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Characterization of Argentinian Honeys Based on their Sugar Profiles and Quality Parameters

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Abstract

The honeys from the Argentinian provinces of Buenos Aires, La Rioja, Catamarca and Misiones were characterised by the sugar profile (fructose, glucose, sucrose, turanose, maltose and erlose) and the physicochemical parameters (free acidity, pH, electrical conductivity (EC), colour and contents of moisture, ash, total soluble solids and hydroxymethylfurfural (HMF)) used for honey quality control. Authentic and traceable honey samples (n = 572) collected along five harvests were analysed using the official analytical methods. All honeys met the specifications of the national and/or international standards for the evaluated parameters, which denoted the blossom origin of most honeys, and confirmed their high quality, good maturity and freshness. The influence of the flora and the pedoclimatic conditions of each phytogeographical region on the physical and chemical properties of honey allowed its characterization. Thus, Buenos Aires produced typical lighter honeys, and Misiones and Catamarca, darker ones. Buenos Aires honeys presented particular lower values of pH, EC, ash, HMF and maltose, and higher concentrations of erlose. Misiones honeys exhibited higher values of moisture, free acidity, EC and turanose amounts, and lower contents of fructose, glucose and total soluble solids. La Rioja honeys showed higher pH and °Brix values; and Catamarca honeys, higher sucrose contents. To the authors' knowledge, the sugar profiles and several quality parameters of honeys from Misiones and Catamarca are here reported for the first time, as well as any physical and chemical data on La Rioja honeys.

Keywords

Honey, Carbohydrate, Physicochemical parameters, Traceability, Phytogeographic province

Introduction

Honey is produced in almost every country worldwide and is widely used as food. Naturally, honey is a sweet substance that bees, mainly *Apis mellifera* species, produce from blossom nectar and/or honeydew (exudates of plants or plant sucking insects) [1]. Carbohydrates are the major constituents of honey, comprising about 80–85 % (w/w) of honey. The most abundant are monosaccharides, mainly fructose and glucose, produced after the enzymatic hydrolysis of sucrose [2]. Natural honey also contains sucrose and other minor sugars, water, proteins, ash, and minor quantities of amino acids, enzymes, vitamins and phenolic compounds [3]. The chemical composition of honey, which is related to its quality, depends on several factors, such as the plant species visited by honey bees, environmental and seasonal factors, as well as its handling, processing and storage.

Nowadays, honey quality is assessed for its commercialization by the analysis of several physicochemical parameters, such as free acidity, colour, pH, electrical conductivity, moisture, the contents of sugars, hydroxymethylfurfural, proline, minerals and ash, and the diastase and invertase activities. International regulatory bodies such as the Codex Alimentarius Commission, European Commission and Mercosur enact specific regulations related to the quality and safety of honey for its commercialization and establish the physicochemical parameters and chemical compounds to be determined in honey by harmonized methods for the quality and safety control of honeys [1, 4-6].

Some honey physicochemical parameters have been used as markers to define the geographical or botanical origin of honey [7-9]. These parameters are influenced by climatic conditions such as humidity, wind, solar irradiation and rainfall regimes of the area. Furthermore, pedoclimatic conditions influence the growth of the plant species in a certain region, and hence its flora, making each region unique. Bees feed on the nectar of plants near the hive. Therefore the composition of honey reflects the characteristics of the nectar of the plants around the hive. Consequently, there is a relationship between the composition of honey and the region where it is produced. This is an interesting added value to the product, which allows economic exploration and preserves the uniqueness of the product [8, 9].

Argentina is one of the major global honey producers, positioned in third place after China and the United States. Argentinian honey represents 70% of the honey produced in the southern hemisphere of the American continent, 25 % of the production of the entire continent, and 6% of the total produced in the world [10]. Approximately 95% of Argentinian honey is exported as non-differentiated product without any regard to its provenance of origin at the regional level [11]. Argentina presents features that favour apiculture exploitation. Indeed, its vast territorial extension and diversity of climates contribute to the development of a large and diversified honey-generating flora that leads to the production of a wide variety of honey. However, since most of the production is fragmented in small primary producers, the structure of the supply chain hinders the differentiation of the products and the quality control related to its origin; therefore it is commercialised in commodity markets without being characterised. Producers, retailers and authorities are interested in given Argentinian honey an added value through different valorisation strategies, ranging from the quality control commonly associated with production and processing practices to the categorical classification of honey, based on their intrinsic quality attributes. In this context, several physicochemical parameters have been used to characterize Argentinian honeys from some provinces, such as Buenos Aires [12], Pampean region [13], Corrientes [14], Córdoba [8], Chubut [15] and Catamarca [16]. However, most of these studies were performed on sample sets with a relatively small number of samples, therefore they allowed just a preliminary characterization of honeys from Argentina, and revealed that they are mainly floral honeys. Besides, the comparison of honeys from the different regions was difficult because only some of the analysed parameters coincided among the studies carried out. In the present work, a large set of Argentinian honeys from the provinces of Buenos Aires, La Rioja, Catamarca and Misiones, which are located at different latitudes and belong to different phytogeographical regions and climates [17, 18], were analysed to determine the sugar profile and physicochemical parameters used for quality control of honey in the international trade, with the aim of typifying the honey produced in these provinces.

Materials and Methods

Honey samples

A total of five hundred seventy-two authentic and traceable multifloral honey samples of *Apis mellifera* were collected from the Argentinian provinces of Buenos Aires (n = 329), La Rioja (n=44), Catamarca (n = 77) and Misiones (n = 122) along several harvests (2013–2017) (Figure 1 and Table S1). Sampling was carried out within the framework of the Argentine National Projects PICT 3264/2014 and PICT 0774/2017, following the instructions depicted on the Projects' analytical plan. The samples (about 1 kg of raw honey each) were provided directly by beekeepers and/or honey producer cooperatives along with farming information (harvest date and conditions, declared botanical origin, field or hive address and GPS coordinates, agricultural system and beehive treatments).

