



Physicochemical parameters and sensory properties of honeys from Buenos Aires region



María F. Silvano^a, María S. Varela^a, María A. Palacio^a, Sergio Ruffinengo^a, Diego K. Yamul^{b,*}

^a Cátedra de Apicultura y Calidad y Tecnología de miel, Unidad Integrada Balcarce, Facultad de Ciencias Agrarias, UNMdP – Estación Experimental Agropecuaria, INTA, Argentina

^b Centro de Investigación y Desarrollo en Crioteología de Alimentos (CIDCA), Facultad de Ciencias Exactas, UNLP – CCT La Plata – CONICET, 47 y 116, 1900 La Plata, Argentina

ARTICLE INFO

Article history:

Received 28 August 2013

Received in revised form 25 November 2013

Accepted 3 December 2013

Available online 10 December 2013

Keywords:

Multifloral honey
Chemical traceability
Multivariate analysis
Geographic origin

ABSTRACT

The physicochemical parameters (moisture, hydroxymethyl furfural, colour, electrical conductivity, free acidity, glucose, fructose and sucrose) and the sensory properties (aroma, taste, appearance, texture) were determined in honeys from apiaries of the agricultural, hills and meadow zones of the south east region of Buenos Aires province (Argentina). The analysis of variance showed significant differences among zones in the mean value of hydroxymethyl furfural, colour, electrical conductivity and sucrose content. The principal component analysis explained the 70% of the variance among samples with the first two principal components in both cases. The cluster analysis and linear discriminant analysis showed that samples were grouped in relation to the sampling region coinciding with the results of the principal component analysis. Results suggest that could be possible to classify honeys according to the geographic origin based on the physicochemical parameters; however, the sensory properties were not good predictors.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Argentina is the sixth producer and second exporter of honey in the world, accounting the Buenos Aires (BA) province almost the half of the Argentine's honey production (SAGPyA, 2013). The south east region of BA province could be divided into three different geographical zones: the agricultural, meadow and hills zones which produce mainly multifloral honeys. The honey produced in the region, in spite of its high quality, is mainly exported in bulk without any distinctive reference of its origin. However, honeys might exhibit different characteristics and composition according to the dominant flora around the apiaries. For example, honeys from agricultural zones would have characteristics corresponding to species like *Heliantus annuus*, *Melilotus* sp, *Trifolium* sp, *Triticum aestivum*, *Zea mays*, *Glicine max* and *Medicago sativa*; and, *Colletia paradoxa*, *Baccharis latifolia*, *Brassica rapa*, *Senecio* sp and *Cirsium vulgare* would define the characteristics of honeys from the hills zone. Finally *Eucalyptus* sp, *Pinus* sp, *Mentha* sp and *Minthostachys verticillata* defines the characteristics of the meadow zone honeys. The chemical traceability of honey improves the trust of consumers to certified regional products (Baroni et al., 2009), being the geographical origin criterion a quality parameter to produce certified honey with designation of origin. Hence, a regional classification of honeys according to its zones of production would increase its commercial value, boosting the microeconomy of the region.

Sensory evaluation is a useful tool to define the sensory properties of honey because it can provide complete information about honey quality (Esti, Panfili, Marconi, & Trivisonno, 1997). Honey aroma and taste are related with the volatile compounds (Montenegro, Gomez, Pizarro, Casaubon, & Peña, 2008) and they can be modified as consequence of the seasonal conditions and geographical origin (Anupama, Bhat, & Sapna, 2003).

As a natural complex food, many variables are needed to characterize honey. Thus, chemometrics techniques such as, principal component analysis (PCA), linear discriminant analysis (LDA) and cluster analysis (CA) are the most commonly techniques used to identify the natural clustering pattern and groups of variables on the basis of similarities between samples.

Many scholars have looked for analytical markers of botanical and geographical origin based on sugar profile (Bentabol Manzanares, Hernández García, Rodríguez Galdón, Rodríguez Rodríguez, & Díaz Romero, 2011; Ouchemoukh, Schweitzer, BachirBeya, Djoudad-Kadji, & Louaiche, 2010), mineral composition (Baroni et al., 2009), physicochemical parameters (Corbella & Cozzolino, 2006; Fangio, Iurlina, & Frotz, 2010; Malacalza, Mouteira, Baldi & Lupano, 2007) and sensory properties (Guler, Bek, & Kement, 2008). However, at the moment no information is available concerning the honeys from the meadow, hills and agricultural zones of the south east region of BA province (Argentina). Thus, the purpose of this paper is to study the physicochemical parameters and the sensory characteristics of multifloral honeys using multivariate statistical analysis in order to classify honeys according to the geographical origin.

