-	1.4 ± 0.9	0.2	3.5	-	-	-	-	-	-				
C85	p-Acetanisol	1310	1306	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5 ± 0.2	0.1	0.9		
C86	cis-p-Mentha-1(7),8-dien-1-hydroperoxide	-	1348	-	-	-	-	-	-	-	0.4 ± 0.1	0.2	0.7	-	-	-	-	-	-				
C87	(E)-β-Damascenone	1351	1352	-	-	1.1 ± 0.8	0.3	4.8	-	-	-	-	-	-	-	-	-	-	-				
C88	Decanoic acid	1353	1362	-	-	-	-	-	0.3 ± 0.1	0.1	0.7	1.5 ± 1.1	0.1	6.8	2.0 ± 1.3	0.7	6.7	5.4 ± 4.2	0.4	18.6	1.7 ± 2.0	0.5	10.1
C89	Dodecanal	1389	1385	-	-	-	-	-	-	-	-	-	-	-	0.9 ± 0.5	0.1	2.2	0.6 ± 0.2	0.3	1.0			
C90	4-Methoxypropiofenone	1415	1420	-	-	2.8 ± 1.4	0.2	5.6	-	-	-	-	-	1.1 ± 0.8	0.3	1.9	3.6 ± 3.0	0.2	9.8				
C91	4-Aminoacetophenone	1440	1446	0.3 ± 0.3	0.1	1.3	-	-	-	-	-	-	0.1 ± 0.2	0.3	0.6	-	-	-	-				
C92	Methyl 3,5-dimethoxybenzoate	-	1494	-	-	-	-	-	-	-	0.5 ± 0.2	0.2	0.8	-	-	-	-	-	-				
C93	Methyl vanillate	1516	1520	-	-	-	-	-	-	-	-	-	-	0.4 ± 0.2	0.2	0.5	1.0 ± 0.8	0.3	3.1				
C94	Dodecanoic acid	1556	1554	-	-	-	-	-	-	-	-	-	-	1.6 ± 1.0	0.3	6.0	0.9 ± 0.8	0.3	2.9				
C95	Methyl syringate	-	1722	-	-	-	-	-	-	-	0.8 ± 1.0	0.1	4.1	0.4 ± 0.2	0.1	0.5	0.7 ± 0.6	0.3	1.8				
C96	Tetradecanoic acid	1748	1746	-	-	-	-	-	-	-	-	-	-	1.4 ± 0.8	0.3	5.0	1.1 ± 0.9	0.2	3.8				
C97	Nonadecane	1900	1900	-	-	-	-	-	-	-	-	-	-	1.0 ± 0.7	0.2	3.1	0.6 ± 0.3	0.2	1.1				
C98	Hexadecanoic acid	1959	1960	-	-	-	-	-	-	-	-	-	-	3.5 ± 1.8	0.2	8.5	2.8 ± 1.2	0.7	5.7				
C99	Henicosane	2100	2096	-	-	-	-	-	0.1 ± 0.1	0.1	0.2	-	-	1.3 ± 1.2	0.2	7.0	1.0 ± 0.5	0.1	1.8				
C100	Nonadecanoic acid	-	2160	-	-	-	-	-	-	-	-	-	-	1.9 ± 1.4	0.2	7.0	1.7 ± 0.9	0.3	3.8				
C101	Tricosane	2300	2305	-	-	-	-	-	0.1 ± 0.1	0.1	0.3	0.4 ± 0.2	0.1	0.7	0.9 ± 0.4	0.3	1.7	2.1 ± 1.1	0.5	5.2	2.5 ± 1.3	0.7	5.7
C102	Tetracosane	2400	2400	-	-	-	-	-	-	-	-	-	-	1.1 ± 0.6	0.3	2.6	1.4 ± 0.7	0.5	3.4				

<sup>a</sup>: Order of elution is given on apolar column (Rtx-1)

