Physicochemical Characterization Of Argentinian Honeys From The Phytogeographic Provinces Pampeana, Espinal And Monte Based On Their Sugar Profiles And Quality Parameters

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Abstract.

The honeys from the Phytogeographic Provinces (PP) of the south of Buenos Aires province (Argentina) were characterised by the sugar composition and physicochemical parameters used for honey quality control. A large set (n=329) of traceable raw honey samples obtained from beekeepers were analysed and met the specifications of the national and/or international standards for the evaluated parameters, which denoted their blossom origin and confirmed their authenticity, good maturity and freshness. The influence of flora and the pedoclimatic conditions of each phytogeographical region, as well as their beekeeping practices, on the physical and chemical properties of honey allowed its characterization. Thus, the honeys from the southeast of Buenos Aires province were characterized by higher contents of moisture, fructose, maltose, erlose, hydroxymethylfurfural (HMF) and ash, pH and electrical conductivity (EC) and slightly lighter colours; while southwest honeys showed higher free acidities, sucrose content and ºBrix values. Honeys from the PP Espinal exhibited characteristic lower contents of fructose, HMF and ash and EC values, and larger amounts of sucrose. Honeys from the PP Monte presented typical lower moisture contents and slightly darker colours. Honeys from the PP Pampeana were typified by higher amounts of fructose.

Keywords: *Honey; saccharides; physicochemical parameters; quality; traceability; and geographical origin.*

I. INTRODUCTION

Honey is the natural sweet substance produced by *Apis mellifera* bees from blossom nectar and/or honeydew (exudates of plants or plant sucking insects), according to the Codex Alimentarius Commission (Codex STAN 12-1981 Rev. 2, 2001). Honey is a supersaturated solution of sugars, mainly composed of fructose and glucose, and a wide range of minor components such as minerals, proteins, free amino acids, vitamins, enzymes, phenolic acids and flavonoids [1]. Honey chemical composition and its quality is strongly associated to its botanical origin, closely related to the geographical area where it is produced due to environmental and seasonal factors, and to its handling, processing and storage [2, 3]. The interest of consumers in the quality of food and the traceability of its origin makes the characterization of honey from different botanical and/or geographical origins highly relevant [3]. Moreover, this is also a fundamental issue for the honey market, because every region may present particular quality characteristics that determine its commercial value [4].Among the honey producing countries, Argentina is positioned in third place worldwide, after China and the United States, representing 70 % of the honey produced in the southern hemisphere of the American continent, concentrating 25 % of the production of the entire continent, and 6 % of the total produced in the world [5]. The province of Buenos Aires, situated in the middle-east of the country (33º–41° S and 57º–63° W), is the main honey-producing province, accounting for more than 50 % of the Argentinian honey production with around 915 thousand beehives [5].Most of the production is fragmented in small primary producers and the structure of the supply chain hinders the differentiation of the products and the quality control related to its origin, therefore most of the Argentinian honey is commercialised in commodity markets without being characterised [6].

Producers, retailers and authorities are interested in given Argentinian honey from the different producing regions 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 sense, pedoclimatic conditions determine the botanical species grown in each geographical area, and both influence the physical and chemical characteristics of the honey produced in each region [4, 7, 8]. The province of Buenos Aires presents several Phytogeographic Provinces (PP), districts and vegetation units [9, 10], as well as different climates [11]. The major honey production areas belong to: (*i*) PP Pampeana, where the dominant vegetation type is the steppe or pseudo-steppe combined with grassland (genera *Nassella*, *Piptochaetium* and *Andropogon*) and shrubs (genera *Baccharis* and *Eupatorium*); (*ii*) PP of the Espinal (PP Espinal), with the sclerophytic forest (genus *Prosopis*) and the savannah, including arboreal and shrub species, xerophytic mimosoides legumes and an herbaceous layer as the main vegetation types; and (*iii*) PP of the Monte (PP Monte), presenting the steppe of xerophytic shrubs with perennial and resinous foliage (genus *Larrea*) as the predominant vegetation, and characterised by a shortage of grasses and trees. Nevertheless, part of the wild vegetation has been modified due to agriculture and cattle-raising in the PP Pampeana, and the exploitation of tree species in the PP Monte and the Calden district of the PP Espinal [10].

Regarding the climate of the province of Buenos Aires, a NE-SW thermal and pluviometric gradient causes a gradual variation in the subtropical and temperate vegetation. The Atlantic coast region is subjected to the Oceanic temperate climate; the extreme south of the province to the steppe or semi-arid climate; the region between the steppe and the pampas region to the transition temperate climate; and the rest of the province to the Pampean temperate climate [11].Regulatory entities such as the International Honey Commission (IHC), Codex Alimentarius, European Commission and Mercosur provide international guidelines to enhance quality and safety control of honey. These guidelines (Codex STAN 12-1981 Rev. 2 (2001), Council Directive 2001/110/EC (2001), Mercosur – Res. Nº 89/99 (1999)) outlined several parameters, including the contents of moisture, sugar, total soluble solids, ash and hydroxymethylfurfural (HMF), electrical conductivity (EC), free acidity and diastase activity as benchmarks of honey quality and traceability, and establish their limits and the harmonized methods for their determination [7]. These physicochemical parameters have been used as markers to identify the geographical origin of honey [4, 12], establish the blossom or honeydew origin of honey [7], and disclose honey adulteration [13-15]. Some of these physicochemical parameters have been used to characterize honey from different regions of Argentina [3, 4, 16-20], including the province of Buenos Aires [10, 17]. Argentinian honeys resulted to be mainly floral honeys. However, most of these studies were performed on sample sets with a relatively small number of samples, which just led to preliminary honey characterization. Moreover, the comparison of the physicochemical properties of the honeys from different regions was difficult because the analysed parameters varied among the studies.In the present work, a large set of Argentinian honeys from the PP Pampeana, PP Espinal and PP Monte in the province of Buenos Aires 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 phytogeographical regions.

