Original Article

CANARY HONEYS FROM TENERIFE.

PART 2: COMPOSITION OF EXTRACTIVE COMPOUNDS

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Abstract

The composition of extractive organic compounds of seven samples of Tenerife honey is reported here for the first time. In the extractive composition of the studied samples, gas chromatography-mass spectrometry identified between 74 and 124 representatives of various classes of organic compounds, including aromatics, aliphatic acids, alcohols, and esters, as well as furofuran lignans, which are rarely found in honey. The chemical composition of extractives in the studied samples was highly specific: among 160 registered compounds, only forty were present in all seven samples. The most numerous groups, making the greatest contribution to the total ion current of the chromatograms, were formed by aromatic compounds, the main one being methyl syringate. The second most important group consisted of aliphatic acids, including a series of eleven even hydroxy acids C_8–C_{12}, characteristic of royal jelly and largely responsible for its outstanding antimicrobial activity. The high content of compounds with documented biological activity suggests the high therapeutic potential of the studied Tenerife honey samples.

Keywords: Canary honey, chemical composition, furofuran lignans, hydroxyl acids, norterpenoids, other aromatics

INTRODUCTION

Bee honey is a highly valuable food product and has a wide range of preventive and therapeutic effects (Boukraâ, 2013). While its nutritional value is determined by the consistently high content of easily digestible monosaccharides, its medicinal properties are associated with the presence of minor components, which vary significantly in both composition and quantity (Samarghandian et al., 2017). These parameters are largely determined by the unique chemical composition of the botanical precursors of honey, including flower nectar or honeydew produced by certain species of insects in the order Hemiptera. The composition of nectar and honeydew, in turn, depends not only on the plant species in the honey flora but also on various environmental factors, making it inherently variable (Wang & Li, 2011).

Honey is generally classified based on the plant precursor from which it is derived. It can be obtained from specific types of flower nectars, honeydew, or a mixture of both (Persano Odo et al., 2004). When a particular plant source temporarily predominates and is particularly attractive to bees, they produce monofloral honey. On the European continent, more than one hundred plant species are recognised as botanical precursors of monofloral honeys (Persano Odo et al., 2004). This work lists seven varieties of Canarian honey: malpica, tajinaste azul, tajinaste, tagasaste, relinchón, barrilla, and oregano. The first four varieties originate from plants endemic to the Canary Islands, with the

first two found exclusively on Tenerife and the third only on La Palma (Santos Vilar et al., 2004). A later publication identified additional monofloral honeys produced in Tenerife, including broom honey (also known as retama del Teide), avocado, heather, agave, oregano, and tedera honey (Bentabol Manzanares et al., 2014). Persano-Oddo et al. (2004) categorised all 108 varieties of European monofloral honeys which they reported into three classes based on their relative importance: abundant, medium, and rare. All Canarian honey falls into class 2 (medium), with its registration recorded in the relevant European register and approved by the European Commission in January 2014. Most of the Canarian honey referenced in the report by Persano-Oddo et al. (2004) originates from plants endemic to the Canary archipelago, particularly Tenerife. Additionally, the local honey flora includes numerous other endemic species, whose contributions to polyfloral honey have been confirmed melissopalynologically (Serra Bonvechi et al., 1987, 2004; Santos Vilar et al., 2004; Camancho Santos Vilar et al., 2004; Pérez,1988; Ramos & Ferreras, 2011; Bentabol Manzanares et al., 2017). These unique aspects of Tenerife's honey flora suggest the potential for distinctive features in the chemical composition and medicinal properties of its honey. However, these characteristics remain poorly studied for local honey varieties. Several studies have reported on the mineral content of these honeys (Hernandez et al., 2005; Frias et al., 2008; Diaz et al., 2019), while others focus on their physicochemical characteristics (Serra Bonvechi et al., 2004; Manzanarez et al., 2011; Bentabol Manzanares et al., 2014; Bentabol Manzanares et al., 2017), including water content, water activity, acidity, electrical conductivity, and the presence of such enzymes as invertase and diastase, which are involved in the breakdown of complex saccharides. Chemical analyses have provided data on such components as aliphatic C_2–C_6 acids; mono-, di-, and trisaccharides; proline; and hydroxymethyl furfural. Although these indicators are important, they do not fully explore the healing potential of honeys.

In our research, we aim to conduct a broader and more detailed study of the chemical composition of Tenerife honey. While a recent publication by Zalewsky et al. (2025) reported on the composition of the volatile components of Tenerife honey and largely determine the consumer properties of this valuable product, this publication is devoted to the composition of the extractive components on which its therapeutic potential depends.