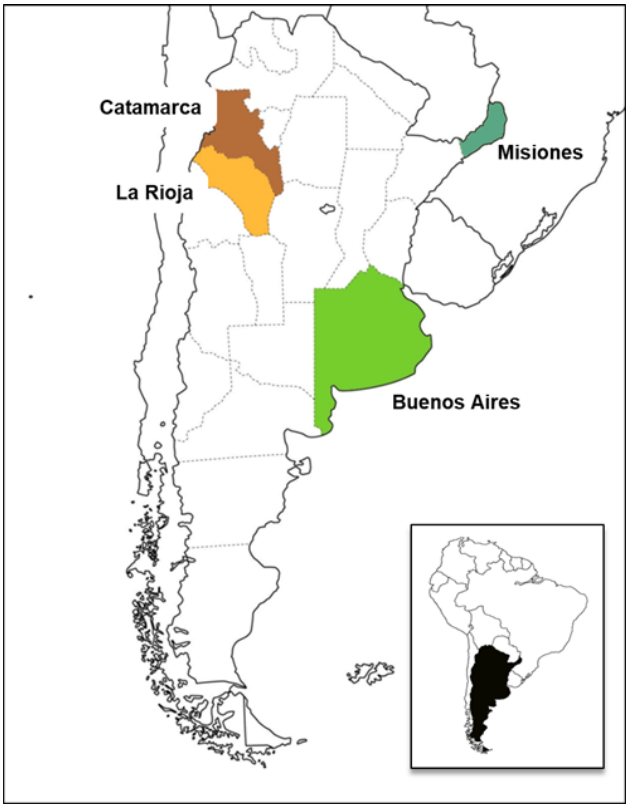

Figure 1: Honey samples were collected in the Argentinian provinces of Buenos Aires, La Rioja, Catamarca and Misiones.

Table 1: Sugar composition and physicochemical parameters of Argentinian honeys from the provinces of Buenos Aires, La Rioja, Catamarca and Misiones.

		Provinces			
Physicochemical parameter		**Buenos Aires**	**La Rioja**	**Catamarca**	**Misiones**
Fructose (g/100 g honey)	n	322	44	68	118
	Mean	39.09^{a}	38.7^{ab}	38.3^{b}	36.3^{c}
	SD	0.76	1.8	1.8	1.5
	Min	37.80	35.8	34.3	33.1
	Max	40.50	41.0	41.4	39.8
	Median	39.10	38.9	38.6	36.2
Glucose (g/100 g honey)	n	315	42	69	119
	Mean	33.4^{a}	32.5^{b}	31.9^{b}	30.7^{c}
	SD	1.3	3.0	2.8	2.9
	Min	30.4	26.6	24.0	23.1
	Max	36.5	37.3	36.2	37.4
	Median	33.2	32.3	32.3	30.4
F+G (g/100 g honey)	n	316	43	69	119
	Mean	72.5^{a}	71.2^{b}	70.3^{b}	67.0^{c}
	SD	1.7	4.0	4.1	3.8
	Min	68.3	63.6	61.4	57.2
	Max	76.5	78.2	77.1	76.5
	Median	72.5	71.2	70.7	66.7
F/G ratio	n	317	42	65	114
	Mean	1.173^{a}	1.200^{b}	1.194^{b}	1.185^{ab}
	SD	0.046	0.092	0.074	0.084
	Min	1.056	1.040	1.033	0.962
	Max	1.284	1.414	1.362	1.360
	Median	1.177	1.210	1.180	1.192
Sucrose (g/100 g honey)	n	324	43	66	119
	Mean	0.18^{a}	0.10^{b}	0.24^{c}	0.16^{ab}
	SD	0.22	0.18	0.23	0.16
	Min	nd	nd	nd	nd
	Max	0.70	0.40	0.80	0.50
	Median	nd	nd	0.30	0.20
Maltose (g/100 g honey)	n	240^{a}	-	35^{b}	60^{b}
	Mean	1.71	-	2.6	2.3
	SD	0.74	-	1.2	1.6
	Min	nd	-	nd	nd
	Max	3.70	-	4.9	6.3
	Median	1.70	-	2.6	2.4
Turanose (g/100 g honey)	n	240	-	34	60
	Mean	1.83^{a}	-	2.04^{a}	2.26^{b}
	SD	0.54	-	0.59	0.44
	Min	0.70	-	1.10	1.20
	Max	3.10	-	3.20	3.00
	Median	1.80	-	1.90	2.30
Erlose (g/100 g honey)	n	240	-	35	60
	Mean	1.00^{a}	-	0.20^{b}	0.19^{b}
	SD	0.65	-	0.24	0.37
	Min	nd	-	nd	nd
	Max	2.70	-	0.70	0.60
	Median	1.00	-	nd	nd

Moisture (%)	n	292	44	62	100
	Mean	17.4[a]	16.5[b]	16.9[b]	18.4[c]
	SD	1.1	1.3	1.5	1.0
	Min	14.6	13.8	13.8	16.6
	Max	20.0	18.9	19.9	20.3
	Median	17.4	16.4	16.9	18.5
Free acidity (meq/kg honey)	**n**	324	43	60	96
	Mean	23.8[a]	24.5[a]	31[b]	37.1[c]
	SD	5.1	7.0	10	8.2
	Min	14.7	13.4	12	16.6
	Max	36.3	43.8	50	50.1
	Median	23.1	24.3	31	37.9
pH	**n**	327	35	61	114
	Mean	3.58[a]	4.32[b]	4.15[c]	3.88[d]
	SD	0.23	0.51	0.41	0.33
	Min	3.09	3.49	3.45	3.18
	Max	4.08	5.29	5.01	4.54
	Median	3.63	4.29	4.18	3.87
EC (µS/cm)	**n**	326	39	59	114
	Mean	295[a]	501[b]	434[c]	545[d]
	SD	76	130	143	131
	Min	132	257	178	275
	Max	490	782	736	790
	Median	288	481	429	553
Ash content (mg/100 g honey)	**n**	326	41	67	119
	Mean	170[a]	300[bc]	281[b]	320[c]
	SD	43	91	117	82
	Min	76	147	102	158
	Max	281	505	553	548
	Median	165	279	264	322
Colour (mm Pfund)	**n**	321	44	70	115
	Mean	37[a]	63[b]	81[c]	84[c]
	SD	10	20	33	18
	Min	18	27	19	52
	Max	54	113	150	119
	Median	36	63	79	82
Total soluble content (°Brix)	**n**	325	44	70	119
	Mean	80.5[a]	81.7[b]	80.8[a]	79.6[c]
	SD	1.6	1.3	2.2	1.2
	Min	77.4	79.0	77.7	76.9
	Max	83.5	84.3	84.5	82.9
	Median	80.8	81.8	81.3	79.6
HMF (mg/kg honey)	**n**	126	21	27	52
	Mean	4.2[a]	9.8[b]	11.3[bc]	13.7[c]
	SD	1.9	6.4	5.6	9.0
	Min	1.0	1.0	6.0	1.0
	Max	7.0	22.0	26.0	34.0
	Median	4.0	9.0	8.0	12.0