* Corresponding author. Tel.: +54 221 4249287; fax: +54 221 4254853.

E-mail address: karim@biol.unlp.edu.ar (D.K. Yamul).

2. Materials and methods

2.1. Honey samples

Honey samples, from multifloral origin, were harvested from apiaries from the south east region of BA province (Argentina) (Fig. 1). A total of 24 honey samples were grouped into different zones namely: meadow zone (11 samples), agricultural zone (8 samples) and hills zone (5 samples). These collection sites were selected to include different botanical origin, soil characteristics and zones. Samples were provided by the beekeepers who obtained honey by cold extraction. Honey samples were stored in fresh and dry place in airtight plastic containers until analysis.

2.2. Physicochemical analysis

Moisture was determined with an Abbe refractometer reading at 20 °C, obtaining the corresponding value of moisture from the Chatway Table (Norma IRAM 15931, 1994) and the electrical conductivity was determined according to the Norma IRAM 15945 (1997). HMF was measured by the method of White, adopted by Normas IRAM (AOAC, 1990; Norma IRAM 15941-2, 1997). The acidity of honey were determined according to Normas IRAM 15933 (1994) and Normas IRAM 15938 (1995). Colour was measured by using the Pfund classifier, adopted by Normas IRAM (Norma IRAM 15937-2, 1995). In this method, homogeneous liquid honey, without air bubbles, is put into the Pfund colorimeter, and the colour is visually compared with standards. Colour grades of honey based on Pfund readings are: average scale reading ≤ 8 mm: water-white; $8 < \text{reading} \leq 16$: extra white; $16 < \text{reading} \leq 34$: white; $34 < \text{reading} \leq 50$: extra light-amber; $50 < \text{reading} \leq 85$: light-amber; $85 < \text{reading} \leq 114$: amber; reading > 114 : dark.

2.3. Sugars profile analysis

About 0.5 g of honey was weighed directly into polypropylen etubes and mixed with 10 ml of 60% methanol. Afterwards, a milliliter of the dissolution was filtered through a 0.45 μm cellulose filter (Osmonics Inc., MN, USA) prior to HPLC analysis. Standards of

glucose, fructose and sucrose were purchased from Sigma–Aldrich. Stock solutions (2 g/l) were prepared for dissolution in deionised water and were stored at 4 °C until analysis. The determination of sugars was performed with Agilent technologies 1100high performance liquid chromatograph (Palo Alto, CA, USA) equipped with a differential refractive index detector. The separation was performed by using an Eclipse Plus C18column (4.6 \times 250 mm) with a particle size diameter of 5 μm (Agilent Technologies, Palo Alto, CA, USA). The column was kept at 25 °C throughout the analysis. The mobile phase was composed of 80% acetonitrile in water. The injection volumes of the samples were 25 μl , with a flow rate of 2 ml/min. The HPLC sample peaks were identified by comparing the retention times obtained from standards. The honey samples were also spiked with standards in order to verify the identity of the chromatographic peaks. Duplicate injections were performed and average peak areas were used for the peak quantification.

2.4. Sensory analysis

The panel was formed by 8 assessors, members of Honey Laboratory Analysis of the Mar del Plata National University, aged ranging from 22 to 50 years and with previous experience in sensory analysis. Sessions were performed in a tasting room, separated from area where the samples were prepared. Room temperature was 25 °C during the evaluation. Coded samples were presented in random order to each assessor in 40-ml glass vials sealed with a twist-off cap and at room temperature. The order of presentation was balanced and randomised to eliminate contrast effect and positional bias. Mineral water was provided for the assessors mouth-rinsing between samples. Sessions were carried out between 10:00 and 12:00 and panelists declared that they were no hungry at the moment of the tests. At initial sessions, assessors underwent training in descriptive analysis where they generated descriptors over the course of several sessions. As suggested by Anupama et al. (2003) the common descriptors chosen by the panel were compiled along with some significant descriptors found in the literature and selected for the formulation of scorecards. Honey samples were evaluated according to quantitative descriptive analysis (QDA) where each sample was individually evaluated