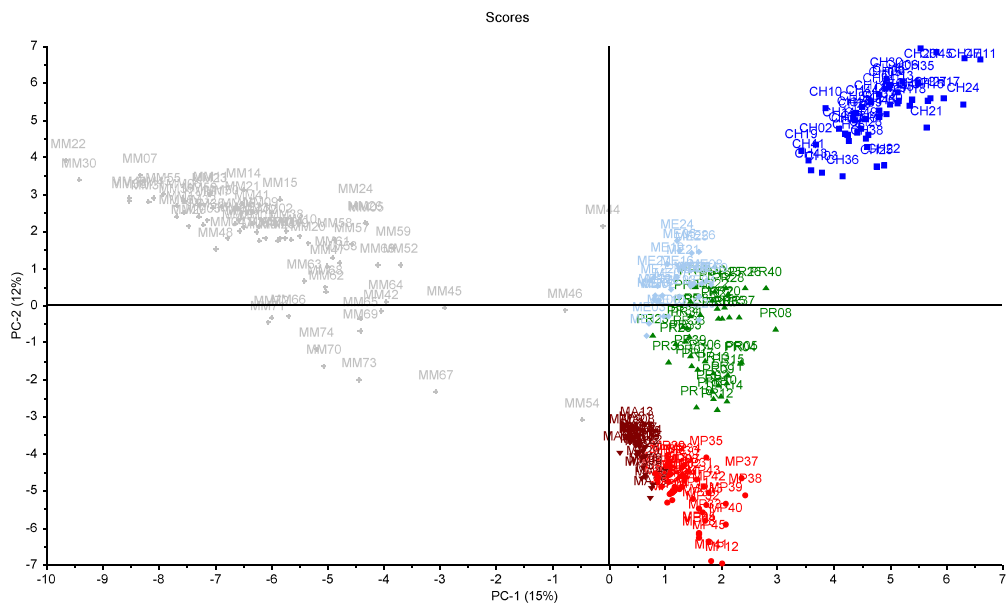
<sup>b</sup>: Retention indice of literature on the apolar column reported from references (König *et al.*, 2001; Nist, 2008)

<sup>c</sup>: Retention indice on the Rtx-1 apolar column

<sup>d</sup>Compound values are expressed as relative percentages obtained by SPME/GC-FID without any internal standardization.

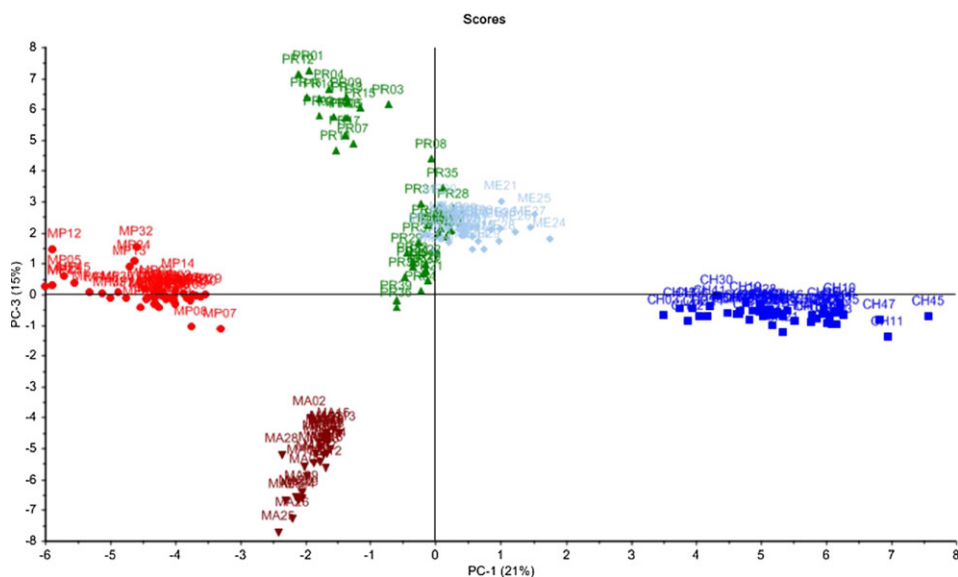
<sup>e</sup>: Volatile composition of "chestnut grove", "spring maquis", "autumn maquis", "summer maquis" honeys had already been reported in Yang *et al.*, 2012a, 2012b, 2014c, 2014a et 2014b, respectively