[1]Abbreviations: n, number of samples; SD, standard deviation; Min, minimum; Max, maximum; nd, not detected; EC, electrical conductivity; F+G, total content of fructose and glucose; F/G ratio, fructose/glucose ratio; HMF, 5-hydroxymethyl-2-furaldehyde.

[2]Different letters within each row indicate significant differences according to Fisher's test ($p < 0.05$).

The honeys were harvested between November and April and some samples from Misiones in May, and manufactured following the guide for Good Beekeeping and Manufacturing Practices provided by the Argentinian Ministry of Agriculture, Livestock and Fisheries [19]. All honey samples were stored in screw-capped plastic containers at 4°C in the dark until analysis.

Reagents and solvents

The analytical standards 5-hydroxymethyl-2-furaldehyde (HMF), fructose, glucose, sucrose, erlose, maltose, trehalose and maltotriose were provided by Sigma-Aldrich (Darmstadt, Germany), as well as the HPLC-grade solvents methanol and acetonitrile. Sodium hydroxide, potassium acid phthalate, phenolphthalein, absolute ethanol, and the sugar standards of turanose, melezitose and raffinose were supplied by Supelco (Bellefonte, PA, USA). All chemicals and reagents used were of analytical quality grade. Water of HPLC-grade was used in all solutions and dilutions.

Determination of physicochemical parameters

The physicochemical parameters, namely moisture, free acidity, pH, electrical conductivity and colour, were measured in honey using the official methods of the Argentine Normalization and Certification Institute (Instituto Argentino de Normalización y Certificación, IRAM) adopted from the International Honey Commission (IHC) [20]. Honey moisture was determined according to IRAM standard 15931 (1994). The measurements of moisture and the total soluble solid content in degree Brix (°Brix) were carried out using an Abbé refractometer 5 (Bellingham & Stanley Ltd, Longfield Road, Tunbridge Wells, United Kingdom) at 20 ± 2 °C. The corresponding moisture value in percentage was obtained from the Chataway table. The electrical conductivity (EC) was determined in a solution of honey at 20% (w/v) at 20 ± 2 °C according to IRAM standard 15945 (1997) using an Adwa AD31 conductometer (Adwa Instruments, Inc., Szeged, Hungary). The ash content in honey was calculated from the EC measurements as described by Bogdanov et al. [4]. Honey free acidity was determined by titration according to IRAM standard 15933 (1994). The pH was determined in a solution of honey at 10 % (w/v) according to IRAM standard 15938 (1995) using a HI 2020-02 HANNA pH-meter (Hanna Instruments Inc., Woonsocket, Rhode Island, USA). The pH was also determined in a solution of honey at 20% (w/v). Honey colour measurements were performed according to IRAM standard 15941-2 (1997) using HI 96785C HANNA colorimeter (Hanna Instruments Inc., Woonsocket, Rhode Island, USA). In the case of crystallized honeys, honey was melted at 55 ± 2 °C in thermostatic bath until complete dissolution of the crystals and elimination of dissolved air, as indicated in the IRAM standard protocol. Then the colour of liquid honey was measured and the results expressed in the Pfund-scale. Honey colour grades regarding Pfund readings are water-white for ≤8 mm Pfund, extra white for 8–16 mm Pfund, white for 16–34 mm Pfund, extra light-amber for 34–50 mm Pfund, light-amber for 50–85 mm Pfund, amber for 85–114 mm Pfund and dark for >114 mm Pfund. Three replicate analyses were done for each sample.

Determination of sugars

The contents of sugars in honey were determined according to IHC [20] on a Agilent Series 1100 HPLC system equipped with a binary pump, a thermostatted autosampler, a thermostatted column compartment and a refractive index detector (RID), connected to an Agilent ChemStation software. A reversed phase Zorbax NH_2 (250 mm × 4.6 mm i.d, 5μm) column was used. The injection volume was 5 μL. The mobile phase was acetonitrile–water (83:17, v/v). The chromatographic separation was carried out in isocratic conditions at a flow rate of 0.65 mL·min^{-1} and 35 ºC. The identification of the saccharides in the HPLC chromatograms of the samples was achieved by comparison with the retention times of the available standards. Saccharides quantitation was performed by reporting the measured integration areas in the calibration equation of the corresponding standards.

Determination of HMF

The HMF content in honey was determined according to IRAM standard 15937-3 (2008) on an Agilent Series 1100 HPLC system equipped with a binary pump, a thermostatted autosampler, a thermostatted column compartment and a UV detector, connected to an Agilent ChemStation software. A reversed-phase Waters Symmetry C18 (250 mm × 4.6 mm i.d, 5μm) column was used. The injection volume was 20 μL. The mobile phase was water–methanol (95:5, v/v). The chromatographic separation was carried out in isocratic conditions at a flow rate of 0.7 mL·min^{-1} and 25 ºC. HMF chromatographic peak was monitored and quantified at 280 nm. HMF identification was performed by comparison with the retention time of the standard; and its quantitation, by reporting the measured integration areas in the calibration equation of the standard.

