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Original Article

CANARY HONEYS FROM TENERIFE:
1. COMPOSITION OF VOLATILE COMPONENTS

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Abstract

Tenerife's melliferous flora is characterised by the presence of a large number of endemic species and a distinct zonation of their growth, which determines the local production of unique varieties of honey not found in other parts of the world. For the first time, the composition of volatile organic compounds (VOCs) in Tenerife honey was studied through the use of nine samples of monofloral (broom, tajinaste, tedera, relinchon, and barrilla) and four samples of multifloral honeys. The VOC composition of the studied samples contained 110 representatives of various classes of organic compounds identified by headspace microextraction in combination with gas chromatography-mass spectrometry (GC-MS): terpenes, alkanes and alkenes, aliphatic and aromatic alcohols and acids, carbonyl compounds, as well as several S-, N- and Cl-containing substances. The chemical composition of the samples turned out to be highly specific; only twenty two compounds were detected in all nine samples. The distinct zonation of Tenerife's honey flora is reflected in the VOC composition of the studied samples. For example, syringic acid hydrazide, a rare component of honey, is completely absent in honey from "high mountain" apiaries but is contained in noticeable quantities in honey from apiaries located at low altitudes. The presence of methyl 3,5-dimethoxybenzoate in Tenerife honeys, as well as some norterpenoids, indicates the likelihood of their high antioxidant and bactericidal activity.

Keywords: Canary honey, chemical composition, norterpenoids, volatiles

INTRODUCTION

From the point of view of commercial interest, fifteen types of multifloral honey in Europe are considered to be the main ones, although more than 100 species of plants producing monofloral honey are known on this continent (Oddo et al., 2004). The list of monofloral European honeys given by these authors mentions seven varieties of Canary honeys with the following Spanish names and their botanical predecessors: malpica (*Carlina xeranthemoides* L., Asteraceae), tajinaste azul (*Echium virenscens* DS, Boraginaceae), tajinaste (*Echium brevirame* Sprague et Huch., Boraginaceae), tagasaste (*Chamaecytisus proliferus* L., Fabaceae), relinchon (*Hirschfeldia incana* L., Brassicaceae), barrilla (*Mesembryanthemum crystallinum* L., Aizoaceae) and oregano (*Origanum virens* Hoffmanns. & Link, Lamiaceae). The first four varieties of honey come from plants endemic to the Canary Islands; the first two are found only on Tenerife and the third only on the island of La Palma (Santos Vilar et al., 2004). This publication does not mention two other varieties of monofloral honeys derived from the nectar of plants endemic to the Canary Islands: broom honey, also called "retama del Teide", the plant predecessor of which is *Spartocytisus supranubius* (Fabaceae), and poleo montuno (*Bystropogon origanifolius*, Lamiaceae). Both of these endemics, as well as the botanical precursor of malpica honey, *C. xeranthemoides*, belong to the flora of the subalpine zone and are found at altitudes up to 2300 m above sea level. A rare variety of monofloral honey is tedera honey, produced by bees from the nectar of the endemic Arabian pea variety, *Bituminaria bituminosa* var. *crassiuscula* (Fabaceae), growing in Tenerife at altitudes from 50 to 1500 m above sea level.

Persano-Oddo et al. (2004) divided all 108 mentioned varieties of European monofloral honeys in terms of their respective importance into three classes: abundant, medium and rare. All honeys from the Canary Islands are classified as class 2 (medium). On 13 January 2014, the European Commission approved the registration of Tenerife honey in the corresponding European registry. Since then it has had the Protected Designation of Origin (DOP) throughout the European community territory (Commission Implementing, 2014) which indicates the growing penetration of Tenerife honey into the pan-European beekeeping market and its growing interest among consumers.

Because of the unique nature of Tenerife's honey flora (Camacho Pérez, 1988; Santos Vilar, et al., 2004; Ramos & Ferreras, 2011), one would expect the chemical composition and properties of its honeys, including aroma, to be determined by volatile components in the nectar. However, the chemical composition of these varieties of honey has been poorly studied. Numerous publications provide data on the ontent of mineral components in them, including toxic metals (Hernanses et al., 2005; Frías et al., 2008; Díaz et al., 2019); others are devoted to the physicochemical characteristics of Tenerife honeys (Serra Bonvehí et al., 2004; Manzanares et al., 2011; Bentabol Manzanares et al., 2014; 2017) but mainly contain information about such basic indicators as water content and activity, acidity, electrical conductivity, invertase and diastase content.

Chemical information is limited to the content of aliphatic C_2–C_6 acids, mono-, di- and trisaccharides, proline and hydroxymethylfurfural. Despite the importance of these indicators, they do not say anything about such important properties as the aroma of honey and its potential medicinal properties. Canarian nectar honeys are among the least studied in terms of their chemical composition, including the compounds that determine their aroma. This paper presents for the first-time data on the VOC content of some varieties of these products.