(A) PCA score plot (PC1/PC2) of volatile composition of 269 Corsican honeys

(CH: “chestnut grove” honey; PR: “spring” honey; ME: “summer maquis” honey; MA: “autumn maquis” honey; MP: “spring maquis” honey; MM: honeydew & blend honey)



(B) PCA score plot (PC1/PC3) of volatile composition of 195 Corsican blossom honeys

(CH: “chestnut grove” honey; PR: “spring” honey; ME: “summer maquis” honey; MA: “autumn maquis” honey; MP: “spring maquis” honey)

**FIGURE 1** A PCA score plot (PC1/PC2) of volatile composition of 269 Corsican honeys. (CH: “chestnut grove” honey; PR: “spring” honey; ME: “summer maquis” honey; MA: “autumn maquis” honey; MP: “spring maquis” honey; MM: honeydew & blend honey). B PCA score plot (PC1/PC3) of volatile composition of 195 Corsican blossom honeys (CH: “chestnut grove” honey; PR: “spring” honey; ME: “summer maquis” honey; MA: “autumn maquis” honey; MP: “spring maquis” honey)

C53 & C56: 20.8%) and *p*-menthen-9-al isomers (C67 & C68: 3.7%), while these components were absent (or present at a very low percentage) in other “spring” samples. Another chemical marker of *Citrus* unifloral honey,<sup>11</sup> methyl anthranilate C84, was also detected in volatile fractions of “spring clementine” honeys. This component was not reported in “spring non-clementine” honey compositions, which exhibited high amounts of benzaldehyde C21 (8.9%) and phenylacetaldehyde C29 (19.9%) compared with “spring clementine” samples.

The general structure of the dendrogram (Figure 2) produced by Ward’s method cluster analysis reinforces the clustering observed by PCA. Indeed, CA performed on volatile data from 195 honey samples allowed us to distinguish the following five groups: “chestnut grove” (CH01–CH50), “spring maquis” (MP01–MP45), “autumn maquis” (MA01–MA30) and “spring clementine” (PR01–PR17) honeys, which were separated into distinctive clusters, while the “spring non-clementine” (PR18–PR41) and

**TABLE 2** Statistics of the PLS regression models for the volatile composition of Corsican honeys

Honey ranges	SEC	R <sup>2</sup>	FN	SEP	Q <sup>2</sup>
Chestnut grove	0.073	0.96	3	0.76	0.96
Autumn maquis	0.082	0.96	3	0.085	0.97
Summer maquis	0.079	0.96	7	0.143	0.88
Honeydew	0.101	0.97	3	0.148	0.95
Spring maquis	0.079	0.97	2	0.098	0.97
Spring	0.099	0.96	5	0.142	0.92

SEC: Standard error of calibration;

R<sup>2</sup>: Coefficients correlation in calibration;

SEP: Standard error or prediction;

Q<sup>2</sup>: Coefficients correlation in prediction;

FN: Factor number.

“summer maquis” (ME01–ME29) honeys were classed into the same group.

### 3.5 | Data analysis of honeydew and blend honeys

Differentiation of Corsican honeydew and blend honeys according to volatile chemical variability is shown in Figure 3. The first and second axes (PC1/PC2) of the PCA represent 43% of the total spectral