Data analysis

For each honey sample, the mean and the standard deviation of the three replicates were calculated for the concentration of the individual sugar compounds and the quality parameters, which indicated that the relative standard deviation (% RSD (n = 3)) were at 5 % or below, confirming the good repeatability of the analytical methodologies performed. The dataset made up of the mean values of the physical and chemical parameters measured on the honey samples were analysed by statistical procedures, such as analysis of variance (ANOVA), Fisher test, and least significant difference test (LSD) and box and whiskers plots. Regarding the box and whiskers plots, the symmetry of data distribution, the mean, median, minimum, maximum, outliers and extreme values were evaluated according to the harvest year and the geographical origin of honeys. Outliers or extremes values that strayed too far from data set were not considered in the final data analysis results for honey characterisation. Bivariate correlations were studied by Pearson's correlation and linear regression. The significance was calculated for $p < 0.05$. Data analysis was performed by means of the statistical software packages SPSS Statistic 17 (SPSS Inc., Chicago, IL, USA, 1993-2007) and Statistica 7.0 (StatSoft Inc., Tulsa, OK, USA, 1984-2004).

Results and Discussion

Honeys from the Argentinian provinces of Buenos Aires, La Rioja, Catamarca and Misiones were characterised by their individual sugar composition and physicochemical quality parameters (Tables 1 and S2). The different pedo-climatic conditions and flora of these provinces are expected to influence the physical and chemical characteristics of the honey produced in each region, giving them an added value. In this sense, the honeys studied were from three phytogeographical regions of Buenos Aires province, i.e. the Phytogeographic Province (PP) of the Espinal, the PP of the Monte and the PP Pampeana [17]. Buenos Aires province presents four different types of climate, i.e. the Pampean temperate climate, the oceanic temperate climate on the Atlantic coast region, the steppe or semi-arid climate in the extreme south of the province, and a transition temperate climate between the steppe and the Pampas regions [18]. The studied honeys from the provinces of La Rioja and Catamarca belonged to both the PP Chaqueña and the PP of the Monte. The main climates observed from NW to SE of these provinces are the mountain arid climate and the sierra & meadow arid climate. The sierra temperate and the sierra subtropical climates are typical of two small areas in La Rioja and Catamarca respectively. In the province of Misiones with a warm subtropical wet climate, two phytogeographical regions are distinguished, the PP Paranaense in the north and the PP Pampeana in the south. The analysed honeys from PP along several harvests presented characteristic sugar profiles and physicochemical parameters (Table 1), which are described in the next sections. In fact, the distinctive vegetation units of each PP and the climate of each region explained the composition and quality parameter values of the studied honeys, which showed a great variability, probably due to the different botanical species flowering at the time of honey production. The effect of the harvest year was not the same for all parameters (Table S2), showing significantly differences among certain harvests depending on the physicochemical parameter considered, as had been already observed [9].

Sugar profiles of honeys

Major sugars

The reducing sugars, i.e. fructose and glucose, represent the largest portion of honey composition. According to the Codex Alimentarius standard [1], blossom honey should present a total content of fructose and glucose higher than 60 g/100 g honey (%, w/w), and honeydew honey and its blends with blossom honey higher than 45 g/100 g honey. This rule was fulfilled by all the honey samples studied along all harvests (Table S2). Significant differences were observed in the honey contents of fructose, glucose and F+G among the provinces, except between Catamarca and La Rioja, and also Buenos Aires and La Rioja for the fructose content (Table 1 and Figure S1). Honeys from Buenos Aires exhibited the lowest variability (38–41 % fructose, 30–37 % glucose and 68–77 % F+G). All honey samples studied contained higher amounts of fructose than glucose, supporting the observation made by Graham et al., who stated that almost all types of honey present greater contents of fructose than glucose [21].

The variation of sucrose contents among honeys is the result of the activity of the invertase enzyme, which breaks down the disaccharide molecule of sucrose in the nectar into glucose and fructose during the ripening process of honey. Although sucrose in honey has minor importance, its presence can provide information about the adulteration and the botanical origin of honey [22]. Unaltered honey should present less than 5 % sucrose according to the Codex Alimentarius standard [1]. Higher contents of sucrose can be due to the addition of exogenous sugars or the early harvesting of honey [2]. The measured sucrose varied in the range from non-detected to 0.8 % (Table S2). These contents being far below from the legislation limit would indicate that all the studied honeys were authentic mature honeys harvested at the proper time, and not subjected to fraudulent practices. Significant differences were observed in the contents of sucrose among the provinces, except between Buenos Aires and Misiones and La Rioja and Misiones (Table 1 and Figure S1). Honeys from Buenos Aires and La Rioja showed higher percentages of samples with non-detected sucrose content, i.e. 51 % and 72 % respectively, than the other provinces.

Honeys from Buenos Aires presented the highest average contents of fructose (39.1 %) and glucose (33.4 %); followed by those from the arid regions of La Rioja (38.7 % fructose and 32.5 % glucose) and Catamarca (38.3 % fructose and 31.9 % glucose), and those from the subtropical region of Misiones (36.3 % fructose and 30.7 % glucose) (Table 1 and Figure S1). As a matter of fact, it was already reported that honey from arid regions presented higher amounts of fructose compared to honey from tropical regions [8]. To the authors' knowledge, data related to the fructose, glucose, sucrose and F+G contents in honeys from Misiones, Catamarca and La Rioja are published here for the first time. The average contents of fructose (39 %, n = 322) and sucrose (0.18 %, n = 324) found in honeys from Buenos Aires were lower than those reported previously (43 % fructose and 1.4 % sucrose, n=24) for honeys from the southeast of the province [23]. However, the average glucose concentration in Buenos Aires honeys (33 %, n = 315) fully agreed with the previously published data (33 %, n = 24) [23]. The F+G range measured in honeys from Misiones (57–77 %) partially overlapped the range observed for honeys from the nearby Argentinian province of Corrientes (68–83 %, n = 141) [14]. The F+G content in honeys from Catamarca (61–77 %) and La Rioja (64–78 %) were close to those found in honeys from other provinces in the northwest of Argentina (68–74 %, n = 13) [24].