MATERIALS AND METHODS

Materials

Nine commercially available samples of monofloral honey from Tenerife, barrilla, relinchón and tedera honey, as well as two samples of broom and four samples of tajinaste honeys were purchased in December 2022, in January, April and December 2023 from different local beekeepers selling their own bee products at local markets. The honey botanical source was as provided by the manufacturers. According to the information received from them, the broom honeys were obtained from apiaries located in the subalpine regions, at an altitude of about 2200 m above sea level. Tajinaste honey came from different apiaries located at altitudes of 1000-1200 m above sea level. The remaining monofloral honey, as well as all four samples of multifloral honey, were obtained from apiaries located at altitudes of 150-800 m above sea level (Tab. 1).

Determination of volatiles

The composition of volatile components of honey was determined according to a previously described method using headspace solid-phase microextraction coupled to gas chromatography-mass spectrometry, HS-SPME/GC-MS (Isidorov et al., 2012; 2015; 2023). Briefly, honey (5 g) was placed in a 50 ml conical flask, and then 20 ml of a saturated solution of NaCl in distilled water was added. It was closed with a polyethylene membrane and stirred until complete homogenisation. The solution was placed on a magnetic stirrer and the membrane was pierced with the needle of a SPME device with Divinylbenzene/Carboxen/Polydimethylsiloxane, DVB/CAR/PDMS fibre (Merck, Germany). After 1 h of exposure at room temperature (21±1°C), the fibre was placed into the injection port of an HP7890A gas chromatograph with a 5975C VL MSD Triple-Axis Detector (Agilent Technologies, USA) for 15 min. The apparatus was fitted with an HP

Table 1.
Studied Tenerife monofloral honey: local names, precursor plants and the altitude level of growth

Name	Species and family of plant precursor	Altitude level
Broom honey (retama del Teide)	*Spartocytisus supranubius*, Fabaceae	1200-2000 m
Tajinaste azul	*Echium virenscens* DS, Boraginaceae	500-1300 m
Tedera	*Bituminaria bituminosa* (L) var. *crassiuscula*., Fabaceae	50-1500 m
Relinchon	*Hirschfeldia incana* L., Brassicaceae	from sea level to 600 m
Barrilla	*Mesembryanthemum crystallinum* L., Aizoaceae	coastal zone

5-ms capillary column (30 m×0.25 mm i.d., 0.25 µm film thickness) with electronic pressure control and split/splitless injector. The latter was operated at 220°C in splitless mode. The helium flow rate through the column was 1 mL min^{-1} in constant flow mode. The initial column temperature was 40°C and rose to 180°C at a rate of 3°C min^{-1}. The mass selective detector acquisition parameters were as follows: the transfer line temperature 280°C, the MS source temperature 230°C, and the MS quadrupole temperature 150°C. The electron ionisation mass spectra were obtained at an ionisation energy of 70 eV. Detection was performed in the full scan mode. After integration, the fraction of separated components in the total ion current (TIC) was calculated. All analyses were carried out in duplicate.

A separate experiment determined the retention times of the *n*-alkanes used as standards in the calculation of chromatographic retention indices on the GC-MS equipment used. From 0.5 to 10 µl of C_5–C_{17}, *n*-alkanes were injected into a 16 ml vial for HS-SPME with a silicone membrane containing 5 ml of pure glycerol with the use of a 10 µl microsyringe, increasing the dose for each subsequent homologue. The mixture was thoroughly mixed and DVB/CAR/PDMS fibre was introduced into the gas phase above it for 2-3 s. The chromatogram of reference alkanes was recorded under the above conditions.

Component identification

To identify the components, two independent analytical parameters were used: mass spectrum and chromatographic retention index (*RI*). The mass spectra recorded during the analysis were compared with the use of a GC-MS data processing system with those contained in the NIST 14 library (NIST/EPA/NIH Library of Electron Ionisation Mass Spectra), as well as in a home library containing mass spectra of more than 650 volatile components of various bee products. The coincidence of spectra (match value) was usually within 800-950. The calculated *RI* values of the components were compared with those given from the collections of the NIST Chemistry WebBook (2022) and Tkachev (2008). Identification was considered reliable if the results of the computer search of the mass spectra library were confirmed by the experimental RI^{Exp} values, i.e., if their deviation from the published database values (RI^{Lit}) did not exceed ±10 u.i. If the result of mass spectrometric identification was not confirmed chromatographically due to the absence of *RI* values in the available databases, or if the RI^{Exp} and RI^{Lit} values differed by more than 10 u.i., identification was considered tentative.

Multivariate statistical analysis

The software RStudio and ggplot2 data package was used to conduct the principal component analysis (PCA) and for processing the results.

RESULTS

The chromatograms recorded during the analysis of volatile components using the described HS-SPME/GC-MS technique contained peaks arising from 67 to 98 components with a specific contribution to the total ion current of the chromatograms was at least 0.02%. According to their chemical structures, they belong to organic compounds of different classes and can be divided on this basis into ten groups shown in Table 2 along with individual representatives of each of them (the names of compounds whose contribution to the TIC in at least one honey sample exceeded 0.15% are given). The eleventh and twelfth groups of the table are formed by components that do not belong to the main groups (Others) and compounds that could not be identified (NN). The studied samples are arranged in Table 2 in order of decreasing altitude above sea level of the location of their apiaries reported by beekeepers: from the highland habitats of *S. supranubius*, the plant precursor of broom honey, to the coastal zone, the main habitat of *M. crystallinum,* the plant precursor of barrilla honey.