II. MATERIALS AND METHODS

2.1. Honey samples

A total of three hundred twenty-nine (n=329) authentic and traceable honey samples of *Apis mellifera* were collected along several seasons (2013–2017) from the southeast (SE) and the southwest (SW) regions of the province of Buenos Aires, located at the east and west of the meridian 60° W and to the south of the 36th parallel S. These regions correspond to: (*i*) the vegetation units 33 (VU-33: meadows of hygrophytes and halophytes) and 34 (VU-34: pseudosteppe of mesophytes with highland scrub) of the Oriental and Austral districts, respectively, of the PP Pampeana; (*ii*) the vegetation unit 22 (VU-22: sclerophyte forest with *Prosopis caldenia*) of the PP Espinal (Calden district); and (*iii*) the vegetation unit 26 (VU-26: Zigofilaceae scrub, e.g, *Larrea* sp., with *Geoffroea decorticans, Prosopis flexuosa* and *Condalia microphylla*) of the PP Monte (Fig. 1 and Table S1) [9, 10]. Sampling was carried out within the framework of the Argentinian 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, apiary location (GPS), agricultural system, colony treatments, etc. The honeys were harvested between November and April, and manufactured following the guide for good beekeeping and manufacturing practices provided by the Argentinian Ministry of Agriculture, Livestock and Fisheries (2019). All honey samples were stored in screw-capped plastic containers at 4°C in the dark until analysis.

2.2. 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.

2.3. Determination of physicochemical parameters

The physicochemical parameters, namely moisture, free acidity, pH, EC 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). Three replicate were analysed for each sample. Honey moisture and the total soluble solid content in degree Brix (ºBrix) was determined according to IRAM standard 15931 (1994), using an Abbé refractometer 5 (Bellingham & Stanley Ltd, Longfield Road, Tunbridge Wells, United Kingdom). The 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. (1999) [7]. 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). 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 air bubbles, as indicated in the IRAM standard protocol. Colour was expressed in the Pfund-scale.

2.4. Determination of sugars

The contents of sugars in honey were determined according to IHC [1] 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 $mL \cdot min^{-1}$ 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.

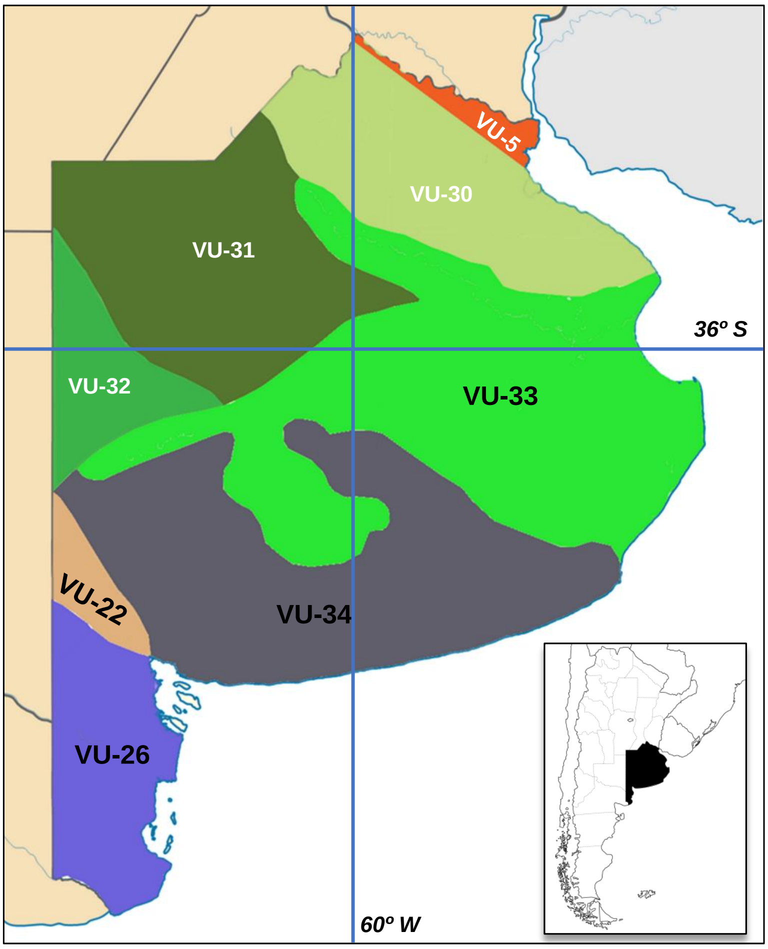

Fig 1. Honey samples were collected in the vegetation units VU-33, VU-34, VU-22 and VU-26 located in the south of the province of Buenos Aires (Argentina).

2.5. 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.

2.6. 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 (n=3) were at 5 % or below, confirming the good repeatability of the analytical methodologies performed. Samples were grouped according to the geographical origin (SE and SW), the vegetation unit of the PP (VU-22, VU-26, VU-33 and VU-34) and the climate (Oceanic and Pampean). 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, least significant difference test (LSD) and box and whiskers plots. Regarding the box and whiskers plots, the symmetry of data distribution, mean, median, minimum, maximum, outliers and extreme values were evaluated according to the geographical origin, the vegetation unit of the PP and the climate. 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).

III. RESULTS AND DISCUSSION

Honeys from four different vegetation units of the PP in the south of the province of Buenos Aires were characterised by their individual sugar composition and physicochemical quality parameters, namely moisture, free acidity, pH, electrical conductivity, colour and the contents of ash, total soluble solids and HMF (Tables 1, 2, S2 and S3). The analysed honeys from these regions along several seasons presented characteristic sugar profiles and physicochemical parameters described in the next sections. The different vegetation units of each PP and the climate of each region explained the composition and values of the quality parameter in the honeys, which exhibited a great variability, likely due to the different botanical species flowering at the time of honey production. Significantly differences were found only among certain seasons and physicochemical parameters (Table S2), as had been already observed [12].

Table 1. Sugar composition and physicochemical parameters of honeys from the south of the province of Buenos Aires depending on their geographical origin.