MATERIAL AND METHODS

Materials

The silylation agent bis(trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane (BSTFA/TMCS) was purchased from TriMen Chemicals (Łódź, Poland). C_8–C_{40} *n*-alkane calibration standards, as well as lignans sesamin and magnolin, were purchased from Sigma-Aldrich (St. Louis, MO, USA). The lignans ashantin and fargesin, along with kojic acid and 8-hydroxyquinone, were produced by TriMen Chemicals. The solvents used in SPE (diethyl ether and methanol) were obtained from POCH (Gliwice, Poland).

Honey samples

Six samples of Tenerife monofloral honeys: broom honey, three samples of tajinaste honeys, relinchon, and barrilla along with one sample of multifloral honey were purchased in December 2022 and January and April 2023 from local beekeepers. Botanical sources of honey were determined by producers based on their floristic observations during the honey collection period and the organoleptic characteristics of the resulting products. Table 1 contains local names of the types of honeys studied, the sample designations adopted in this publication, the names of botanical precursors and the altitude levels of growth of the latter. Honey samples were stored in the dark at +4°C for no more than four months before analysis.

Determination of the chemical composition of honey

To isolate the extractive compounds contained in honey, the solid-phase extraction technique

Table 1.

Studied Tenerife honey samples: local names, sample designation, precursor plants and areas of their growth

Name	Designation	Species and family of plant precursor	Altitude level (m, a.s.l)
Broom honey (retama del Teide)	H1	*Spartocytisus supranubius*, Leguminosae	1200-2000
Tajinaste azul	H2–H4	*Echium virenscens* DS, Boraginaceae	500-1300
Relinchon	H5	*Hirschfeldia incana* L., Cruciferae	from sea level to 600
Barrilla	H6	*Mesembryanthemum crystallinum* L., Aizoaceae	coastal zone
Multifloral honey	H7	-	800 m

was used, as described in earlier publications (Isidorov et al., 2011, 2015) with minor modifications. In brief, honey samples (10 g) were diluted in 50 mL of distilled water and filtered through an extraction column pre-conditioned with methanol and water containing 6 g of C18 sorbent. After the column was purged with a strong stream of air for 3-4 min, the adsorbed compounds of low and medium polarity were eluted with 50 mL of diethyl ether. The eluates collected in glass beakers were placed in a fume hood to evaporate the solvent. The dry residue was washed off the walls with 300 µL of dry pyridine, the solution was transferred into a 2-mL vial, and 100 µL of BSTFA/TMCS was added and heated for 30 min at 60°C to complete the derivatisation.

The obtained samples were chromatographed on an HP7890A gas chromatograph with a 5975C VL MSD triple-axis detector (Agilent Technologies, USA). The instrument was equipped with an HP 5-ms capillary column (30 m × 0.25 mm internal diameter, 0.25 µm film thickness) with electronic pressure control and a split/splitless injector. The latter was operated at a temperature of 220°C in the split (1:10) flow mode. The helium flow rate through the column was 1 ml/min in the constant flow mode. The initial column temperature was 40°C and increased to 320°C at a rate of 3°C/ min. Data acquisition parameters for the mass-selective detector were as follows: transfer line temperature -280°C, MS source temperature -230°C, MS quadrupole temperature -150°C. Electron ionization mass spectra were acquired at an ionization energy of 70 eV. Detection was performed in full-scan mode. After integration, the fraction of separated components in the total ion current (TIC) was calculated. All analyses were performed in duplicate.

To identify the components, two independent analytical parameters were used: chromatographic retention indices (RI) and mass spectrum. Under the given conditions, a calibration mixture of C_8-C_{40} *n*-alkanes was separated and the registered retention times were used to calculate RI^{Exp} values according to equation:

$$RI^{Exp} = 100[n + (t_x - t_n)/(t_{n+1} - t_n)]$$

where t_x is the retention time of the analyte, and t_n and t_{n+1} are the retention times of *n*-alkanes eluting directly before and after the analyte, respectively.

The mass spectra recorded during the analysis and the RI^{Exp} values were compared with the use of a GC-MS data processing system against those in the NIST 14 library (NIST/EPA/NIH Library of Electron Ionisation Mass Spectra), the NIST Chemistry WebBook collections (the match value was usually within 800-950), and a recently published atlas containing mass spectra and RIs of more than 1750 organic components of various origins in the form of trimethylsilyl derivatives, including bee products (Isidorov, 2020). In several cases, mass spectrometric

identification was confirmed through GC-MS analysis of specially purchased standard substances for which RIs were not available in existing databases under the specified gas chromatographic separation conditions.

Multivariate statistical analysis

The software RStudio and ggplot2 data package have been used to principal component analysis and to process the results.