The chemical composition of VOCs in the studied samples is quite specific. Only twenty-two of 110 identified compounds were registered in all thirteen samples. These include five C_6–C_{17} alkanes, five aromatic compounds (toluene and *p*-cymene, benzaldehyde, benzeneacetaldehyde, and methyl 3,5-dimethoxybenzoate), four C_7–C_{10} straight aliphatic aldehydes, three monoterpenes (α-pinene, 3-carene, and limonene), two sulfur-containing components (dimethyl sulfide and dimethyl disulfide), as well as acetic acids, furfural, and chloroform. The compounds with the largest contribution to TIC include C_6–C_{19} alkanes and alkenes. In samples of monofloral honey, they reached 35%, but in three samples of multifloral honey, they did not exceed 14%.

The chromatograms of all the studied samples contained peaks in aliphatic carbonyl compounds, whose specific contribution to the TIC ranged between 10.7 and 32.1% in monofloral honeys and 16 and 28% in multifloral honeys. A large contribution to the TIC chromatograms was also made by the group of aromatic compounds formed by both alkylbenzenes (toluene, *p*-xylene, *p*-cymene, and *p*-cymenene) and their oxygen derivatives belonging to the group of aromatic aldehydes, alcohols, and esters. Terpene compounds, the next largest group of VOCs, contributed between 3.7 and 17.4% to the TIC in the case of monofloral honeys and from 1.1 to 7.4% in samples of multifloral honeys.

The remaining VOCs were represented by a few acids, of which acetic acid was present in all samples in amounts ranging from 0.9 to 4.2% TIC, C_2–C_8 alcohols (0.3–6.1% TIC), esters of aliphatic C_5–C_{10} acids (the richest in these compounds was one of multifloral honeys), as well as S- and Cl-containing compounds.

A comparison of the data shown in the Table 2 group composition of monofloral and multifloral honeys revealed some differences. Monofloral honeys turned out to be richer in terpene hydrocarbons (3.7-17.4% TIC) than multifloral honeys (1.1-7.4% TIC) as well as in alkanes (5.6-35.3% TIC and 6.6-23.9% TIC, respectively).

No indicator compounds were found among the VOCs of monofloral honeys, pointing to a specific plant precursor. At the same time, the studied samples contained compounds rarely mentioned as honey VOCs, including methyl 3,5-dimethoxybenzoate and 4-hydroxy-3,5-dimethoxybenzylhydrazide (syringic acid hydrazide), as well as several compounds usually classified as anthropogenic pollutants.

To point out differences among honey samples based on apiaries location, principal component analysis was used in the processing of relative TIC percentage of volatile compounds. Results are summarised in Fig. 1. The first and second principal components (PC1 and PC2) were used as axes. The PC1 explained 19% of the total variance and was positively related to (Z)-linalool oxide, linalool, lilac aldehydes, octanoic acid, acetol, 1-nonanol, 1-octene-3-ol, 2-heptanone, benzeneacetaldehyde, and damascenone; however, methyl-3,5-dimethoxybenzoate, 2,5-dimethylfuran, 2,3,5-trimethylfuran and 4-hydroxy-3,5-dimethoxybenzohydrazide contributed negatively to the PC1. On the other hand, the PC2 explained 14.2% of the variance and was mainly related to two terpene compounds (3-carene and γ-terpinene), several aliphatic esters, decanoic acid, (Z)-3-hexen-1-ol, cumene, methyl 3,5-dimethoxybenzoate, and 4-hydroxy-3,5-dimethoxybenzohydidrazide.

Fig. 1 shows a graph of the trends in honey composition according to their origin. Broom samples from high altitude regions were

Table 2.

Relative group composition (% of TIC) of volatiles of Canarian (Tenerife) monofloral and multifloral honey