Physicochemical parameter		Geographical origin	
		SE	**SW**
Fructose (g/100 g honey)	**n**	267	55
	Mean	39.2[a]	38.4[b]
	SD	0.6	1.1
	Min	37.6	35.6
	Max	42.0	41.0
	Median	39.2	38.2
Glucose (g/100 g honey)	**n**	267	55
	Mean	33.4[a]	33.3[a]
	SD	1.4	1.9
	Min	29.3	26.8
	Max	39.0	37.2
	Median	33.2	33.2
F+G (g/100 g honey)	**n**	267	55
	Mean	72.6[a]	71.7[b]
	SD	1.7	2.3
	Min	68.3	67.4
	Max	76.7	76.0
	Median	72.5	72.1
F/G ratio	**n**	267	55
	Mean	1.176[a]	1.152[b]
	SD	0.046	0.063
	Min	0.995	1.038
	Max	1.331	1.320
	Median	1.179	1.155
Sucrose (g/100 g honey)	**n**	269	56
	Mean	0.14[a]	0.38[b]
	SD	0.18	0.30
	Min	n.d.	n.d.
	Max	0.70	0.90
	Median	n.d.	0.30
Maltose (g/100 g honey)	**n**	209	31
	Mean	1.77[a]	1.30[b]
	SD	0.75	0.53
	Min	n.d.	0.50
	Max	3.70	2.30
	Median	1.80	1.40
Turanose (g/100 g honey)	**n**	209	31
	Mean	1.85[a]	1.75[a]
	SD	0.55	0.49
	Min	0.70	1.00

Physicochemical parameter		Geographical origin SE	SW
	Max	3.10	2.70
	Median	1.80	1.60
Erlose (g/100 g honey)	n	209	31
	Mean	1.04[a]	0.77[b]
	SD	0.66	0.58
	Min	n.d.	n.d.
	Max	2.70	1.90
	Median	1.00	0.60
Moisture (%)	n	261	55
	Mean	17.8[a]	17.2[b]
	SD	1.3	1.7
	Min	15.0	14.6
	Max	20.6	20.8
	Median	17.6	16.8
Free acidity (meq/kg honey)	n	268	56
	Mean	22.9[a]	28.5[b]
	SD	4.6	4.6
	Min	14.7	18.0
	Max	33.2	37.3
	Median	22.0	28.1
pH	n	271	56
	Mean	3.61[a]	3.47[b]
	SD	0.22	0.25
	Min	3.13	3.09
	Max	4.11	4.08
	Median	3.64	3.42
EC (µS/cm)	n	271	55
	Mean	301[a]	266[b]
	SD	76	69
	Min	148	132
	Max	565	425
	Median	296	248
Ash content (mg/100 g honey)	n	271	55
	Mean	173[a]	153[b]
	SD	43	40
	Min	85	76
	Max	281	234
	Median	170	142
Colour (mm Pfund)	n	270	55
	Mean	36.8[a]	40[b]
	SD	9.8	14
	Min	17.3	22
	Max	55.5	59
	Median	36.1	37
Total soluble content (°Brix)	n	268	56
	Mean	80.4[a]	81.0[b]
	SD	1.5	1.7
	Min	77.4	77.5
	Max	83.3	83.5
	Median	80.7	81.6
HMF (mg/kg honey)	n	84	41
	Mean	4.9[a]	2.8[b]
	SD	1.6	1.9
	Min	1.0	1.0
	Max	9.0	6.0
	Median	5.0	3.0

[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; SE, southeast; SW, southwest.

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

Table 2. Sugar composition and physicochemical parameters of honeys from the Phytogeographical Provinces (PP) and vegetation units (VU) located in the south of the province of Buenos Aires.[1,2]

Physicochemical parameter		PP Pampeana		PP Espinal	PP Monte
		VU-33	VU-34	VU-22	VU-26
Fructose	**n**	77	201	29	15
(g/100 g honey)	**Mean**	39.23[c]	39.22[c]	38.0[a]	38.53[b]
	SD	0.48	0.61	1.2	0.97
	Min	38.30	38.00	36.1	37.10
	Max	40.20	40.60	40.0	40.50
	Median	39.20	39.20	37.9	38.50
Glucose	**n**	77	201	29	15
(g/100 g honey)	**Mean**	33.4[a]	33.4[a]	33.1[a]	33.3[a]
	SD	1.6	1.3	2.0	2.3
	Min	29.3	29.6	27.1	26.8
	Max	39.0	39.0	37.2	36.1
	Median	33.2	33.4	33.0	33.0
F+G	**n**	77	201	29	15
(g/100 g honey)	**Mean**	72.6[b]	72.6[b]	71.2[a]	71.9[ab]
	SD	1.9	1.7	2.5	2.2
	Min	68.3	68.4	67.4	69.6
	Max	75.7	76.7	76.0	74.7
	Median	72.4	72.6	71.3	72.2
F/G ratio	**n**	77	201	29	15
	Mean	1.178[b]	1.175[b]	1.152[a]	1.162[a]
	SD	0.052	0.043	0.073	0.101
	Min	1.000	0.995	1.038	1.059
	Max	1.331	1.311	1.320	1.455
	Median	1.186	1.178	1.150	1.155
Sucrose	**n**	78	202	29	16
(g/100 g honey)	**Mean**	0.19[b]	0.13[c]	0.50[a]	0.26[b]
	SD	0.20	0.17	0.33	0.22
	Min	n.d.	n.d.	n.d.	n.d.
	Max	0.70	0.70	1.40	0.60
	Median	0.20	n.d.	0.50	0.25
Maltose	**n**	56	161	12	11
(g/100 g honey)	**Mean**	1.90[b]	1.69[ab]	1.39[a]	1.33[a]
	SD	0.81	0.72	0.62	0.59
	Min	0.30	n.d.	0.60	0.50
	Max	3.50	3.40	2.30	2.00
	Median	1.90	1.50	1.70	1.40
Turanose	**n**	56	161	12	11
(g/100 g honey)	**Mean**	1.95[a]	1.80[a]	1.66[a]	1.92[a]
	SD	0.55	0.55	0.47	0.52
	Min	0.80	0.70	1.00	1.30
	Max	2.90	3.10	2.50	2.70
	Median	2.00	1.70	1.50	1.80
Erlose	**n**	56	161	12	11
(g/100 g honey)	**Mean**	1.26[b]	0.94[a]	1.05[ab]	0.60[a]
	SD	0.61	0.65	0.61	0.57
	Min	0.30	n.d.	0.20	n.d.
	Max	2.40	2.60	1.70	1.90
	Median	1.10	0.90	1.20	0.60
Moisture	**n**	76	196	29	15