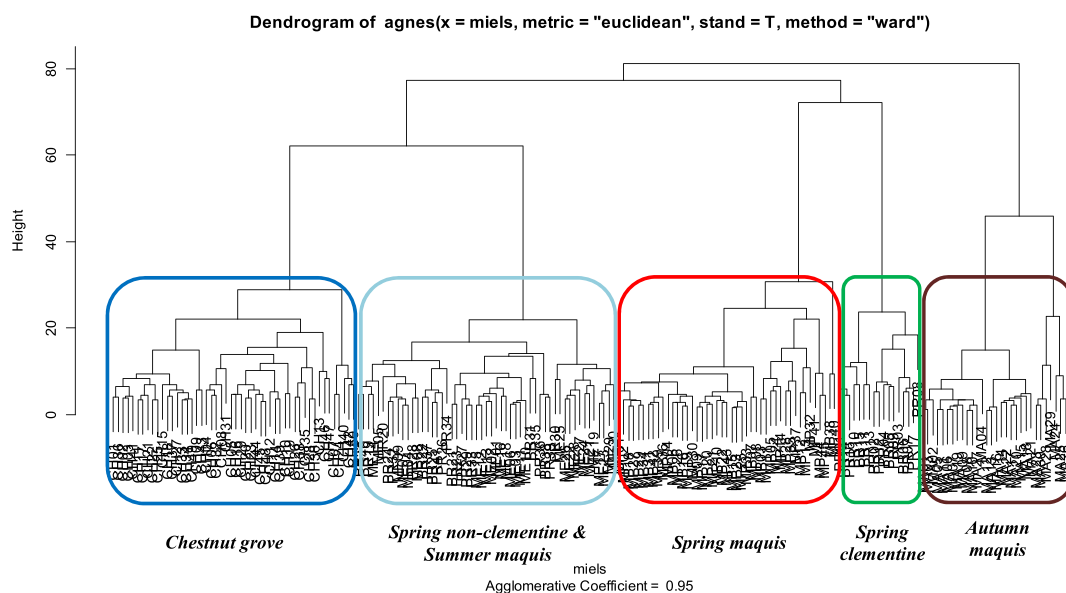
variance. The honeydew and blend honeys were separated by PCA into two main groups. The first group (negatively correlated on the PC1 axis) of 50 honey samples, including 43 *Metcalfa* honeydew (MM01–MM43), two traditional honeydew (MM47 and MM48), and five blend honeys (MM49–MM53), were characterized by higher amounts of 3-furaldehyde (C10: 24.2%) and linear acids (C77 and C88: 23.6%) than samples in the second group (positively correlated on the PC1 axis), which included 20 blend honeys (MM55–MM74, C10: 13.4%, C77 and C88: 11.1%). The latter samples showed complex chemical compositions leading to three subgroups according to nectariferous origins: seven honeys (MM55–MM61) exhibited a high content of 2-aminoacetophenone C79 (21.3%), a chemical marker of *C. sativa* nectar contribution; seven samples (MM68–MM74) were characterized by high amounts of two specific components of nectariferous *E. arborea* input, *p*-anisaldehyde C70 (12.5%) and 4-propylanisol C75 (16.1%); and six samples (MM62–MM67) possessed an intermediate chemical profile between the two previous subgroups with 2-aminoacetophenone C79 (8.2%) associated with *p*-anisaldehyde C70 (6.6%) and 4-propylanisol C75 (7.5%), suggesting combined nectar contributions of *C. sativa* and *E. arborea*.

Finally, three “traditional honeydew” samples (MM44–MM46) and one blend honey (MM54) exhibited an atypical volatile composition with high content of benzaldehyde (C21: 10.2–14.3%) associated with

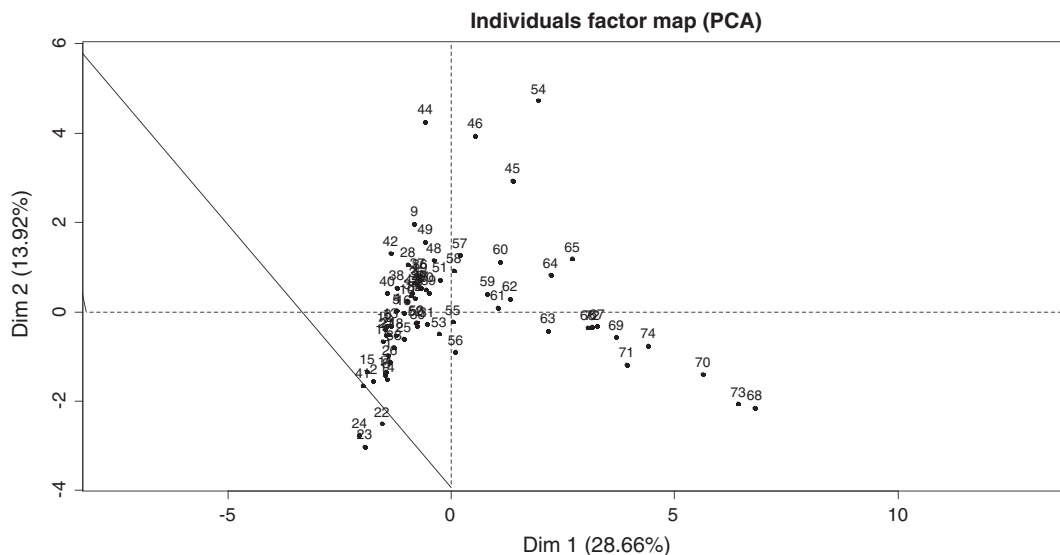
**TABLE 3** Classification matrix obtained in prediction (PLS-DA regression) honey origin