Group	RI^{Exp}	Monofloral honey									Multifloral honey			
		broom 1	broom 2	tajinas-te 1	tajinas-te 2	tajinas-te 3	tajinas-te 4	tedera	Relinch-ón	barrilla	mf 1	mf 2	mf 3	mf 4
Terpene compounds, including:		**14.00 (12)***	**7.45 (8)**	**3.67 (9)**	**5.76 (14)**	**15.02 (15)**	**11.71 (8)**	**17.38 (20)**	**6.49 (10)**	**3.66 (8)**	**1.07 (6)**	**3.30 (5)**	**2.88 (7)**	**7.38 (6)**
- α-pinene	936	trace	trace**	0.37	0.43	trace	-***	0.23	0.95	0.38	0.20	0.25	0.19	trace
- 3-carene	1011	trace	-	0.46	0.82	0.41	-	0.40	0.58	0.35	0.42	0.31	trace	-
- limonene	1028	1.66	1.12	1.88	1.29	1.13	0.63	2.32	1.18	1.32	0.08	2.37	0.17	3.02
- β-(Z)-ocimeme	1042	-	-	-	0.47	trace	-	-	-	-	-	-	-	-
- β-(E)-ocimene	1048	-	-	trace	1.88	0.62	-	-	-	-	-	-	-	-
- γ-terpinene	1059	-	-	0.26	trace	0.21	-	0.31	0.70	0.35	trace	-	-	trace
- (Z)-linalool oxide	1074	4.45	1.98	0.48	-	1.22	2.78	1.68	0.44	0.36	0.24	0.23	0.31	1.78
- (E)-linalool oxide	1084	1.85	-	-	-	5.69	0.89	-	-	-	-	-	-	trace
- linalool	1101	0.92	-	-	-	-	0.60	-	-	-	0.24	0.23	0.31	-
- lilac aldehyde A	1141	0.99	1.46	-	-	-	trace	-	-	-	-	-	-	-
- lilac aldehyde B	1149	1.03	trace	-	-	1.02	0.73	-	-	-	-	-	-	-
- nerol oxide	1154	0.98	trace	-	-	0.74	0.60	0.47	0.94	-	-	-	-	0.88
- lilac aldehyde C	1164	1.24	0.97	-	-	0.43	0.73	-	-	-	-	-	-	-
- α-terpineol	1189	trace	1.60	-	-	1.30	-	0.40	-	-	-	-	-	-
- bornyl acetate	1286	-	-	-	-	0.38	-	0.13	-	-	-	-	-	-
- β-caryophyl-lene	1417		-	trace	trace	-	-	-	0.22	0.27	0.14	0.13	1.44	-
Aliphatic acids, including:		**4.72 (5)**	**8.75 (6)**	**1.21 (5)**	**2.21 (6)**	**2.99 (4)**	**5.20 (6)**	**8.03 (4)**	**2.61 (4)**	**2.41 (4)**	**4.01 (4)**	**5.54 (4)**	**4.43 (5)**	**8.76 (4)**
- formic acid	520	1.79	1.20	-	0.25	0.34	0.65	3.09	1.19	0.80	1.38	2.24	1.79	4.55
- acetic acid	602	1.54	1.67	1.04	0.94	0.88	1.93	3.99	0.70	1.11	2.34	2.82	1.52	4.21
- hexanoic acid	982	-	-	trace	trace	-	-	0.43	-	-	-	-	-	-
- octanoic acid	1182	0.67	1.23	-	trace	0.30	1.47	-	-	0.16	-	0.25	0.25	trace
- nonanoic acid	1270	0.72	3.55	trace	0.81	1.48	1.16	0.52	0.51	0.33	trace	-	0.21	trace
- decanoic acid	1379	trace	0.44	-	0.21	-	trace	-	0.22	-	0.29	0.24	0.67	-
Aliphatic alco-hols, including:		**4.84 (8)**	**4.39 (10)**	**2.72 (3)**	**1.06 (2)**	**6.07 (11)**	**1.69 (3)**	**4.53 (8)**	**0.31 (1)**	**2.40 (4)**	**3.25 (4)**	**4.28 (6)**	**4.54 (5)**	**1.83 (3)**
- ethanol	<500	trace	-	-	0.78	0.23	-	1.51	-	0.69	-	0.39	0.67	trace
- acetol	673	-	0.18	0.94	0.27	0.20	0.45	0.28	0.31	1.04	1.49	1.86	1.30	1.83
- 3-meth-yl-1-butanol	734	0.57	trace	0.20	-	trace	-	0.45	-	0.44	1.34	1.30	1.32	trace
- 2-meth-yl-1-butanol	737	trace	trace	-	-	-	-	0.39	-	0.23	-	-	-	-
- 3-meth-yl-2-butenol (prenol)	780	-	0.18	-	-	-	-	-	-	-	-	0.22	-	-
- 1-hexanol	866	0.78	0.38	1.58	-	-	-	-	-	-	-	-	-	-
- (Z)-3-hexen-1-ol	855	-	-	-	-	0.39	0.39	-	-	-	0.29	0.36	0.37	-
- 1-nonanol	1171	1.04	0.74	-	-	0.73	-	0.55	-	-	-	-	-	-
- 1-octene-3-ol	981	1.48	0.83		-	1.19	1.19	-	-	-	-	-	-	-
- 3-octanol	992	-	-	-	-	0.52	-	-	-	-	-	-	-	-
- 2-nonanol	1102	-	-	-	-	-	-	-	-	-	0.13	0.14	0.37	-