The fructose/glucose ratio (F/G) has been related to the ability of honey to crystallize; thus, honey seemed to remain liquid when its F/G ratio is high and vice versa, and honey crystallization seemed to be slower when the F/G ratio exceeded 1.3, and faster when the ratio was below 1.0. However, the F/G ratio-based crystallization remained not clearly demonstrated because honey contains other sugars (sucrose, maltose, etc.) and insoluble substances (dextrin, colloids, etc.) able to influence the crystallization process [25]. In fact, in the present study, the F/G ratios of the honey samples analysed did not show significant differences according to their physical state (crystallized or uncrystallised at r.t. before analysis).

Relative to the botanical origin, Bentabol Manzanares et al. reported an average F/G ratio of around 1.2 for blossom honey and around 1.3 for honeydew honey [26]. In this regard, the average F/G ratio in all the studied honeys was 1.2, infering the blossom origin of most of the honeys.

Minor sugars

Minor sugars were analysed in the honeys from Buenos Aires, Catamarca and Misiones, collected in the harvests 2013, 2014 and 2015 (n = 355) (Table S2). Trehalose, melezitose, raffinose and maltotriose were not detected in most of the honey samples. Significant differences were observed in the honey contents of turanose, maltose and erlose among the provinces, except between Catamarca and Buenos Aires for turanose and Catamarca and Misiones for maltose and erlose (Table 1). The mean concentration of turanose in the honeys from Misiones (2.3%), Catamarca (2.0%) and Buenos Aires (1.8%) were double than those reported for honeys from other Argentinian phytogeographic regions, while the average amounts of maltose (2.6% for Catamarca, 2.3% for Misiones and 1.7% for Buenos Aires) were similar [27]. Honey from Buenos Aires contained 1% erlose on average, and those from Catamarca and Misiones 0.2%. To the authors' knowledge, data related to the minor sugars of honeys from Misiones and Catamarca has not been previously published.

Physicochemical quality parameters of honeys

Moisture

The water content in honey generally depends on the botanical and geographical origins, the soil, the climatic conditions, the harvest season, the degree of maturity, and the agricultural practices used by beekeepers during extraction, processing and storage of honey [28-30]. Honey moisture is related to its preservation and storage, since a high-water content can lead to the growth of yeast and moulds, responsible of honey sugar fermentation, causing off-flavours and short shelf life. According to the Codex Alimentarius standard for honey, the moisture content of good quality honey cannot be higher than 20 g/100 g of honey (%, w/w) [1]. Thus, honey moisture content lower than 20 % is important for the stability of the product during its storage. All the honey samples studied presented moisture contents (17.0–17.8 % on average) within the limits established by the international standards (Table S2). These moisture values confirmed the good sanitary conditions of all the honeys analysed, and that the fermentation rate was very low [15, 28, 29]. The water contents were consistent with mature honeys, and the average values corresponded to honeys extracted in summer [30]. Moisture was significantly different among the honeys from the four provinces, except for those from Catamarca and La Rioja (Table 1 and Figure S2). This is explained by the fact that both provinces, Catamarca and La Rioja, are next to each other in an area with close climatic and pedoclimatic characteristics, and belong to the same phytogeographical regions (PP Chaqueña and PP of the Monte). The highest average moisture value was presented by honeys from Misiones (18.4%,), followed by those from Buenos Aires (17.4%), Catamarca (16.9%) and La Rioja (16.5%). The different PP present in each province, which contain different vegetation units, and thus different botanical species, are probably responsible for the differences observed in honey moistures [31]. Moreover, honey is hygroscopic, i.e. it is capable of absorbing or losing water depending on environmental conditions (wet or dry respectively) [25]. In this sense, honey from Misiones exhibited higher moisture values probably due to its subtropical climate without a dry season, characterised by high temperatures (15.6–25.5 °C in average) and abundant rainfall throughout the year (1970 mm of annual mean) [32]. Moisture variability in honeys from Misiones was lower than in the other provinces, probably due to the fact that the whole Misiones province is under the influence of the same type of climate, while the other provinces are influenced by several different climates depending on the region. The median moisture observed for honey from Misiones (18.5%, n = 100) were similar to those reported before for this province (18.4%, n = 13) [11]. The influence of rainfalls on honey moisture content was previously reported for honeys from the Argentinian province of Córdoba; thus honeys from the southern region of the province, which receives more annual precipitations, presented the highest moisture values [8]. This was also observed in honeys from the Tabasco region (Mexico) [3] and West Bank (Palestine) [33]. The water content measured in honeys from Buenos Aires agreed with those found in literature for honeys from the same PP (17 %, n=107) [12] and the southeast of Buenos Aires (17%, n = 24) [23], and for clover and eucalyptus honeys (17.1% and 17.3%, respectively) from the PP Pampeana [13]. The moisture of honeys from Buenos Aires were comparable to those reported for Italian multifloral honeys (17.4 %, n = 40) [28], and to the average value obtained in a study of about one thousand honey samples from all over the world (17.9 %) [34]. Moisture variability for Buenos Aires honeys (14–20 %, n=292) was similar to that reported before (13–20 %, n=30) [35]. The average moisture values observed for honeys from Buenos Aires, Catamarca and La Rioja were close to those found previously for Argentinian multifloral honeys (17.0%, n = 16) [36]. Data related to the moisture of honeys from Catamarca and La Rioja is reported here for the first time to the authors' knowledge. Honeys from La Rioja exhibited similar moisture to Spanish honeys of thyme (16.3 %, n = 25), a floral genus also grown in this Argentinian province [30]. The low moisture in honeys from Catamarca and La Rioja could be attributed to the dryness of these arid regions. These results are consistent with other reported data for honeys from the provinces of Chubut and Santa Cruz (Argentina), which present also an arid climate [15].