RESULTS

The chromatograms recorded during the analysis of extractives contained peaks corresponding to 74 to 124 components, with each contributing at least 0.01% to the total ion current (TIC) of the chromatograms. Based on their chemical structure, these organic compounds were classified into eight groups, as shown in Table 2, along with representative examples of each group (components within each group are listed in ascending order of their retention index). The table lists compounds whose contribution to the TIC in at least one honey sample exceeded 0.15%. The final two rows of the table represent components that do not belong to the main groups and compounds that could not be identified. The samples in Table 2 are arranged according to the decreasing altitude of their apiaries, as reported by the beekeepers: from the high-altitude habitats of *Spartocytisus supranubius*, the plant precursor of broom honey, to the coastal zone, the primary habitat of *Mesembryanthemum crystallinum*, the plant precursor of barrilla honey. The chemical composition of extractives in the studied samples was highly specific: among 160 registered compounds, only forty were present in all seven samples. These included seventeen aliphatic acids, nine aromatic compounds, seven long-chain C_{19}–C_{31} alkanes, and six C_7–C_{10} aliphatic alcohols. The largest contribution to the TIC of the chromatograms (24%-66% of TIC) was recorded for the group of aromatic compounds. The main contribution to this group (56%-89% of TIC) was provided by methyl syringate (MESY). Phenolic carboxylic acids including β-phenyllactic, 4-hydroxybenzoic, vanillic, syringic, and *p*-coumaric acids, along with benzoic and phenylacetic acids, were present in all Tenerife honey samples. Flavonoids, however, were absent in extracts from tajinaste, barrilla and monofloral honey. Lignans with a furofuran group, which are rarely mentioned as honey components and are formally classified as aromatic compounds, are presented in a separate group for clarity. These components were found in only two of the four monofloral honeys, tajinaste and barrilla, and were entirely absent in multifloral honey. This group also included a rare compound, 4-hydroxy-3,5-dimethoxybenzoylhydrazide (syringic acid hydrazide). To our knowledge, this compound has previously only been identified in cotton honey (Alissandrakis et al., 2005).

The second most important group consisted of aliphatic acids, which accounted for 13%-36% of the TIC. Another subset was identified within this group, comprising eleven saturated and unsaturated aliphatic hydroxy acids and two genetically related unsaturated dicarboxylic acids: 2-octene-1,8-dioic acid and 2-decene-1,10-dioic acid. This distinction is based on their specific common origin, which is discussed in the next section. The studied samples also contained significant amounts of unbranched alkanes and alkenes, reaching up to 16% in monofloral honeys and 6% in polyfloral honey.

Esters and ethers were also identified in the extracts. The esters included two glycerol acetates, while the ethers consisted of monosubstituted glycerol derivatives. Additionally, monosubstituted ethers of glycerol and C_{18}–C_{22} alcohols were detected in the honeys, with 1-*O*-eicosylglycerol present in all analysed samples. The chromatograms of all extracts displayed peaks for thirty-four unidentified components, accounting for 5%-15% of the total ion current. Most of them belong to minor components for which spectra of the quality required for identification could not be recorded.

To know how the analysed chemical variables are presented and how the studied honeys are grouped, a principal components analysis (PCA) was carried out. It was observed that approximately one-third (32) of the 108 chemically identified compounds

Table 2.

Relative group composition (% of TIC) of extractives of Canarian (Tenerife) honey. Designations: H1 - broom honey; H2 - tajinaste 1; H3 - tajinaste 2; H4 - tajinaste 3; H5 - relinchon; H6 -barrilla; H7- multifloral honey.