Aliphaic esters, including:		**-**	**-**	**-**	**-**		**-**	**-**	**-**	**1.18 (2)**	**0.17 (1)**	**0.15 (1)**	**1.39 (7)**	**-**
- isoamyl acetate	875	-	-	-	-	-	-	-	-	0.87	0.17	0.15	trace	--
- 2-methyl-1-butanol acetate	879	-	-	-	-	-	-	-	-	0.31	-	-	trace	-
- methyl hexanoate	926	-	-	-	-	-	-	-	-	-	-	-	0.15	-
- ethyl hexanoate	1001	-	-	-	-	-	-	-	-	-	-	-	0.29	-
- methyl octanoate	1126	-	-	-	-	-	-	-	-	-	-	-	0.17	-
- ethyl octanoate	1198	-	-	-	-	-	-	-	-	-	-	-	0.30	-
- methyl decanoate	1325	-	-	-	-	-	-	-	-	-	-	-	0.20	-
- ethyl decanoate	1394	-	-	-	-	-	-	-	-	-	-	-	0.28	-
Aliphatic carbonyls, including:		**26.50 (11)**	**19.50 (17)**	**29.16 (11)**	**10.73 (7)**	**19.22 (12)**	**32.11 (9)**	**23.17 (9)**	**19.93 (9)**	**20.61 (12)**	**24.03 (10)**	**21.24 (10)**	**16.00 (11)**	**27.7 (9)**
- acetone	501	-	1.31	-	-	-	-	-	-	-	-	1.41	trace	-
- isobutanal	555	-	trace	-	-	-	-	-	-	1.40	0.63	-	-	2.38
- isopentanal	650	0.33	0.27	1.03	-	0.09	0.90	1.24	-	2.55	2.32	2.23	1.98	2.75
- 2-methylbutanal	658	0.26	0.13	0.56		0.13	0.87	0.82	-	1.55	1.02	1.13	0.94	2.22
- 3-methyl-2-butenal (prenal)	776	-	0.53	-	-	trace	-	-	-	-	0.13	0.31	trace	-
- 2-heptanone	890	1.42	trace	0.50	-	-	1.07	0.67	-	-	-	-	-	trace
- heptanal	903	3.29	0.69	0.73	trace	0.72	3.62	2.03	0.33	0.53	0.68	0.54	0.97	trace
- 3-octanone	988	-	-	-	-	0.40	-	-	-	-	-	-	-	-
- octanal	1002	4.65	2.25	6.29	2.14	4.47	9.52	3.30	2.93	3.11	7.35	6.55	2.32	4.62
- nonanal	1104	13.42	6.79	13.29	6.01	7.70	12.44	9.82	12.19	7.88	9.28	7.40	8.15	11.60
- decanal	1107	0.85	3.50	5.65	2.03	2.89	3.19	3.36	3.44	2.37	2.33	1.45	1.20	4.06
- undecanal	1310	trace	0.48	0.35	0.55	-	0.51	0.32	0.60	0.36	0.18	0.22	0.34	-
- dodecanal	1412	-	-	0.52	trace	-	trace	-	0.44	0.23	0.11	trace	0.14	-
Aromatics, including		**15.60 (11)**	**27.60 (17)**	**13.05 (8)**	**24.62 (10)**	**24.54 (14)**	**8.03 (7)**	**18.89 (14)**	**15.54 (10)**	**16.06 (8)**	**23.40 (12)**	**25.99 (11)**	**31.60 (9)**	**9.81 (5)**
- toluene	766	1.37	trace	6.72	14.67	0.52	0.65	2.41	5.50	5.10	3.90	3.26	2.82	trace
- p-xylene	866	-	-	-	-	-	-	0.98	-	-	0.28	0.34	0.20	-
- benzaldehyde	962	4.67	10.12	0.60	4.16	8.30	1.09	1.12	0.20	2.01	0.75	0.98	0.51	2.40
- p-cymene	1023	trace	trace	1.06	0.60	0.18	trace	2.13	0.92	1.46	0.73	0.92	0.65	trace
- benzyl alcohol	1036	trace	1.50	0.44	-	0.92	0.83	0.52	trace	-	0.30	0.42	-	-
- benzeneacetaldehyde	1047	6.64	4.94	1.26	0.69	4.50	3.41	1.98	2.75	0.85	2.26	1.94	1.85	4.83
- p-cymenene	1089	-	-	1.32	trace	-	-	5.17	2.91	1.34	0.39	0.42	0.24	-
-2-phenylethanol	1112	-	1.16	0.58	-	1.37	0.90	-	1.42	-	0.09	0.22	-	-
- methyl salicylate	1194	1.96	0.63	-	-	-	-	0.72	-	1.07	-	-	-	-
- (E)-cinnamaldehyde	1270	-	0.28	-	-	-	-	-	-	0.24	0.49	0.45	-	-
- thymol	1295	-	-	-	-	-	-	-	0.53	-	-	-	-	-
- dehydro-ar-ionone	1350	-	-	-	-	-	-	-	-	-	0.25	0.47	-	-
- methyl 3,5-dimethoxybenzo-ate	1582	0.18	1.55	1.07	2.82	4.14	0.53	0.22	1.32	2.92	13.57	16.75	25.34	2.58