Free acidity

The free acidity in honey is owed to the presence of organic acids in equilibrium with their corresponding lactones or internal esters, and some inorganic ions, such as phosphate or sulphate [30]. The organic acids present in honey vary according to the characteristic flora in each phytogeographical region [17, 37]. Free acidity is an important quality criterion because honey fermentation causes an increase in this parameter [4]. The fermentation of honey is favoured by high moisture content; therefore free acidity can be correlated with the humidity of the honey and the environment [15, 25]. The

Codex Alimentarius standard fixed the free acidity at 50 meq of acid/kg of honey [1]. The free acidities of all honey samples analysed (22.2–29.5 meq/kg on average) were within the limits established by the international standards, indicating the absence of undesirable fermentation processes (Table S2). Significantly different free acidities were observed among the honeys from the studied provinces, except between Buenos Aires (23.8 meq/kg) and La Rioja (24.5 meq/kg) (Table 1 and Figure S2). Honey collected in Misiones presented the highest average free acidity (37.1 meq/kg), in agreement with the higher moisture contents observed for these samples. Honeys from Misiones presented an average free acidity higher than honeys from the border province of Corrientes, even though the free acidity range of Misiones (17–50 meq/kg, n = 96) partially overlapped that of Corrientes (11–50 meq/kg, n=141) [14]. Both provinces have a sub-tropical wet climate but the sites where the samples were collected, in the present study and in that carried out by Fechner et al., belong to different phytogeographic provinces. Honeys from Catamarca contained on average 31 meq/kg, which was higher than the free acidity found in honeys from these province before (26 meq/kg, n = 39) [16]. It is known that honey free acidity can present a large variability [4]. The free acidity range in honeys from Buenos Aires (14.7–36.3 meq/kg, n = 324) was similar to that reported for Buenos Aires honeys from the same PP (8.2–36.1 meq/kg, n=107) [12] and the Austral district of the PP Pampeana (14.9–28.7 meq/kg, n = 30) [35]. The free acidity of honeys from La Rioja is described for the first time in this work as far as the authors know.

pH

The microorganism's growth in honey depends on honey pH, and can change its texture, stability and shelf life. Honey pH has a great importance during the extraction and storage of honey [8, 30]. The IRAM standard 15938 (1995) for honey interprets pH between 3.5 and 4.5 for blossom honey and between 4.5 and 5.5 for honeydew honey. Indeed, low pH values, even lower than pH 3.5, are associated with blossom honeys while high pH values with honeydew honeys [26, 30]. Most of the honey samples studied showed pH values (pH 3.4–4.0 on average) in the range of the blossom honeys (Table S2). However, some honey samples of harvest 2017 from La Rioja presented higher extreme pH values between 5.7 and 7.9. Significant differences were observed among the four provinces (Table 1 and Figure S2). Honeys collected in La Rioja presented an average pH value (pH 4.3, excluding extreme samples) higher than those in Catamarca (pH 4.2), Misiones (pH 3.9) and Buenos Aires (pH 3.6). The pH values found for honeys from Misiones (pH 3.2–4.6, n = 114) were similar to those reported in literature for this region (pH 3.4–4.5, n = 13) [11], and close to those previously reported for honeys from the northeast region of Argentina (pH 3.7–5.4, n = 141 [14]; pH 3.7–5.0, n = 19 [7]). The pH of honeys from Buenos Aires (pH 3.1–4.1) agreed with those previously published for honeys from the Austral district of the PP Pampeana (pH 3.3–3.7, n = 30) [35]) and the other PP in Buenos Aires (pH 3.2–4.0, n = 53), even though the pH of honeys from the Oriental district of the PP Pampeana were higher (pH 3.3–5.8, n = 54) [12]. The measured pH of honeys from Buenos Aires and Misiones indicated that they were blossom honeys. In contrast, honeys from Catamarca and La Rioja presented pH ranges of 3.5–5.0 and 3.5–5.3 respectively; the box and whiskers plots revealed that the pH of about 25 % of these samples were inside the pH range of honeydew honey according to the IRAM standard. However, such a high pH values were also observed in multifloral honeys from semi–arid regions in Palestine [33]. Moreover, Baroni et al. found that honeys obtained from typical native flora from the semi–arid region in the north of Córdoba province (Argentina) presented higher pH values [8]. This agreed with current observations as expected, since La Rioja and Catamarca are border provinces with the north of Córdoba, present mainly arid climates, and are considered to be arid and semi–arid regions [17, 38]. To the authors' knowledge, pH data related to honeys from Catamarca and La Rioja has not been previously reported in literature.

Additionally, in the present study, a satisfactory linear regression model was developed to relate the pH of the honey solution (20%, w/w) prepared for the determination of honey EC (IRAM standard 15945, 1997) and the pH determined in honey according to the official method (IRAM standard 15938, 1995) with a correlation coefficient of 0.994 (Table S3 and Figure S3). This model allows the determination of both parameters, EC and pH, using the same honey solution, reducing the time for sample preparation and the sample amount required for analysis, which are relevant issues for quality control laboratories.

Electrical conductivity

The honey EC is directly related to the concentration of minerals and salts in the soil of each area, and organic acids and proteins from the nectar of plants [2, 3, 14, 30, 37]. The EC variability in honey depends on the flowers visited by the honey bees, being a relevant parameter for the differentiation of honeys according to their floral origin [2, 23]. EC can be used as a quality indicator for the discrimination between blossom and honeydew honeys [2]. The Codex Alimentarius standard establishes that honey EC should not exceed 800 μS/cm, except for honeydew honey and certain unifloral blossom honeys [1]. The honey samples studied were declared multifloral, and showed EC (248–442 μS/cm on average) within the limits for blossom honey of the international standards (Table S2). Honey EC were significantly different among the provinces studied (Table 1 and Figure S2). Honeys from Misiones displayed a mean EC of 545 μS/cm; La Rioja, 501 μS/cm; Catamarca, 434 μS/cm; and Buenos Aires, 295 μS/cm. The median EC values of honeys from Misiones (553 μS/cm, n=114) were similar to those reported previously for this province (550 μS/cm, n = 13) [11]. The EC range measured in honeys from Buenos Aires (132–565 μS/cm) was included in that found in literature for honeys from the same PP (120–640 μS/cm, n = 107) [12]. EC data of honeys from Catamarca and La Rioja are described here for the first time to the authors' knowledge. The EC values exhibited by all the studied honeys (378 ± 148 μS/cm, range = 132–790 μS/cm) were lower than those observed in about one thousand honey samples collected all over the world (640 ± 400 μS/cm, range=150–1640 μS/cm) [34].