Group of compounds	RI^{Exp}	*RI^{Lit}	M^+	H1	H2	H3	H4	H5	H6	H7
Aromatic compounds, including:				65.8	41.54	41.6	23.97	52.11	58.53	58.01
- benzyl alcohol, TMS	1156	1152±1	180	0.12	-	trace	-	trace	0.06	trace
- 2-phenylethanol, TMS	1228	1224±1	194	-	trace	-	-	0.31	-	-
- benzoic acid, TMS	1246	1249±2	194	0.07	trace	0.52	0.19	0.31	0.34	0.12
- benzeneacetic acid, TMS	1301	1303±3	208	0.07	trace	3.4	1.44	0.55	0.13	trace
- thymol, TMS	1321	1322±2	222	0.85	7.59	2.84	0.97	1.59	2.29	0.99
- hydroquinone, di-TMS	1410	1409±1	254	-	-	-	0.06	-	-	-
- 2-hydroxyacetophenone?, TMS	1417	1378	208	-	-	0.32	-	0.12	-	-
- cinnamyl alcohol, TMS	1430	1426±7	206	0.09	-	-	-	-	-	0.17
- mandelic acid, di-TMS	1490	1491±1	-	-	-	-	0.08	-	-	-
- salicylic acid, di-TMS	1519	1522±3	-	-	-	trace	-	0.05	0.24	-
- cinnamic acid, TMS	1545	1550±9	220	-	-	0.14	0.11	-	0.09	-
- 4-hydroxyphenylethanol, di-TMS	1578	1579±1	282	-	0.25	0.95	0.69	-	-	-
- methyl 3,5-dimethoxybenzoate	1591	1591±0	196	-	-	-	-	-	0.61	2.47
- β-phenyllactic acid, di-TMS	1597	1596±2	310	0.33	trace	1.24	1.15	16.74	0.31	0.43
- 4-hydroxybenzoic acid, di-TMS	1636	1635±2	282	0.31	0.83	0.57	0.46	0.55	0.55	0.43
- 4-hydroxybenzeneacetic acid, di-TMS	1646	1648±2	196	-	-	0.13	0.18	0.07	0.08	-
- veratric acid, TMS	1708	1682±2	254	-	trace	0.15	-	0.08	0.69	0.84
- 4-hydroxy-3,5-dimethoxybenzoyl-hydrazide	1772	1775±2	212	0.16	0.36	0.4	-	0.61	1	1.01
- vanillic acid, di-TMS	1776	17762	312	0.13	trace	0.17	0.12	0.14	0.25	trace
- 3,4-dihydroxyphenyl ethanol, tri-TMS	1782	1781±2	370	-	trace	-	-	-	0.18	-
- (Z)-p-coumaric acid, di-TMS	1798	1798±3	308	-	-	-	0.12	0.27	0.19	-
- methyl syringate (MESY), TMS	1816	1816	284	58.6	31.54	29.69	17.79	29.19	44.19	48.27
- protecatehuic acid, tri-TMS	1836	1835±1	370	-	-	trace	-	-	0.38	-
- syringic acid, di-TMS	1915	1815±2	342	0.73	0.74	0.58	0.41	0.58	6.34	0.84
- (E)-p-coumaric acid, di-TMS	1947	1949±3	308	0.24	0.24	0.4	0.2	trace	0.32	0.32
- ferulic acid, di-TMS	2101	2104±3	338	trace	-	trace	-	trace	0.08	0.18
- caffeic acid, tri-TMS	2154	2154±6	396	0.27	0.27	0.1	-	0.09	0.19	0.3
- pinocembrin, di-TMS	2549	2544±5	400	0.21	-	-	-	trace	-	0.08
- unidentified flavonoid, TMS	2597	-	416	-	-	-	-	0.18	-	-
- pinobanksin, di-TMS	2610	2607±4	488	0.54	-	-	-	0.18	-	0.17
- chrysin, di-TMS	2745	2750±4	-	0.13	-	-	-	-	-	1.28
- galangin, tri-TMS	2755	2768±1	486	trace	-	-	-	-	-	0.04
- sakuranetin, di-TMS	2877	2877±3	430	-	-	-	-	-	-	trace