S-containing compounds, including		**2.27 (2)**	**trace (2)**	**8.77 (3)**	**11.03 (3)**	**4.99 (3)**	**7.53 (2)**	**4.03 (2)**	**8.35 (5)**	**4.43 (4)**	**9.58 (4)**	**7.01 (4)**	**3.75 (3)**	**4.42 (3)**
- methyl mercaptan	<500	-	-	-	-	-	-	-	0.25		-	-	-	-
- dimethylsulfide	518	1.89	trace	2.10	2.38	0.32	6.25	4.03	trace	2.55	trace	trace	trace	2.52
- dimethyldisulfife	742	0.38	trace	3.08	7.25	1.94	1.28	trace	1.58	1.49	3.53	3.09	1.44	0.85
- dimethyltrisulfide	965	-	-	3.59	1.39	2.74	-	-	6.09	0.39	4.90	3.89	2.32	1.05
- dimethyltetrasulfide	1211	-	-	-	-	-	-	-	0.44	-	0.28	0.03	-	-
Cl-containing compoinds, including:		**1.99 (1)**	**0.67 (3)**	**0.69 (2)**	**3.13 (3)**	**0.66 (2)**	**4.79 (1)**	**1.33 (1)**	**1.79 (2)**	**1.26 (2)**	**1.33 (1)**	**1.44 (1)**	**1.26 (1)**	**2.16 (1)**
- chloroform	615	1.54	0.12	0.69	1.88	0.41	4.79	1.33	0.70	1.06	1.33	1.44	1.26	2.16
- tetracloroethylene	806	-	-	-	-	-	-	-	1.09	-	-	-	-	-
- 1-hexyl chloride	866	-	-	-	0.61	-	-	-	-	-	-	-	-	-
- 1-octyl chloride	1060	-	0.32	-	0.64	0.25	-	-	-	0.20	-	-	-	-
Furans, including:		**5.45 (3)**	**13.70 (5)**	**5.14 (5)**	**0.93 (2)**	**6.00 (4)**	**5.62 (2)**	**2.00 (4)**	**1.64 (3)**	**14.08 (6)**	**8.03 (5)**	**8.94 (6)**	**7.65 (5)**	**14.2 (5)**
- 2,5-dimethylfuran	710	-	-	0.61	0.66	trace	-	trace	trace	3.39	2.07	2.03	1.99	trace
- 2,3,5-trimethylfuran	812	-	-	0.65	-	-	-	-	-	1.87	1.00	1.22	1.69	trace
- furfural	835	3.67	10.97	3.24	0.27	4.56	2.03	0.47	1.29	7.23	4.45	5.09	3.08	11.50
- furfurol	853	-	1.33	-	-	-	0.59	0.37	-	-	-	-	-	-
- 2-acetylfuran	912	-	0.94	0.20	-	0.88	-	-	-	-	0.24	0.27	0.24	0.60
- 2-pentylfuran	993	0.89	-	-	-	-	-	-	-	-	-	-	-	-
- 2-acety-5-methylfuran	1013	-	0.28	-	-	-	-	-	0.35	1.09	0.27	0.16	0.65	2.09
- 3-phenylfuran	1220	0.89	-	-	-	-	-	-	-	-	-	-	-	-
Alkane & alkenes, including:		**8.96 (9)**	**4.04 (11)**	**25.97 (16)**	**35.34 (16)**	**5.60 (13)**	**11.50 (11)**	**11.57 (10)**	**23.86 (18)**	**21.47 (20)**	**8.40 (14)**	**6.61 (13)**	**10.50 (12)**	**19.83 (11)**
- isoprene	508	-	-	-	-	-	-	-	-	-	-	-	3.20	-
- n-hexane	600	1.56	0.08	3.20	1.59	0.68	2.66	2.78	1.17	1.11	1.84	1.75	1.46	trace
- n-heptane	700	0.57	0.80	2.69	1.35	0.27	0.22	0.80	0.58	0.90	0.88	-	-	1.22
- 1-octene	791	0.81	trace	0.22	2.55	0.10	0.71	0.17	0.24	0.46	0.13	0.12	0.18	0.59
- n-octane	800	5.15	0.12	11.40	21.39	1.38	5.75	4.21	11.40	7.36	4.58	4.10	4.48	8.28
- n-pentadecane	1500	0.44	0.71	1.64	0.55	0.26	0.79	1.26	1.10	1.19	0.26	0.20	0.33	2.49
- 8-heptadecene	1677	-	0.90	1.31	1.80	-	0.53	0.40	0.93	2.58	0.29	0.14	0.27	trace
- n-heptadecane	1700	0.62	1.73	2.04	0.95	0.35	0.74	0.95	2.31	4.19	0.60	0.23	0.37	4.11
- 9-nonadecene	1890	-	-	-	-	-	-	-	trace	0.39	-	-	-	-
- n-nonadecane	1900	-	-	-	-	-	-	0.20	0.77	0.96	0.18	-	-	1.03
Other, including:		**12.30 (4)**	**8.03 (3)**	**4.24 (4)**	**0.49 (2)**	**2.91 (5)**	**3.58 (6)**	**4.28 (5)**	**4.07 (2)**	**5.43 (4)**	**4.80 (4)**	**4.40 (6)**	**0.82 (2)**	**2.70 (5)**
- diethyl ether	<500	2.94	-	2.82	-	0.54	0.93	2.68	-	-	-	-	-	trace
- 2,6-dimethylpyrazine	912	-	-	-	-	-	-	-	-	1.71	-	-	-	-
- isophorone	1119	-	-	-	-	-	0.64	-	-	-	-	-	-	trace