Physicochemical parameter		PP Pampeana		PP Espinal	PP Monte
		VU-33	VU-34	VU-22	VU-26
(%)	Mean	17.6[bc]	17.8[c]	17.2[ab]	16.7[a]
	SD	1.2	1.3	1.8	1.6
	Min	15.3	15.0	14.6	15.2
	Max	21.0	21.0	20.4	17.0
	Median	17.5	17.6	16.6	16.2
Free acidity (meq/kg honey)	n	78	201	29	16
	Mean	21.2[b]	23.8[c]	28.5[a]	28.7[a]
	SD	3.1	5.0	4.9	4.7
	Min	15.0	14.7	24.1	20.6
	Max	29.7	35.0	36.0	37.3
	Median	20.8	23.0	28.1	29.8
pH	n	78	204	29	16
	Mean	3.68[b]	3.57[c]	3.47[a]	3.56[abc]
	SD	0.20	0.23	0.25	0.28
	Min	3.36	3.09	3.09	3.16
	Max	4.11	4.01	3.88	4.08
	Median	3.70	3.60	3.48	3.44
EC (µS/cm)	n	78	204	29	15
	Mean	309[b]	296[b]	249[a]	308[b]
	SD	88	69	66	77
	Min	155	148	132	192
	Max	526	461	361	425
	Median	313	288	235	284
Ash content (mg/100 g honey)	n	78	204	29	15
	Mean	177[b]	170[b]	143[a]	177[b]
	SD	51	40	38	44
	Min	89	85	76	110
	Max	302	265	207	244
	Median	180	166	135	163
Colour (mm Pfund)	n	78	203	29	15
	Mean	35.5[b]	38[b]	38[ab]	44[a]
	SD	9.2	10	13	16
	Min	17.5	21	23	22
	Max	52.8	54	51	54
	Median	35.3	37	35	40
Total soluble content (°Brix)	n	76	203	29	16
	Mean	80.6[ab]	80.3[b]	81.1[a]	81.3[a]
	SD	1.2	1.5	1.7	1.9
	Min	77.7	77.2	78.0	81.5
	Max	83.0	83.3	83.5	83.0
	Median	80.7	80.6	81.6	81.9
HMF (mg/kg honey)	n	22	73	20	10
	Mean	4.0[bc]	4.8[b]	2.5[a]	3.6[ac]
	SD	1.7	1.6	1.7	2.6
	Min	2.0	1.0	1.0	1.0
	Max	7.0	9.0	6.0	9.0
	Median	4.0	5.0	2.0	3.0

[1] Abbreviations: See Table 1.

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

3.1. Sugar profiles of honeys

3.1.1. Major sugars

The reducing sugars, i.e. fructose and glucose, are the major compounds in honey. According to the Codex Alimentarius standard (Codex STAN 12-1981 Rev. 2, 2001), blossom honey should present a total content of fructose and glucose (F+G) 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. The F+G content was higher than 60% for all the honeys studied, confirming their blossom origin (Table S2). The amounts of fructose and glucose and the F+G content varied in the range of 36–42 % fructose, 29–37 % glucose and 63–78 % F+G. All samples contained higher amounts of fructose than glucose, supporting that almost all types of honey present greater contents of fructose than glucose [21].The contents of fructose and F+G in honeys from the SE and SW of the province of Buenos Aires were significantly different (Table 1 and Fig. S1). The fructose contents of SE honeys (38.0–40.6 %) exhibited lower variability than SW honeys (35.6–41.0 %). Significant differences were observed in the fructose concentrations among the honeys from the three PPs; and in the F+G content, only between honeys from PP Espinal and those from PP Pampeana (Table 2 and Fig. S2). Honeys from PP Espinal exhibited the highest variability (36–40 %) in the fructose content and the lowest mean value (38.0 %) compared to honeys from the other regions (38.5 % for PP Monte and 39.2 % for PP Pampeana). The F+G average concentration in honeys from the PP Pampeana (72.6 %) was significantly higher than in those from the PP Monte (71.9 %) and the PP Espinal (71.2 %).The presence of sucrose in honey can provide information about its adulteration and its botanical origin [22]. A high sucrose concentration in honey means, in most cases, an early harvest of honey because sucrose has not been fully transformed to glucose and fructose by the activity of the invertase enzyme, and/or the addition of exogenous sugars [13].

Unaltered honey should present less than 5 % sucrose according to the Codex Alimentarius standard (Codex STAN 12-1981 Rev. 2, 2001). The sucrose measured in the studied honeys varied in the range from non-detected to 0.9 %, except for one sample with 1.4% (Table S2). These contents being far below 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. SE and SW honeys showed significantly different concentrations of sucrose; the median being 0.3 % for SW honeys and under the limit of detection for SE honeys (Table 1 and Fig. S2). Thus, sucrose was not detected in 20 % of SW honeys and in 57 % of SE honeys. The same trend was observed for SW and SE honeys from VU-34 (Table S3). Moreover, the sucrose contents of honeys from VU-34 were significantly influenced by the Oceanic or Pampean temperate climates of the production site (Fig. S5). Significant differences were observed in the sucrose contents of honeys from the studied vegetation units, except between VU-26 and VU-33 (Table 2 and Fig. S3). The mean sucrose content of honeys from VU-22 (0.50 %) was significantly higher than those from VU-26 (0.26 %), VU-33 (0.19 %) and VU-34 (0.13 %).The average content of fructose (39 %) and sucrose (0.14 %) in SE honeys was lower than that reported previously (43% fructose and 1.0–1.6 % sucrose, n=24), whereas the average glucose concentrations (33 %) were coincident [23]. The mean fructose and glucose contents of honeys from the PP Pampeana (39 % fructose and 33 % glucose) was higher than those reported previously for honeys from the same phytogeographical region (35 % fructose and 27 % glucose, n=6), whereas the sucrose contents (0.13–0.19%) were lower (0.27 %, n=6) [24]. However, the mean concentrations of fructose, glucose and sucrose measured in honeys from the PP Pampeana were lower than those found for clover and eucalyptus honeys from this PP (41 % fructose, 34% glucose and 0.9–1.0% sucrose, n=81), while the average F+G content (72.6 %) was higher than those reported for eucalyptus (71.2 %, n=28) and clover (71.8 %, n=53) honeys [17].