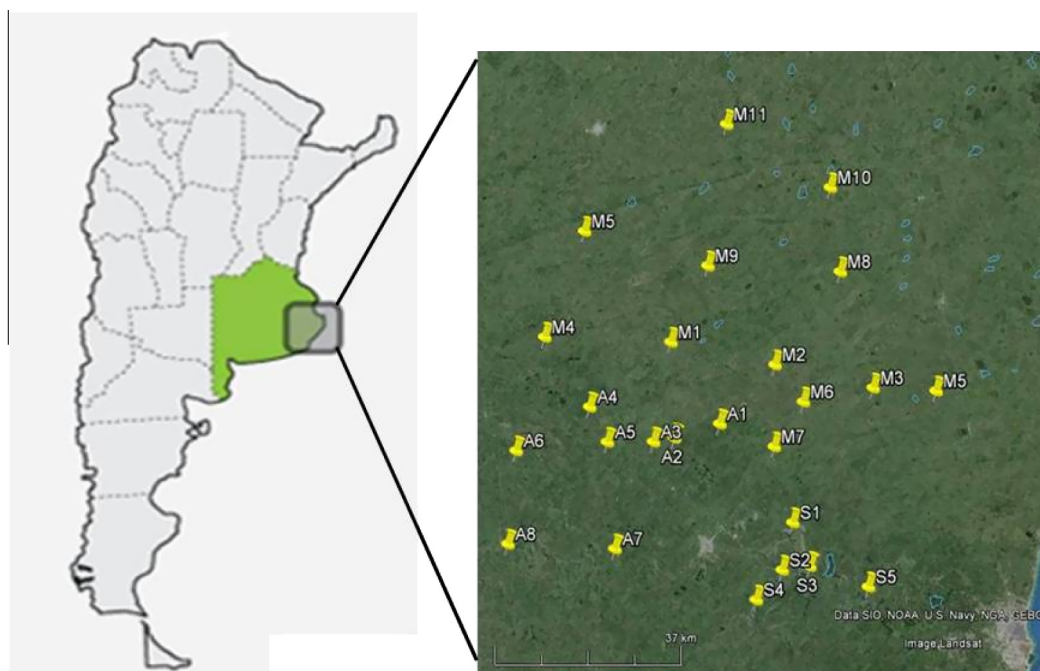


Fig. 1. Location of apiaries from the southeast region of the Buenos Aires province

using a list with previously defined descriptors (flowery, sweetness, degree of crystallization, viscosity, adhesiveness and grainy). The assessors used a 10 cm non-structured scale, from 0 to 10, to rate the intensity of each attribute, previously selected. The performance of the assessors was checked by giving duplicate samples at the start of each session. Sensory analysis of 24 honey samples was performed in 6 sessions.

2.5. Data analysis

The multivariate and sensory analysis was performed by using the Infostat software (Córdoba National University, Córdoba, Argentina) and PASW Statistics 18 software (SPSS Inc., Chicago, IL, USA), respectively.

To compare the physicochemical parameters of honeys from the different zones, the percentage of each parameter was calculated. A

one way analysis of variance of the data was performed and the least significant differences (LSD) were calculated to compare the means at a level of 95% using the Fisher test. A p -value of less than 0.05 was considered significant.

PCA was conducted to examine the relationship among physicochemical parameters and zones. The original data matrix was auto-scaled for column, subtracting the media of each column to every sample and dividing it for their standard deviation (standardized data) to ensure that all the elements had equal weighting in the results. A varimax rotation was carried out to minimise the number of variables that influences each factor. Only the principal components with eigenvalue higher than one were considered significant. The PCA model was validated by the cross validation method, meaning that a sample is left out one time and used to find the validation error. Then, all samples are left out one time and the total error is obtained (Camiña et al., 2008).