- safranal	1202	6.41	0.54	-	0.49	2.13	1.66	-	-	0.16	-	-	-	0.98
- HMF	1230	trace	-	-	-	-	2.99	-	-	-	-	-	-	-
- megastigmatriene $C_{13}H_{20}$	1282	-	-	-	-	-	-	-	-	-	0.28	0.42	0.08	-
- megastigmatriene $C_{13}H_{20}$	1340	-	-	-	-	-	-	-	-	-	0.33	0.40	trace	-
- 1,1,5-trimethyl-1,2-dihydronaphthalene	1350	-	-	1.41	-	-	-	0.31	-	-	-	-	-	-
- β-damascenone	1384	0.60	1.06	-	trace	-	0.34	-	-	-	0.11	trace	trace	trace
4-Hydroxy-3,-5-dimethoxybenzohydrazide	1772	-	-	-	-	-	-	0.10	0.22	0.20	0.35	0.71	0.82	trace
NN		**2.96 (3)**	**8.03 (9)**	**4.26 (5)**	**4.70 (6)**	**11.79 (12)**	**8.30 (7)**	**4.81 (11)**	**4.07 (7)**	**5.00 (10)**	**11.35 (13)**	**10.39 (15)**	**15.40 (11)**	**1.14 (1)**

* - the size of the group is given in parentheses; ** - less than 0.02% TIC; *** - substance not detected.

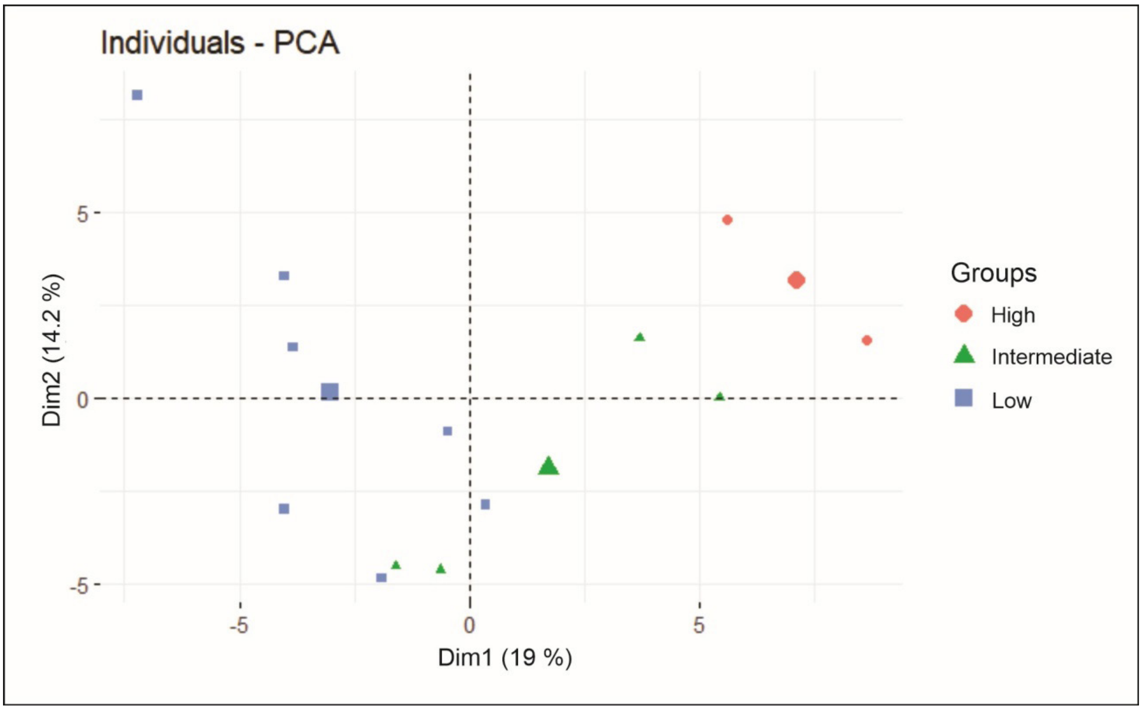

Fig. 1. Principal component analysis plot of the thirteen Canarian (Tenerife) honeys. Dim1 axis: first component; Dim2: second component. Different colour reflects the altitude above de sea level where honey samples were obtained: high (ca. 2200 m, broom), intermediate (1000-1200 m, tajinaste), and low (150-800 m, barrilla, relinchón, tedera and multifloral).

characterised by high positive values (>5) of the PC1 (on the right), while most samples from lower regions (barrilla, relinchón, tedera, and multifloral) had negative values in the same component (on the left). The honey samples from middle altitudes (tajinaste) were in a likewise position between high- and low-region honey. The plot reflects the relatively high concentration of those compounds with high positive loading scores in the PC1 in broom honey from the high lands, which shows the presence of 2,5-dimethylfuran and methyl 3,5-dimethoxybenzoate, and 2,5-dimethylfuran in the honey from low altitudes.

The third and fourth components showed a 11.3% and a 10.2% data variance, respectively. The relatively low cumulative variance explained by the first four components (54.7%) suggests considerable dispersion in the VOC composition across the samples.

DISCUSSION

The composition of volatile components contained in products used for human consumption is an important consumer characteristic. In the case of honey, this primarily depends on the aroma of the plant precursor material that the bees collect: nectar, honeydew or other sugar-rich plant secretions. The enormous chemical diversity of these precursors determines the equally wide range of VOC compositions of different honey varieties (Maga, 1983; Overton & Manura, 1994; Isidorov, 2021). They can be expected to be especially pronounced in areas whose melliferous flora is characterised by many endemic species, as well as by a well-defined zonality of plant belts. These features are inherent in beekeeping in the Canary Islands, particularly Tenerife. At the same time, Canarian nectar honeys are among the least studied in terms of their chemical composition.