Ash content

Certain nitrogen compounds, minerals, vitamins, pigments and aromatic substances contribute to the ash content of honey; thus it is mainly determined by soil and climatic characteristics but also by the flora physiology of the area [3]. This parameter has been usually used for honey classification in blossom, mixed or honeydew honey [8]. According to the Mercosur and Argentinian national regulation, the ash content of honey should not be higher than 600 mg/100 g of honey, except for honeydew honey or blends of honeydew and blossom honeys [6, 39]. All honeys analysed in this work contained ash below 600 mg/100 g honey, denoting their blossom origin (Table S2). The ash contents of honeys from the studied provinces were significantly different, except between honeys from La Rioja and Catamarca and La Rioja and Misiones (Table 1 and Figure S2). The average ash contents were 320 mg/100 g honey for Misiones, 300 mg/100 g honey for La Rioja and 281 mg/100 g honey for Catamarca, whereas honeys from Buenos Aires showed the lowest value (170 mg/100 g honey). The differences could be attributed to different weather conditions, soil characteristics and floral species in each province [8]. The ash contents of honeys from La Rioja and Misiones have not been published yet to the authors' knowledge. Regarding the ash contents of honey from Catamarca, the average value was slightly higher than that reported previously for the honey of this province (260 mg/100 g honey, n=39) [16]. The ash content measured in honeys from Buenos Aires (76–281 mg/100 g honey, n = 326) were barely higher respect to the data previously published for the same PP of this province (4–230 mg/100 g honey, n = 107 [12]; and 20–150 mg/100 g honey, n = 34 [40]). It should be noted that the set of samples in the present study is considerably larger and more representative of the honey produced in the three PP considered.

Colour

The honey colour is due to the presence of polyphenols, terpenes and carotenoids, therefore it is considered as an index of its antioxidant power [27]. In general, light-coloured honey has lower total phenol contents, and dark honey contains a larger amount of phenolics. Regarding that these compounds come from the flowers that feed honey bees, the colour of honey can provide information related to its botanical origin. Agricultural practices and production methods can also influence the colour of honey. Honey colours differed significantly among the provinces studied (Table 1 and Figure S2), except for Catamarca and Misiones with mean values of 81.0 and 83.8 mm Pfund respectively (light amber, but close to the amber colour range). The honeys from these two provinces exhibited the darkest colours and the largest variability. In contrast, the honey from Buenos Aires with an average of 37 mm Pfund (extra light amber) showed the lightest and the most homogenous colour. Honey from La Rioja presented an intermediate average colour value of 63 mm Pfund (light amber). Colour measurements of honeys from Catamarca and La Rioja are reported here for the first time as far as the authors know. The colour range of honey from Misiones (51–119 mm Pfund, n=115) was included in that observed before (55–150 mm Pfund, n=13) [11]. The honeys from Buenos Aires (18–54 mm Pfund, n = 321) presented colours similar to those previously reported (8–54 mm Pfund, n = 34) [40], but lighter than those observed in honeys from the southeast of Buenos Aires (29–71 mm Pfund, n = 24) [23]. The honeys from Catamarca (19–150 mm Pfund, n = 70) exhibited similar distribution of colours to those from Corrientes (29–150 mm Pfund, n =141) [14], and close to those from the northwestern region of Argentina (10–126 mm Pfund, n = 13) [24]. The colour of the analysed honeys disclosed that darker colours were linked to higher ash contents and EC measurements, as previously observed [27, 30]. Honeys from Buenos Aires exhibited lighter colours and lower EC and ash contents than honeys from the other provinces, which presented medium-high EC and ash contents. A linear fit of colour and ash content data of honeys from Buenos Aires, La Rioja and Catamarca displayed a correlation coefficient of 0.75, whereas no correlation was found between these two parameters for honey from Misiones. Honey colours were from white to light amber in Buenos Aires, white to amber in La Rioja, white to dark in Catamarca and light amber to dark in Misiones. This fact is a competitive advantage for honeys from Buenos Aires since they are preferred in the international market. Regarding consumers perception, in general, lighter colours are associated to delicate flavours, and darker colours with strong flavours and less attractive appearance. Honey can undergo darkening and experiment changes in its organoleptic properties during shipping and storage. Therefore, colour is a very relevant grading and commercial factor that determines the price of honey in the world market [14].

Total soluble solid content

The total soluble solid content is a measure of the total sugar content in honey, expressed as grams of sucrose in 100 grams of honey (°Brix). Honey typically contains about 83 ºBrix (ºBx) [28-30]. All honey samples analysed presented total soluble solid contents (80–81 °Bx on average) within this °Brix value (Table S2). The total soluble content of honey is strictly correlated to its humidity; the correlation coefficient being –0.98 at $p < 0.05$, as previously observed [28-30]. On the one hand, the higher the water content in the honey, the greater the dilution of the sugars and, hence, the honey presents a lower ºBrix value. On the other hand, a higher moisture content in honey increases the probability of sugar fermentation during honey storage, which leads to a decrease in its °Brix value [41]. In this sense, honeys collected in Misiones exhibited a significantly lower average °Brix value (79.6 °Bx) than those from Buenos Aires (80.5 °Bx), Catamarca (80.8 °Bx) and La Rioja (81.7 °Bx) (Table 1 and Figure S1). The low °Brix value of Misiones honeys was explained by the wet subtropical climate, which favours higher moisture contents in honey, resulting in lower °Brix values, as explained above [41]. The total contents of total soluble solids of honeys from La Rioja, Catamarca and Misiones have not been reported previously to the authors' knowledge. The average °Brix values of honeys from La Rioja was similar to those published for honeys from Spain (81.9 °Bx, n = 24) [30]. The ºBrix values of honeys from Buenos Aires and Catamarca were comparable to those reported for Italian multifloral honeys (80.9 °Bx, n = 40) [28] and for honeys from Le Marche (Italy) (81.2 °Bx, n = 69) [29].