In contrast with previous observations [4], honeys from the transition temperate and the steppe or semi-arid climates in the PP Espinal and PP Monte, respectively, presented lower fructose concentrations than honeys from Pampean temperate climate (PP Pampeana), indicating that the main influence on this parameter is due to the flora of each PP and no directly to climate. However, significant differences were observed between the sucrose content in honeys from VU-34 depending on the climate; thus inland honeys under the Pampean temperate climate presented higher sucrose contents than those under the Oceanic temperate climate on the Atlantic coast. Regarding all studied honeys from the south of the province of Buenos Aires, the F+G range (67–77 %) partially overlapped with that reported for honeys from the Argentinian provinces of Corrientes (68–83 %, n=141) [3] and La Pampa (63–73 % w/w, n=38) [25].The ability of honey to crystallize has been related to the fructose/glucose ratio (F/G); thus, honey with high F/G seemed to remain liquid and vice versa [21].Besides, honey crystallization seemed to be slower when F/G exceeded 1.3, and faster when the ratio was below 1.0. However, F/G-based crystallization remained not clearly demonstrated, because honey contains other sugars and insoluble substances able to influence the crystallization process [26]. Indeed, F/G of all studied honeys varied in the range from 0.99 to 1.33 (Table S2), and were found to be either crystallized or uncrystallised at r.t. before analysis. Relative to the botanical origin, Bentabol Manzanares et al. (2011) reported an average F/G around 1.2 for blossom honey and around 1.3 for honeydew honey [27]. In this regard, the mean and standard deviation F/G values of the studied honeys were 1.18±0.05 for the PP Pampeana, 1.15±0.06 for the PP Espinal and 1.14±0.07 for the PP Monte, supporting their blossom origin.

3.1.2. Minor sugars

Minor sugars were determined in honeys of harvests 2013, 2014 and 2015 (Table S2). The contents varied in the range of 0.8–3.1 % turanose, 0.3–3.7 % maltose and nd–3.1 % erlose. Trehalose, melezitose, raffinose and maltotriose were not detected in most of the honey samples. Significantly different amounts of maltose and erlose were found in honeys from SE (1.8 % maltose and 1.0 % erlose) and SW (1.3 % maltose and 0.8 % erlose) (Table 1); SE honeys showing larger variability than SW ones. This trend was also exhibited for SW and SE honeys from VU-34 (Table S3). Significant differences were observed in the average content of maltose among honeys from VU-33 (1.9 %) and both VU-22 (1.4%) and VU-26 (1.3%), and erlose among honeys from VU-33 (1.3 % erlose) and both VU-34 (0.9%) and VU-26 (0.6%) (Table 2). The average maltose content of honeys from PP Espinal was lower than those measured before (1.8 %, n=6) [24]. However, honeys from the PP Pampeana with 1.9 % and 1.7 % maltose for VU-33 and VU-34 respectively, presented higher mean maltose concentrations than those previously reported for this PP (1.3 %, n=6) [24]. The average turanose content of honeys from PP Espinal (1.7 %) and PP Pampeana (2.0 % for VU-33 and 1.8 % for VU-34) were higher than those found for honeys from these PPs, i.e. 0.98 % (n=6) and 1.0 % (n=6) respectively [24].

3.2. Physicochemical parameters of honeys

1.2.1. Moisture

The water content in honey generally depends on its botanical and geographical origins, pedoclimatic conditions, harvest season, maturity and agricultural practices during extraction, processing and storage [14, 28, 29]. Honey moisture is a relevant issue regarding its conservation and storage, since a high-water content can cause the growth of yeasts and moulds responsible for the fermentation of sugar in honey, causing bad flavours and a short shelf life [22]. According to the Codex Alimentarius standard for honey (Codex STAN 12-1981 Rev. 2, 2001), the moisture content of good quality honey cannot be higher than 20 g/100 g (%, w/w), except for honeys from some botanical species, such as *Tifolium* (<21%) . Thus, honey moisture content lower than 20 % is important for the stability of the product during its storage. Most the honey samples studied presented moisture contents within the limits established by international standards (Table S2). Nine honey samples exhibited moisture values higher than 20% but in agreement with the characteristic moisture of honey of the botanical species *Tifolium*. These samples had been declared as multiforal including pasture, which typically contains *Tifolium* species in the studied regions. The moisture values of all the honeys analysed confirmed their good sanitary conditions, and that the fermentation rate was very low [14, 18, 28]. These water contents were consistent with mature honeys, and the average values corresponded to honeys extracted in summer [29].Honey is hygroscopic, i.e. it is capable of absorbing or losing water depending on environmental conditions (wet or dry respectively) [26].

Thus, honey moisture content is influenced by the climate of the geographical origin where it is produced. Significant differences were found between the moisture contents of SE and SW honeys (Table 1 and Fig S3); SE honeys exhibited higher average moisture contents (17.8 %) than the SW honeys (17.2 %). Regarding the phytogeographical regions, mean moisture contents were not significantly different between honeys from VU-26 (16.7 %) and VU-22 (17.2 %), and between VU-33 (17.6 %) and VU-34 (17.8 %) (Table 2 and Fig. S4). These observations may be due to the different botanical species grown in these regions and also to their climate, since the humidity decreases from the NE towards the SW of the province [11]. Indeed, more humid climates occur in the PP Pampeana, i.e. the Oceanic temperate climate on the Atlantic coast and the Pampean temperate climate inland, than in the other two PPs. The moisture of honeys from VU-26 displayed the least variability, and VU-26 gave the highest percentage of honeys with the lowest moisture contents, which could be correlated with the semi-arid climate of this area.

The influence of rainfalls on honey moisture contents was also previously reported for honeys from the Argentinian province of Córdoba [4]; the highest moisture values corresponded to honeys from the southern region of this province, which receives more precipitations. Studies on honeys from the Tabasco region (Mexico) [8] and West Bank (Palestine) [30] also disclosed that their moisture contents depended on the climate conditions of each region. The average moisture contents were higher in honeys from the PP Espinal (VU-22) and the Oriental (VU-33) and Austral (VU-34) districts of the PP Pampeana than those already reported for honeys collected from the same regions, i.e., 15.1 % (n=7), 17.1 % (n=54) and 16.9 % (n=36) respectively; and lower in honeys from the PP Monte (18.6 %, n=10) [10]. The mean moisture contents of SE honeys were higher than those found in literature (17 %, n=24) [23], and for clover (17.1 %) and eucalyptus (17.3 %) honeys from the PP Pampeana [17]. The average moisture values observed for SW honeys were close to those found previously for multifloral honeys from Argentina (17.0 %, n=16) [31] and Italy (17.4 %, n=40) [28]. The moisture range for SE honeys (15–21 %, n=261) were close to that reported before (13–20 %, n=30) [32], as well as their average value (17.8 %) was comparable to that found for about one thousand honey samples from all over the world (17.9 %) [15].