The VOC composition of the studied Tenerife honey varieties given in Table 2 is, in general terms, typical for nectar honeys produced by *Apis mellifera* bees. All the groups of organic compounds that form it are characteristic of this species' honey in different parts of the world (Overton & Manura, 1994; Soria et al., 2009; Isidorov, 2021). However, several features can be noted in the groups and individual composition of representatives of these groups, most likely related to local geographical conditions.

Intragroup differences in individual monofloral honeys (broom and tajinaste) are natural and can be caused because they were produced in different apiaries and purchased at different times. In the group composition of VOCs, some noted features indicate the zonality of nectar sources for individual varieties of honey. For example, 4-hydroxy-3,5-dimethoxybenzylhydrazide (syringic acid hydrazide) was present in appreciable quantities in honeys from apiaries located at low altitudes above sea level but was completely absent in the products of "high mountain" apiaries, i.e., broom and tajinaste honey. This unusual chemical compound was previously discovered in Greek cotton honey with an average concentration of 209 $\mu g \cdot kg^{-1}$ (Alissandrakis et al., 2005), but its plant precursor has remained unidentified to date.

A distinctive feature of three multifloral honeys from "low-level" apiaries is the presence of cyclic unsaturated hydrocarbons $C_{13}H_{20}$, or megastigmatrienes. Previously, these compounds were found in the juice of the passion fruit *Passiflora edulis* Sims (Casimir et al., 1981), as well as in exudates of birch (*Betula pubescens* Erch.) buds and in European "birch-type" propolis (Isidorov et al., 2021). As far as we know, their presence in any honey has not previously been reported. It is noteworthy that here is a high content of methyl 3,5-dimethoxybenzoate in all analysed samples of Tenerife honey without exception. Its relative content in "high-mountain" honeys ranged between 0.2 and 4.4% TIC but reached 25% TIC in multifloral honeys from apiaries located at lower altitudes. This compound was probably first discovered in heather honey from New Zealand (Tan et al., 1989). High levels of this aromatic ester have previously only been reported in Manuka honey prepared by bees from the nectar of *Leptospermum scoparium*, which grows in New Zealand and Australia. The outstanding antimicrobial non-peroxide activity of this honey (Molan & Russell, 1988) is largely due to the presence of this compound and its biochemical precursor, leptosperine glycoside (gentibioside 3,5-dimethoxybenzoic acid) (Kato et al., 2019; Shen et al., 2016).

Among the volatile components of Tenerife honeys, there are also other compounds with well-documented biological activity. These include compounds with a 3,5,5-trimethylcyclohex-2-ene skeleton: isophorone, safranal, and β-damascenone. These cyclic compounds, which are degradation products of carotenoids, exhibit high radical scavenging capacity (Assimopoulou et al., 2005; Hosseinzadeh & Sadeghnia, 2005; Gómez-Caravaca et al., 2006). In addition, these norterpenoids are largely responsible for the aroma of Sardinian honey (Bianchi et al., 2005). For example, β-damascenone is the main compound responsible for the rose scent, and only a small concentration of this compound is needed to produce the aroma.

The presence of chloroform in all honeys studied is also noteworthy. Some authors state that this compound, like the aromatic hydrocarbon toluene, is of anthropogenic origin, i.e. a pollutant (Karabagias, 2022). However, in the case of Tenerife honey, it is difficult to agree with the total anthropogenic contamination of honey with these compounds, primarily due to the absence of any industrial or other sources of these substances on the island. In addition, chloroform and toluene are not components exclusively produced by humans: the release of these compounds has been recorded for many terrestrial plants (Isidorov, 1990).

From our point of view, chloroform, like other chlorine-containing compounds in Tenerife honey, is of natural origin, associated with the continuous addition of chlorides from the marine aerosol deposited everywhere on the soil of the island. Recent years have seen great progress in understanding the chlorine cycle in terrestrial ecosystems, including the recognition that emissions of volatile organic chlorines could be a significant export pathway of chlorine (Svensson et al., 2021). Plants intolerant to soil salinity must excrete excess chlorine even though chlorine is an essential element for living plants. One of the effective mechanisms may be conversion into a volatile form by biomethylation, whereby three chlorine atoms and one carbon atom are released into the gas phase as part of the $CHCl_3$ molecule. However, ours hypothesis needs to be confirmed.

Summarizing the above observations, the chemical composition of the volatile components of the studied samples of Tenerife honey is characterised by a relatively low percentage of monoterpene compounds, which are largely responsible for the aroma of honeys from the European continent. Their inherent odour is probably determined by the presence of norterpenoids. These carotenoid degradation products are characterised not only by a pleasant odour at a low olfactory threshold but also by high biological activity. The same important property is also characteristic of methyl 3,5-dimethoxybenzoate, present in all tested samples, a breakdown product of leptospermine glycoside with high antimicrobial potential. All this serves as a prerequisite for a detailed study of the chemical composition of the extractive components of Tenerife honey and the determination of its antibiotic potential.

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