Honey ranges	Number of latent variables	CH	MA	ME	MM	MP	PR	False negative samples	False positive samples
CH (n = 25)	3	25	0	0	0	0	0	0	0
MA (n = 22)	3	3	0	22	0	0	0	0	0
ME (n = 20)	7	7	0	0	20	0	0	1	0
MM (n = 14)	3	3	0	0	0	14	0	0	0
MP (n = 14)	2	2	0	0	0	0	14	0	0
PR (n = 36)	5	5	0	0	0	0	0	35	1

CH: “chestnut grove” honey; MA: “autumn maquis” honey; ME: “summer maquis” honey; MM: “honeydew maquis”; MP: “spring maquis” honey; PR: “spring” honey



**FIGURE 2** Dendrogram of volatile composition of 195 Corsican blossom honeys



**FIGURE 3** PCA score plot (PC1/PC2) of volatile composition of 74 Corsican honeydew and blend honeys (MM01 – MM74)

an abundance of linear aldehydes (62.2%) for sample MM44 or with a high content of isophorone for samples MM45 and MM46 (**C46**: 9.4%, 13.5%, respectively). Finally, MM54 was dominated by isophorone **C46** (15.1%), 2,3,4-trimethylphenol **C73** (9.8%), and 3,4,5-trimethylphenol **C83** (38.6%), which assumes a contribution of *A. unedo* nectar.

## 4 | CONCLUSIONS

The volatile fraction of 269 Corsican honeys was characterized by 105 compounds amounting to 60.7–99.7% of the total composition. This study is the first to report the chemical composition of Corsican honeydew honey, especially Metcalfa honeydew. This approach allowed differentiation of Corsican honeydew honey and blossom honey based on their richness of 3-furaldehyde in the category of “honeydew maquis”. For the different blossom honeys, some characteristic compounds were also identified for different botanical origins, including 2-aminoacetophenone (“chestnut grove” honey), *p*-anisaldehyde and 4-*n*-propylanisole (“spring maquis”), isophorone and 3,4,5-trimethylphenol (“autumn maquis”), and isomers of lilac aldehyde and *p*-menthen-9-*al* (“spring clementine”). The “spring non-clementine” and “summer maquis” honeys possessed similar volatile compositions with a high content of toluene and phenylacetaldehyde. The volatile classification of Corsican honeys was in accordance with the pollinic and sensorial typologies of honeys obtained using a traditional approach.

These results also showed that chemometric analysis of volatile fraction data is useful for detecting the nectar contributions of plant species in honeys with complex melliferous origins. As shown for the blend samples, the high content of 2-aminoacetophenone (marker of “chestnut grove”), *p*-anisaldehyde (marker of “spring maquis”), isophorone (marker of “autumn maquis” honey) and 3-furaldehyde (marker of “honeydew”) indicated the *C. sativa*, *E. arborea*, *A. unedo* nectar and honeydew contributions, respectively. The results of this study are expected to contribute to the

development of an innovative approach using statistical analysis of volatile fractions, thereby allowing researchers to obtain discriminant chemical markers to determine the botanical origins of honeys. In addition, PCA analysis and PLS-DA regression could be effective for identifying class and/or predicting Corsican honeys’ botanical origins in new production through comparisons with the database established in this study.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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