1.2.2. Free acidity

Honey free acidity is due to the presence of organic acids in equilibrium with their corresponding lactones or internal esters, and some inorganic ions [29]. The organic acids present in honey vary according to the characteristic flora in each phytogeographical region [9]. Free acidity is an important quality criterion, as moisture is, since honey fermentation, which is favoured by a high moisture content, causes an increase in its acidity [7, 26]. In fact, the increase of honey acidity may be due to the fermentation of its sugars to alcohol by microorganisms, and further oxidation to carboxylic acids. The Codex Alimentarius standard (Codex STAN 12-1981 Rev. 2, 2001) fixed the free acidity at 50 meq of acid/kg of honey. The free acidities of all honey samples analysed (14.7–44.7 meq/kg honey) were within the limits established by the international standards (Table S2), indicating the absence of undesirable fermentation processes. SE honeys (23 meq/kg honey) exhibited significantly lower mean acidity values than SW ones (29 meq/kg honey) (Table 1 and Fig. S3). This trend was also observed for SW and SE honeys from VU-34. Significant differences were found among honeys from the studied vegetation units, except between VU-22 (28.5 meq/kg honey) and VU-26 (28.7 meq/kg honey) (Table 2 and Fig S4).

Honeys from VU-33 (21.2 meq/kg honey) and VU-34 (23.8 meq/kg honey) exhibited the lowest average acidities. Moreover, it was observed the influence of the climate on VU-34, thus honeys from the Pampean temperate climate presented mean free acidities significantly higher than those from the Oceanic temperate climate (Fig. S5). The average free acidity of SE honeys (22.9 meq/kg honey) was higher than those reported before, i.e. 17.0 meq/kg honey (n=24) [23], as well as for honeys from the Austral district of the PP Pampeana (VU-34), i.e. 20.2 meq/kg honey (n=30) [32]. The mean free acidity of the honeys from the different vegetation units studied (21.2–28.7 meq/kg honey, n=324) was higher than those reported previously for unifloral honeys (16.7–22.8 meq/kg honey, n=148) [33] and for unifloral and multifloral honeys (17.3–21.3 meq/kg honey, n=107) from the same regions [10]. The average free acidity of SE honeys was comparable to those found in Portuguese honeys (23 meq/kg honey, n=20) [2]. Honey free acidity can present a large variability [7], as observed in the present study. However, the free acidity range of all the honeys studied (15–37 meq/kg honey, n=324) presented less variability than those reported for honeys from Corrientes (12–50 meq/kg honey, n=141) [3], and similar to those from Spain (18–40 meq/kg honey, n=25) [29].

1.2.3. pH

The microorganism's growth in honey depends on its pH, and can change its texture, stability and shelf life. Honey pH is affected by extraction and storage conditions [4, 29]. The IRAM standard 15938 (1995) for honey sets 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 [27, 29]. All the honeys studied presented pH values (pH 3.1–4.1) in the range of blossom honeys (Table S2). Significant differences were observed among SE and SW honeys (Table 1 and Fig. S3); the former showing a higher mean pH value. This tendency was also found in honeys from VU-34 (Tables S3). The pH of honeys from VU-22 (pH 3.5±0.2), VU-34 (pH 3.6±0.2) and VU-33 (pH 3.7±0.2) were significantly different among them, but not from that of honeys from VU-26 (pH 3.6±0.3) (Table 2 and Fig. S4). These pH values agreed with those previously published for these phytogeographical regions, i.e. pH 3.4 (n=7), pH 3.6 (n=36), pH 3.7 (n=54) and pH 3.7 (n=10) respectively [10]. SE honeys (pH 3.1–4.1) included the pH range already reported for honey from this geographical origin (pH 3.2–3.7, n=30) [32]. Honeys from VU-33 exhibited the highest pHs (pH 3.4–4.1) in agreement with previous results for honeys from the Oriental district of the PP Pampeana (pH 3.3–5.9, n=54) [10]. All honeys studied presented a pH range (pH 3.1–4.1, n=327) partially overlapping but with lower values than those reported for honeys from the northeast region of Argentina (pH 3.4–4.9, n=50) [34], Corrientes (pH 3.7–5.4, n=141) [3], Spain (3.7–4.7, n=77) [27] and Mexico (pH 3.7–4.2, n=15).

1.2.4. Electrical conductivity

The EC is a honey quality indicator assisting in the identification and distinction of blossom honey. The Codex Alimentarius standard establishes that honey EC should not exceed 800 µS/cm, except for honeydew honey and certain unifloral blossom honeys (Codex STAN 12-1981 Rev. 2, 2001). The honeys studied were declared multifloral, and their EC (132–565 µS/cm) were within the limits for blossom honeys according to international standards (Table S2). The honey EC is directly related to the concentration of minerals and salts in the soil of each area, and of organic acids and proteins from the nectar of plants [3, 8, 13, 29]. Taking into account that each region presents particular botanical species, soil and pedoclimatic characteristics, honey EC can be related to its phytogeographical origin. The average EC of SE honeys were significantly higher than those from the SW (Table 1 and Fig. S3), as well as occurred for SE and SW honeys from VU-34 (Table S3). Honeys from VU-22, presenting lower mean EC, differed significantly respect to honeys from the other vegetation units studied (Table 2 and Fig. S4).