- kaempherol, tetra-TMS	3114	3115±3	574	-	-	-	-	-	-	0.03
Furofuran lignane, including:				-	4.6	1.5	1.26	-	1.69	-
- episesamin**	3138	3139±2	354	-	0.49	0.16	-	-	0.17	-
- fargesin**	3195	3200±3	370	-	1.11	0.31	0.11	-	0.36	-
- aschantin**	3332	3332±3	400	-	1.59	0.51	0.09	-	0.55	-
- magnolin, isomer 1**	3369	3371±2	416	-	0.01	trace	trace	-	-	-
- magnolin, isomer 2**	3382	3388±4	416	-	0.46	0.14	0.33	-	0.15	-
- yangambin, isomer 1**	3508	3510±3	446	-	trace	0.04	0.2	-	0.07	-
- yangambin, isomer 2**	3523	3519±4	446	-	0.52	0.18	0.33	-	0.19	-
- unidentfied lignan	3567	-	430	-	0.44	0.15	0.2	-	0.19	-
Aliphatic acids, including:				5.26	13.31	15.23	26.68	11.96	8.99	6.12
- lactic, di-TMS	1074	1073±5	-	0.7	0.64	1	0.23	1.29	0.97	0.57
- succinic, di-TMS	1324	1321±2	262	0.06	trace	trace	0.16	0.2	0.58	0.1
- suberic (1,8-octanedioic), di-TMS	1715	1707±3	-	0.27	trace	0.99	0.48	0.62	0.93	0.37
- azelaic (1,9-nonanedioic), di-TMS	1808	1806±6	-	trace	0.19	0.31	0.2	0.28	-	-
- sebacic (1,10-denedioic), di-TMS	1906	1899±5	-	0.96	2.07	3.79	2.05	2.69	2.57	0.95
- palmitic, TMS	2052	2049±2	328	0.66	1.95	1.77	3.3	1.16	0.76	0.69
- 3-hydroxysebacic, di-TMS	2090	2091±4	-	-	-	0.11	-	0.18	0.15	-
- linoleic, TMS	2215	2210±4	352	0.18	0.17	0.24	0.49	0.22	0.28	0.19
- oleic, TMS	2222	2217±4	354	2.1	6.21	5.23	13.64	3.54	1.86	1.8
- elaidic, TMS	2228	2219±4	354	-	0.22	0.18	0.76	0.13	0.07	-
- stearic, TMS	2248	2243±4	356	0.17	0.47	0.48	1.38	0.26	0.16	0.14
- tetracosanoic, TMS	2845	2838±4	440	-	trace	0.45	0.47	0.41	0.14	0.73
- heneicosanedioic, TMS	2992	-	-	trace	0.22	0.22	0.75	0.1	0.19	0.21
Aliphatic hydroxy acids, including:				7.79	12.2	15.74	8.67	12.41	13.11	7.75
- 3-hydroxyoctanoic, di-TMS	1486	1488±4	-	-	trace	0.13	0.15	0.07	0.09	-
- 7-hydroxyoctanoic, di-TMS	1560	1559±2	-	0.1	0.2	0.29	0.04	0.31	0.35	0.14
- 7-hydroxy-2-octenoic, di-TMS	1610	1612±8	-	2.58	0.29	0.69	0.25	0.22	1.38	2.18
- 8-hydroxyoctanoic, di-TMS	1627	1627±3	-	0.24	trace	0.31	0.13	0.33	0.34	0.36
- 3-hydroxydecanoic, di-TMS	1669	1669±2	-	trace	trace	0.16	0.14	0.26	0.26	2.18
- 8-hydroxyocten-2-oic, di-TMS	1675	1672±3	-	0.02	trace	0.01	0.01	trace	trace	0.03
- 9-hydroxydecanoic (9-HDAA), di-TMS	1752	1752±2	-	trace	trace	0.13	0.12	0.14	0.2	trace
- 2-octene-1,8-dioic, di-TMS	1762	1762±2	-	0.39	0.58	0.41	0.22	0.35	0.82	0.7
- 9-hydroxy-2-decenoic, di-TMS	1802	1802±1	-	0.25	0.63	0.95	0.52	0.82	0.87	0.34
- (E)-10-hydroxy-2-decenoic (10-HDA), di-TMS	1874	1875±2	-	0.02	-	trace	0.02	trace	trace	0.03
- (E)-2-decene-1,10-dioic (2-DecDA), di-TMS	1960	1958±2	344	3.57	10.49	12.33	7.09	9.25	8.16	3.25