HMF content

The HMF content in honey indicates the degree of honey deterioration caused by intense and/or extended thermal treatment and/or inadequate or prolonged storage conditions. HMF content increases upon storage depending on the pH of the honey and the storage temperature [4]. Indeed, HMF is formed by the decomposition of monosaccharides during the Maillard reaction, which occurs slowly during storage, and quickly when honey is heated [11]. The Codex Alimentarius standard defined a maximum content of 40 mg HMF/kg of honey from non-tropical regions and 80 mg HMF/kg of honey from tropical regions [1]. HMF was determined in the honeys collected in harvests 2015, 2016 and 2017 (Table S2); all samples complied with the HMF contents limits established by international standards. This was indicative of good quality, fresh and unprocessed honeys, and suggests good practices by beekeepers. The formation of HMF, through the Maillard reaction, is favoured by the water content in the media. Therefore, a higher moisture in honey results in the presence of a higher amount of HMF. Honey from Buenos Aires presented the lowest HMF amounts and variability, displaying a mean value of 4.2 mg HMF/kg, which was significantly different from those of the other provinces (Table 1 and Figure S4). The average HMF content of Misiones, Catamarca and La Rioja were 13.7, 11.3 and 9.8 mg HMF/kg respectively. Moreover, the HMF results were consistent with the concentration of fructose and glucose in the honeys from the studied provinces, since the honeys with higher HMF values presented lower fructose and glucose contents (Figure S1 and S4). The significant differences revealed between the HMF contents of honeys from diverse provenances could be also due to different beekeeping practices [9]. The average HMF content in the multifloral honeys from Buenos Aires was similar to that previously described for honeys from the same PP (4.3 mg HMF/kg, n = 107) [12], but lower than those reported for clover honey (6.7 mg HMF/kg, n = 53) and eucalyptus honey (7.2 mg HMF/kg, n = 28) from this province [13]. The median HMF concentration in honeys from Misiones (12 mg HMF/kg, n = 52) was higher than the reported in the literature (6 mg HMF/kg, n = 13) [11], but the present measurements exhibited less variability (1–34 mg HMF/kg, n = 52) than in the mentioned report (1–70 mg HMF/kg, n = 13). According to Ávila et al., the HMF content in honey can be influenced by climate [37]. In tropical regions, where honeys are exposed to high temperatures for long periods, sugar decomposition pathways that lead to the formation of HMF are favoured, and therefore, these honeys can present higher HMF amounts. Moreover, Baroni et al. observed that honey from the southern region of Córdoba (Argentina), which has a Pampean temperate climate with relatively high levels of rainfall, contained higher concentrations of HMF than honey from the northern region of Córdoba with arid climate [8, 18]. Therefore, the higher HMF contents observed in honeys from Misiones were explained by its characteristic wet subtropical climate and higher moisture content [17, 18, 38]. The mean HMF content of honeys from Catamarca was lower than those reported previously for honey from this province (20 mg HMF/kg, n = 39) [16]. Data related to the HMF contents of honeys from La Rioja are published here for the first time. Most of the honey samples from Catamarca and La Rioja were collected in regions under arid climate, which explained their close HMF contents, even though Catamarca exhibited a higher maximum value due to the honeys collected in the region under the sierra subtropical climate [18]. The contents of water and HMF in honey also depend on the method used for extraction, processing and storage of honeys, therefore these parameters cannot be considered as completely representative of the honey nature but rather as indicators of freshness [8].

Conclusions

The honeys from the Argentinian provinces of Buenos Aires, Misiones, Catamarca and La Rioja were characterized according to their sugar profiles and typical physicochemical quality parameters. All honeys were in compliance with the national [39] and the international regulations established by the Codex Alimentarius Commision, EU Council and Mercosur [1, 5, 6], except for few samples that were close to the established limits for some parameters. The analytical results disclosed that the honeys from the different provinces were high quality honeys obtained under adequate beekeeping and processing practices. Several parameters, i.e. fructose/glucose ratio, ash content, EC and pH, disclosed to the blossom origin of the honeys. The contents of sucrose, water and HMF evidenced the good maturity and freshness of the honeys harvested in the proper time and season. The moisture and free acidity measurements revealed the absence of undesirable fermentation in the honeys. Low EC and contents of HMF and sucrose were indicative of a high control of production, good beekeeping practices and good preservation state of samples. The results of the present study proved the impact of the vegetation units in each PP and the pedoclimatic conditions of each province on the physical and chemical parameters of honeys. In this sense, the honeys from the four provinces presented significantly distinctive pH and EC values. Honeys from Buenos Aires exhibited characteristic lighter colours, lower pH and EC values and contents of ash, HMF and maltose, intermediate moistures, and higher concentrations of erlose. In contrast, honeys from Misiones were typified by higher moistures, free acidities, EC values and turanose contents, intermediate pH values, and lower amounts of reducing sugars and total soluble solids. Honeys from La Rioja showed particularly higher pH and ºBrix values, intermediate colours and medium-high EC values. Honeys from Catamarca were characterised by medium-high pH, medium-low EC and higher sucrose content. Besides, Misiones and Catamarca produced the darkest honeys. However, none of the physical and chemical parameters measured were completely discriminant among the honeys from the four provinces studied. To the best of the authors' knowledge, data related to the physicochemical quality parameters of honeys from La Rioja, and the moisture, pH, EC and total soluble solid content of honeys from Catamarca, as well as the sugar profiles of honeys from Misiones, Catamarca and La Rioja are reported here for the first time. In addition, the relevance of the present work also lies in the extended knowledge generated with the study of the 572 Argentinian honey samples of five harvests. This large sample set was traceable and representative of the honeys from the regions studied, and included harvest variability, which is a requirement to characterise any agricultural food product. The typification of the honeys from each of the studied provinces will provide them with an added value and allow them to access new markets. Furthermore, typified honey has a higher commercial value than standard quality honey. Indeed, there is currently a growing global demand for differentiated products. In this framework, the importance of having typified honeys is evident, and the contribution of this study to the characterization of honeys from Argentina is noteworthy.

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