The average EC of honeys from VU-22 (248 µS/cm) and VU-33 (309 µS/cm) were higher than that reported for honeys from the same regions (230 µS/cm (n=7) and 260 µS/cm (n=54) respectively) by Malacalza et al. (2007). However, honeys from VU-26 displayed considerably lower mean EC values (308 µS/cm) than those observed before (370 µS/cm, n=10), whereas honeys from VU-34 (296 µS/cm) exhibited a similar average EC values (290 µS/cm, n=36) [10 55]. The EC of honeys from VU-22 (132–361 µS/cm), VU-26 (192–425 µS/cm) and VU-33 (155–526 µS/cm) showed lower variability and partially overlapped with the EC ranges measured in a previous study (130–550 µS/cm (n=7), 300–520 µS/cm (n=10) and 120–640 µS/cm (n=54), respectively), except for honeys from VU-34 (148–461 µS/cm), which presented a similar variability (160–430 µS/cm, n=36) [10 55]. Regarding all studied honeys from the south of the province of Buenos Aires, the median EC of (288 µS/cm) was lower than that reported for honeys from other Argentinian provinces at northern latitudes, such as Misiones (550 µS/cm, n=13), Formosa (430 µS/cm, n=10), Chaco (480 µS/cm, n=10) and Corrientes (730 µS/cm, n=16) [34]; and the average EC (295 µS/cm) was lower than those observed in honeys from Corrientes (470–790 µS/cm, n=141) [3] and Chaco (668 µS/cm, n=189) [16], and in a study of about one thousand honeys from all over the world (640 µS/cm) [15].

1.2.5. Ash content

The ash content in honey constitutes a quality parameter reflecting its richness in certain nitrogen compounds, minerals, vitamins, pigments and aromatic substances, which are determined by its botanical origin, and the soil and climatic characteristics of its geographical origin [8]. This parameter has been usually used to classify honey as blossom, mixed or honeydew type [4]. According to the Mercosur (Mercosur – Res. Nº 89/99, 1999) and the Argentinian National (Código Alimentario Argentino Ley 18284, Res. MSyAS N° 003, 1995) regulations, 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. All honeys analysed in this study contained ash below 600 mg/100g, inferring their blossom origin (Table S2). SE honeys had significantly higher average ash content (173 mg/100 g honey) than SW ones (153 mg/100 g honey) (Table 2 and Fig.

S3), which was also observed regarding only samples from VU-34 (Table S3). The mean ash content of honeys from VU-22 (143 mg/100 g honey) was significantly lower than those from the other vegetation units (Table 2 and Fig. S4). All ash contents were higher than those reported before (80–83 mg/100 g honey for VU-22 and VU-33, 70–73 mg/100 g honey for VU-34, and 105–110 mg/100 g honey for VU-26) and exhibited a different trend [10 55, 35]. The average ash content found in honeys from the PP Pampeana were close to that described for clover honeys from this PP (160 mg/100 g honey, n=148) [17].Comparing with honeys from the other Argentinian provinces, the studied honeys from the south of the province of Buenos Aires exhibited an average ash content (170 mg/100 g honey, n=326) higher than that of honeys from La Pampa (110 mg/100 g honey, n=38) [25] and Chubut (110 mg/100 g honey, n=62) [18], which are located at a similar or southern latitudes, respectively; and lower than that of honeys from Catamarca (260 mg/100 g honey, n=39) [20] and Jujuy (240–430 mg/100 g honey, n=58) [19], located at northern latitudes.

1.2.6. Colour

Honey colour depends on its alkalinity, ash content and antioxidant compounds, such polyphenols, terpenes and carotenoids [8]. Thus, honey colour is considered as an index of its antioxidant capacity, since generally dark honeys present higher amounts of phenolic compounds and antioxidant activities, whereas the opposite occurs in light honeys. Regarding that the antioxidant compounds come from the flowers that feed honeybees, the colour of honey can provide information related to its botanical origin. Agricultural practices and production methods can also influence the colour of honey [36]. In this sense, the use of old wax combs, the presence of antibiotics and pesticides residues, honey contamination with heavy metals during extraction, and honey exposure to either high temperatures or light can alter honey colour. The studied honeys presented colours ranging from water-white (5.75 mm Pfund) to light amber (83.75 mm Pfund), with average colours in the extra light amber grade (Table S2). SE honeys presented significantly lighter mean colour values (36.8 mm Pfund) than SW honeys (40.2 mm Pfund). The colour grades observed in SE honeys (17–56 mm Pfund, n=270) were lighter than those reported previously (29–71 mm Pfund, n=24) [23]. Honeys from VU-26 (47.7 mm Pfund, n=15) exhibited an average colour significantly higher than those from the other units, i.e. VU-22 (38.0 mm Pfund, n=29), VU-34 (37.5 mm Pfund, n=203) and VU-33 (35.5 mm Pfund, n=78), probably due to the characteristic vegetation and pedoclimatic conditions of VU-26.

These mean colour values of honeys from VU-22, VU-34 and VU-33 were considerably higher than those observed previously in honeys from the same phytogeographical regions (2.0 mm Pfund (n=7), 24.0 mm Pfund (n=36) and 19.0 mm Pfund (n=54), respectively), while the colour of honeys from VU-26 were slightly lower than that reported (53.0 mm Pfund, n=10) [10]. In contrast, a preliminary study with few honey samples from the PP Espinal (58.2 mm Pfund, n=6) and the PP Pampeana (28.0 mm Pfund, n=6) [24] reported darker and lighter colours, respectively, than those observed in the current study. The average colours of honeys from the PP Pampeana (VU-33: 36±9 mm Pfund; VU-34: 38±10 mm Pfund) were within the colours displayed by clover honeys from the same PP (32±20 mm Pfund, n=53) [17]. The colour of all the studied honeys (17–54 mm Pfund, n=325) were lighter than those described for honeys from Misiones (55–150 mm Pfund, n=13), Chaco (35–132 mm Pfund, n=11), Corrientes (29–150 mm Pfund, n=141) and Formosa (17–>150 mm Pfund, n=10) [3, 34]. This fact is a competitive advantage for honeys from Buenos Aires since honey with lighter colours 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 [3, 33].