- 3,10-dihydroxydecanoic, tri-TMS	2009	2009±2	-	0.47	trace	0.44	0.25	0.67	0.56	0.77

- 3,11-dihydroxydodecanoic, tri-TMS	2126	2125±1	-	-	-	-	-	-	0.09	-
Aliphatic alcohols, including:				0.82	1.79	1.27	3.29	1.12	1.08	0.78
- 2,3-butanediol, isomer 1, di-TMS	1042	1032±8	-	-	-	-	-	trace	trace	-
- 2,3-butanediol, isomer 1, di-TMS	1049	-	-	-	-	-	-	0.08	0.1	-
- glycerol, tri-TMS	1298	1289±6	-	0.06	trace	0.24	0.04	0.06	0.05	0.09
- 1-octadecanol, TMS	2163	2154±5	-	0.12	trace	0.11	0.26	0.09	0.05	0.05
- 1-eicosanol, TMS	2360	2351±2	-	trace	0.23	0.15	0.46	0.12	0.11	0.1
- 1-docosanol, TMS	2557	2542±3	-	0.18	0.31	0.23	0.62	0.17	0.16	0.23
- 1-tetracosanol, TMS	2754	2754±1	-	0.28	0.79	0.54	1.22	0.36	0.4	0.14
- 1-hexacosanol, TMS	2951	2945±5	-	0.18	0.46	0.25	0.69	0.24	0.26	0.15
Aliphatic esters, including:				-	-	1.46	3.32	-	0.85	0.33
- diacetin, TMS	1333	1326±3	-	-	0.3	-	-	-	0.06	-
- triacetin	1355	1350±4	-	-	1.34	-	-	trace	0.1	-
Glyceride ethers, including:				1.32	1.53	3.22	7.5	0.65	1.6	0.73
- 1-O-octadecyl glycerol (batyl alcohol), di-TMS	2701	2659±N/A	-	0.75	0.89	2.4	4.84	-	1.03	0.36
- 1-O-eicosyl glycerol, di-TMS	2893	-	-	0.57	0.64	0.82	2.66	0.65	0.57	0.29
- 1-O-docosyl glycerol, diTMS	3086	-	-	-	-	-	-	-	-	0.08
Alkanes & alkenes, including:				1.95	15.01	12.86	15.7	8.42	4.14	5.8
- n-nonadecane	1900	1900	268	trace	0.18	trace	0.13	0.11	0.21	0.31
- n-eicosane	2000	2000	282	0.22	0.44	0.29	trace	0.09	0.08	0.23
- n-heneicosane	2100	2100	296	0.26	0.29	0.26	0.33	0.27	0.24	0.25
- n-tricosane	2300	2300	324	0.22	0.92	0.68	1.56	0.51	0.34	0.22
- n-pentacosane	2500	2500	352	0.21	1.07	0.84	1.58	0.63	0.32	0.33
- n-heptacosane	2700	2700	380	0.25	2.8	2.4	0.13	1.79	0.53	0.18
- n-nonacosane	2900	2900	408	0.21	0.64	1.67	1.77	0.98	0.53	0.75
- 9-hentriacontene	3075	3075±1	434	-	1.43	0.69	1.8	0.6	0.4	0.35
- 7-hentriacontane	3082	3082±1	434	-	2.18	1.1	2.32	0.92	0.59	0.14
- n-hentriacontane	3100	3100	436	trace	2.18	0.91	0.87	0.54	0.22	0.35
Other compounds, including:				4.49	1.92	3.18	4.1	1.85	3.77	11
- dihydroacetone (DHA), di-TMS	1233	-	234	2.74	-	trace	0.05	0.2	0.78	2.73
- maltol, TMS?	1274	1293±N/A	-	-	-	-	-	-	0.22	-
- 5-hydroxymethylfurfural (HMF), TMS	1321	1319±3	198	1.17	-	-	-	-	-	-
- 3-hydroxy-2,3-dihydromaltol, di-TMS	1461	-	-	-	-	-	-	trace	0.23	-
- 5-hydroxymaltol, di-TMS	1494	-	286	-	-	-	0.16	0.15	0.24	-
- 8-hydroxyquinoline, TMS**	1622	1622±1	217	-	-	-	-	-	1.67	5.85
- kojic acid, di-TMS**	1683	1686±3	-	-	-	-	-	trace	0.08	0.3
- fructopyranose, penta-TMS	1888	1886±3	-	0.58	-	-	-	-	-	-
- (E,E)-abscisic acid, TMS	2303	2308±1	-	-	-	-	-	-	0.08	-

- all-trans-retinol, TMS	2571	-	358	-	-	2.31	-	-	-	-
- cholesterol, TMS	3149	3150±3	458	-	trace	0.18	-	-	-	-
- α-tocopherol, TMS	3149	3149±2	502	-	-	-	0.31	-	-	
- 24-methylenecholesterol, TMS	3244	-	472	-	0.28	0.1	0.95	0.09	0.1	-
- β-sitosterol, TMS	3345	3347±2	486	-	-	0.19	1.05	-	-	-
NN				15.22	8.39	4.96	7.24	11.51	7.44	10.22
Number of peaks				74	91	124	97	121	118	110

*According to Wiley 12th NIST 2020 Library and (Isidorov, 2020).
**Identification confirmed by mass spectra and chromatographic parameters of a commercial standard.

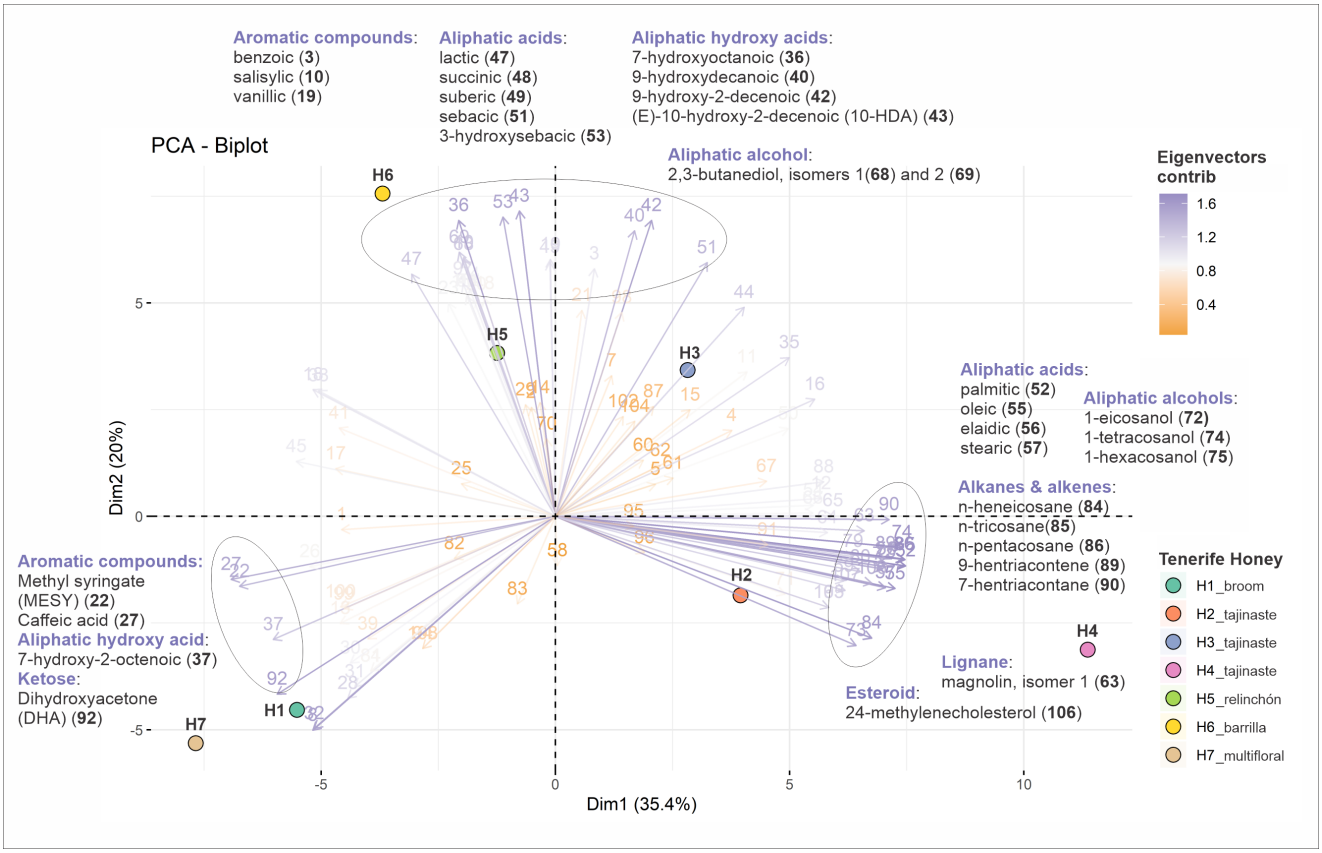

Fig. 1. Biplot of the first two components obtained by PCA.
Arrows indicate the eigenvectors for all chemical compounds and the colours represent the contribution of each one. Blue, yellow, and red indicate a high, medium, and low contribution, respectively. Open circles highlight compound groups that contributed the most to each component. The parentheses indicate the number of metabolites from each chemical group. Black dots represent the honey samples.

were the most relevant, allowing us to infer a possible grouping of the honeys (Fig. 1). In this regard, we found that eighteen compounds had a strong correlation with PC1, which accounted for a significant proportion of the total variance (35.4%). These included several aliphatic acids and alcohols, alkanes and alkenes, the lignan magnolin (isomer 1), and the steroid 24-methylenecholesterol, all with positive loadings on PC1 and plant origin. These compounds prevailed in the monofloral tajinaste honeys (H2, H3, and H4) originating from mid-altitude regions. On the same PC1, but with an opposite sense (negative values), we found the aromatic compounds MESY and caffeic acid, the hydroxy acid 7-hydroxy-2-octenoic acid, and the dihydroxyacetone (DHA). These compounds were representative of the high-altitude monofloral broom honey (H1) and the multifloral honey (H2). PC2 accounted for a smaller proportion

of the variance (20%) and grouped numerous compounds possibly originating from bees (7-hydroxyoctanoic acid, 9-hydroxydecanoic acid, 9-hydroxy-2-decenoic acid, (E)-10-hydroxy-2-decenoic acid) and microbes (lactic acid, succinic acid, 2,3-butanediol).

DISCUSSION

Aromatic compounds represent the largest group of biologically active components in the studied Tenerife honeys, contributing the most to the TIC of all chromatograms. The phenolic carboxylic acids within this group, like other phenolic compounds, are a key focus for researchers studying the biological activity of beekeeping products because they exhibit not only antimicrobial but also antiviral, antioxidant, and anti-inflammatory effects (Estevinho et al., 2008; Jaganathan & Mandal, 2009; Cornara et al., 2017; Thungmunnithum et al., 2018; Hassain et al., 2021; Martinello Mutinelli, 2021; Nader et al., 2021; Nainu et al., 2021). Furthermore, they demonstrate inhibitory effects on various forms of cancer, particularly by preventing the proliferation of cancer cells (Elaminea et al., 2021).

In all the studied samples, MESY was the predominant component, not only within the group of aromatic compounds but overall, accounting for 18% to 63% of the TIC. According to Elaminea et al. (2021), this compound is found in significant quantities only in monofloral honeys whose botanical precursors belong to the orders Apiales, Asparagales, and Myrtales. For instance, in six samples of Zantaz honey derived from the nectar of *Bupleurum spinosum* (Apiales), the MESY content averaged 340±56 mg/kg, corresponding to 40%-58% of the total phenolic compound content. Similarly, in Asphodel honey, derived from the nectar of *Asphodelus microcarpus* (Asparagales), MESY is also one of the main components (Tuberoso et al., 2009). All these honeys exhibit high antimicrobial activity. Among other types of honey, Manuka honey, derived from the nectar of *Leptospermum scoparium* (Myrtales), has the highest clinically proven antimicrobial and wound-healing activity. Its high MESY content is considered a primary factor contributing to its antiseptic properties (Oelschaegel et al., 2012; Kato et al., 2016; Gill et al., 2019).