1.2.7. 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 (ºBrix). Honey typically contains about 83 ºBrix (ºBx) [14, 28, 29]. All honeys studied contained between 74.8 and 83.5 ºBx (Table S2). The total soluble content of honey is strictly correlated to its humidity [14, 28, 29]. Indeed, the correlation coefficient observed for these two parameters in the present study was –0.98 at $p < 0.05$. On the one hand, the higher the water content in honey, the greater the dilution of the sugars, and hence, honey presents a lower ºBx 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 ºBx value [37]. SW honeys showed significantly higher ºBx values than SE honeys (Table 2 and Fig. S3) which could be explained by the NE-SW pluviometric gradient observed in the province. Thus, the lower ºBx value of SE honeys maybe be associated to the higher rainfall regime occurring in the SE respect to the SW of the province, which favours higher moisture contents and lower ºBx values in honey [37]. The same trend was observed for honeys from the different phytogeographical regions studied, displaying median values of 80.6 ºBx for VU-34, 80.7 ºBx for VU-33, 81.6 ºBx for VU-22 and 81.9 ºBx for VU-26. The average ºBx value of all honeys studied (80.5 ºBx, n=324) was close to those reported for multifloral honeys from Italy (80.9 ºBx, n=40) [28] and Le Marche (Italy) (81.0 ºBx, n=69) [14]; and lower than that found in Spanish honeys (81.9 ºBx, n=24) [29].

1.2.8. 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 results from the decomposition of monosaccharides during the Maillard reaction, being found only in small amounts in fresh honey. HMF concentration increases slowly with prolonged storage of honey and quickly when honey is heated [34]. The Codex Alimentarius 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 (Codex STAN 12-1981 Rev. 2, 2001). HMF contents were determined in honeys collected in harvests 2015 and 2017 (Table S2); all samples complied with the HMF content limits established by international standards. This was indicative of good quality, fresh and unprocessed honeys, and suggested good practices by beekeepers. Significant differences were observed in the mean HMF contents of SE and SW honeys (4.9 and 2.8 mg HMF/kg honey, respectively) (Table 1 and Fig. S6). The formation of HMF, through the Maillard reaction, is favoured by the water content in the media. Thus, higher moisture in honey results in the presence of a higher amount of HMF [38]. The HMF trend observed could be explained by the NE-SW pluviometric gradient described to occur in the province with higher rainfalls in the SE respect to the SW, which favours higher moisture contents in SE honey and would result in higher HMF contents [4, 37]. This was also observed in honeys from the SE and SW of VU-34. Honeys from VU-22 contained the lowest average HMF content (2.5 mg HMF/kg honey), followed by those from VU-26 (3.6 mg HMF/kg honey), VU-33 (4.0 mg HMF/kg honey) and VU-34 (4.8 mg HMF/kg honey) (Table 2 and Fig. S6).

HMF contents of honeys from VU-34 under the Oceanic temperate climate were higher than for honeys under Pampean temperate climate (Fig. S5). This observation could be also justified by the rainfall regimes of these climates, since more abundant precipitations occur on the coastal region under the Oceanic temperate climate than inland with Pampean temperate climate. The average HMF content of honeys from VU-33 was similar to data found in literature (4 mg HMF/kg honey, n=54); from VU-22 and VU-26, lower (5 mg HMF/kg honey, n=7 and 10 respectively); and from VU-34, higher (3 mg HMF/kg honey, n=36) [10]. The mean HMF content of honeys from the PP Pampeana was lower than those reported for clover (6.7 mg HMF/kg honey, n=53) and eucalyptus (7.2 mg HMF/kg honey, n=28) honeys from this PP [17], and close to honeys from Spain (4.1 mg HMF/kg honey, n=40) [39]. The median HMF content of all the studied honeys (4.0 mg HMF/kg honey, n=126) was lower than that of honeys from Misiones (6.0 mg HMF/kg honey, n=13), Formosa (33 mg HMF/kg honey, n=10), Chaco (28 mg HMF/kg honey, n=10) and Corrientes (11 mg HMF/kg honey, n=16) [34]. Besides, the average HMF content in all studied honeys (4.2 mg HMF/kg honey, n=126) was lower than in those from Catamarca (20 mg HMF/kg honey, n=39) [20] and Portugal (average: 9.4 mg HMF/kg honey, n=38) [40]. Since the contents of water and HMF in honey also depend on the method used for extraction, processing and storage of honeys, these parameters cannot be considered as completely representative of the honey nature but rather as indicators of freshness [4].

IV. CONCLUSIONS

The Argentinian honeys from different vegetation units of the PPs Pampeana, Espinal and Monte in the south of the province of Buenos Aires were characterized according to their sugar profiles and typical physicochemical quality parameters. All honeys were in compliance with the national (Código Alimentario Argentino Ley 18284, Res. MSyAS N° 003, 1995) and the international regulations established by the Codex Alimentarius Commision (Codex STAN 12-1981 Rev. 2, 2001), EU Council (Council Directive 2001/110/EC, 2001) and Mercosur (Res. Nº 89/99, 1999). The analytical results disclosed that all the studied honeys were high quality honeys obtained under adequate beekeeping and processing practices. Several parameters, i.e. F+G content, F/G ratio, EC, ash content and pH, indicated the blossom origin of the honeys. 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 present study confirmed the impact of the vegetation and the climate, in particular the precipitation regime of each area, on the physical and chemical parameters of honeys. In this sense, the results evidenced that honeys from the SE and SW of the province of Buenos Aires presented significantly distinctive quality parameters and carbohydrate compositions (except for the concentrations of glucose and turanose), which were influenced by both the flora and the pedoclimatic conditions of each region. SE honeys were characterized by higher contents of moisture, fructose, maltose, erlose, F+G, HMF and ash, F/G ratio, pH and EC and slightly lighter colours; while SW honeys showed higher free acidities, sucrose content and °Brix values.

Honeys from the PP Espinal (VU-22) exhibited characteristic lower contents of fructose, HMF and ash and EC values, and larger amounts of sucrose. Honeys from the PP Monte (VU-26) contained typical lower moisture contents and slightly darker colours. Honeys from the PP Pampeana (VU-33 and VU-34) were typified by higher amounts of fructose and F/G ratios; and in particular, honeys from VU-33 by lower free acidities and higher pH, and honeys from VU-34 under Oceanic temperate climatic conditions by smaller sucrose contents and higher HMF contents. However, none of the physical and chemical parameters measured were completely discriminant among the honeys according to their geographical or phytogeographical origin, the vegetation unit which it belongs to, or the climate of the region.The relevance of the present work lies in the extended knowledge generated with the study of the more than three hundred honey samples collected along five seasons from the province with the largest honey production in Argentina. This large sample set was traceable and representative of the honeys from the regions studied, and included seasonal variability, which is a requirement to characterise any agricultural food product. The typification of the honeys from each of the studied phytogeographical regions 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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