Among the flora of Tenerife, the botanical source of furofuran lignans also remains unidentified. All compounds of this group that we discovered are known for their biological activity. Antioxidant, anti-inflammatory, cytotoxic and antimicrobial activities have been reported for ashanthin and magnolin (Patel, 2023; Lee et al., 2024). These properties are also shared by yangambin and fargesin, the former of which also exhibits cardiovascular activity (Tibiriçá, 2001) and the latter has therapeutic potential in the treatment of chronic migraine, a severe neurological disorder (Rushendran & Chitra, 2024).

To the best of our knowledge, furofuran lignans have previously been reported only in sesame honey from West Bengal (Das et al., 2015). The existence of an unidentified botanical source in the Canary Islands is further supported by the presence of all compounds from this group mentioned in Table 2 in propolis from the island of Gran Canaria (Bankova et al., 1989).

By contrast, the source of eleven even-numbered aliphatic C_8–C_{12} hydroxy acids and two unsaturated C_8 and C_{10} dicarboxylic acids, which were also present in all samples, can be identified with certainty. This unique set of compounds is found exclusively in royal jelly (RJ), secreted by the glands of worker bees (*Apis mellifera*) and used to feed larvae. It has not been found in any other natural objects. This indicates that these acids are of animal, not plant origin. This fact was reflected in our results in the principal components analysis, in which most aliphatic hydroxy acids were represented by PC2, which is independent of PC1. Their presence in honeys from different countries has been previously demonstrated (Isidorov et al., 2011; 2015). Subsequent studies of honey from Scotland, Greece, and Egypt also confirmed the presence of individual representatives of this group (File et al., 2017; Kasiotis et al., 2023). The main component in this group is the unsaturated 2-decene-1,10-dioic acid (2-DecDA), which, according to Plettner et al. (1996), is formed as

a result of the enzymatic oxidation of 10-hydroxy-2-decenoic acid (10-HDA), which is the main component of the hydroxy acid complex of royal jelly. Interestingly, significant amounts of this acid have been found in the urine of people treated with royal jelly (Isidorov, 2020). Similarly, its homologue, the unsaturated dicarboxylic acid 2-octene-1,8-dioic acid, is likely formed from 8-hydroxy-2-octenoic acid through the same process. High levels of 2-DecDA were first reported in Manuka and white clover honey from New Zealand (Tan et al., 1988).

The presence of RJ hydroxy acids in honey is not unexpected, particularly in light of findings from studies characterising its protein content using proteomic tools (Chua et al., 2014; Di Giralomo et al., 2012). Both studies cited reported that all proteins identified in honey were of *Apis mellifera* origin and not plant-derived. Chua et al. (2014), using mass spectrometry, identified major RJ proteins (MRJPs) such as MRJP-1, MRJP-2, MRJP-5, and MRJP-7 in honey, demonstrating a proteome similar to that of RJ. However, there is limited information in the literature regarding the presence of low-molecular-weight components of RJ in honey, such as even-numbered C_8–C_{12} hydroxy acids. This scarcity is likely due to technical challenges: these acids lack chromophore groups in their molecules, making them undetectable by the ultraviolet detectors commonly used in high-performance liquid chromatography. Additionally, their high polarity and low volatility, resulting from the presence of two polar functional groups, -COOH and -OH, necessitate derivatisation for successful detection with the use of gas chromatography-mass spectrometry (GC-MS) technology (Molnar-Perl, 1999, 2000; Isidorov, 2020).

It can also be assumed that hydroxy acids of RJ, along with low-molecular representatives of this class, such as lactic, succinic and malic acids, significantly influence the overall acidity of honey. The average pH of 3.9 is primarily attributed to the presence of gluconic acid, which is produced by glucose oxidase activity (Nishizawa et al., 2021). However, this enzymatic process occurs only after the honey is diluted, and it also results in the production of a second compound-hydrogen peroxide. In this context, RJ acids, which contribute to the formation of several important characteristics of honey, merit closer attention from researchers.

The presence of many endemic species in the melliferous flora of Tenerife, including those found only on this island of the Canary archipelago, determines the unique composition of local honey varieties. These honeys consist of a variety of such characteristic and rare compounds as furofuran lignans, kojic acid, syringic acid hydrazide, and ethers of glycerol and normal C_{18}–C_{22} alcohols. The presence of a wide range of compounds with documented antimicrobial activity makes these honeys an interesting and promising subject of study with potential practical applications, especially in light of the onset of the 'post-antibiotic era'.

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