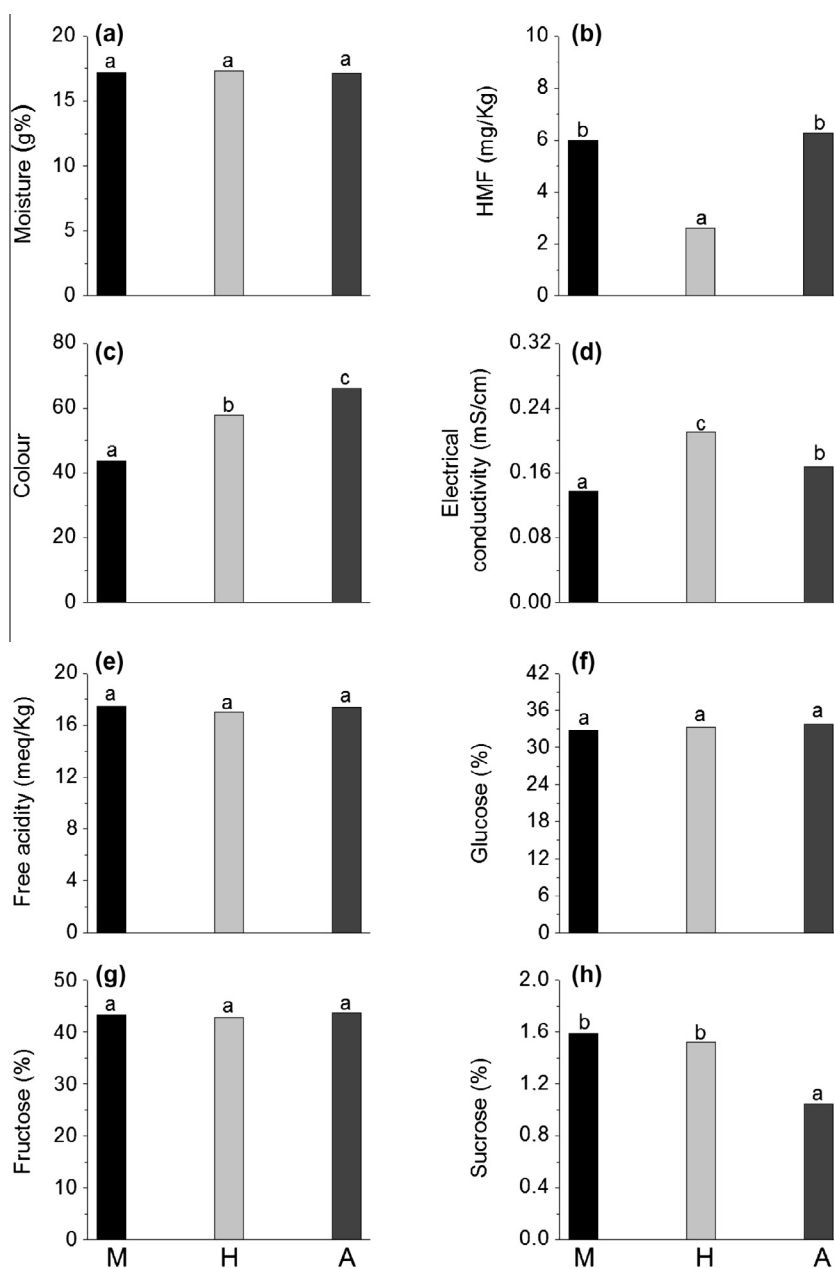


Fig. 2. Physicochemical parameters and sugar composition of honeys from the meadow (M), hills (H) and agricultural (A) zones. Values in the same graph with the same letter are not significantly different ($p > 0.05$). (a): Moisture; (b): Hydroxymethylfurfural content; (c): Colour; (d)Electrical conductivity; (e): Free acidity; (f): Glucose content; (g): Fructose content; (h) Sucrose content.

Table 1
Results of the sensory analysis. Values in the same column with the same letter are not significantly different ($P > 0.05$).

Samples	Flowery	Sweetness	Degree of crystallisation	Viscosity	Adhesivness	Grainy
<i>Sensory attributes</i>						
M1	1.60	4.43	7.02	5.54	2.90	6.65
M2	3.05	5.56	4.16	5.88	2.30	4.23
M3	2.10	5.15	4.12	6.56	5.04	2.83
M4	3.70	4.96	3.79	6.30	3.15	2.59
M5	3.33	4.64	3.15	6.16	3.64	1.81
M6	2.90	5.94	3.61	4.67	1.73	4.36
M7	2.60	3.66	6.99	7.53	2.95	6.41
M8	2.53	5.13	6.73	6.40	3.78	6.10
M9	2.60	5.05	6.16	7.94	4.87	2.93
M10	2.15	4.63	4.74	7.56	2.08	2.01
M11	3.15	4.03	4.43	7.01	1.86	4.17
Mean	2.70 ^a	4.83 ^a	4.99 ^a	6.50 ^a	3.12 ^a	4.01 ^a
A1	3.50	4.37	8.21	6.14	3.92	7.38
A2	4.30	3.72	1.39	5.07	1.00	0.90
A3	4.18	3.50	5.63	6.55	1.33	3.66
A4	4.47	4.79	5.03	5.51	2.80	4.35
A5	3.20	4.30	4.56	6.64	3.40	4.40
A6	3.87	5.13	5.60	6.88	1.53	5.45
A7	3.70	3.83	2.73	5.33	3.20	1.50
A8	4.25	3.85	6.66	6.97	2.85	6.43
Mean	3.93 ^b	4.19 ^a	4.98 ^a	6.14 ^a	2.50 ^a	4.26 ^a
H1	4.00	4.81	5.66	7.13	4.27	2.25
H2	4.38	2.84	4.90	7.60	6.43	3.25
H3	3.90	4.00	3.64	6.60	1.50	2.93
H4	4.60	5.86	6.01	5.50	3.68	4.94
H5	4.45	3.21	5.75	6.03	3.70	3.36
Mean	4.27 ^b	4.14 ^a	5.19 ^a	6.57 ^a	3.92 ^a	3.35 ^a
LSD	0.54	0.82	1.76	0.93	1.34	1.94

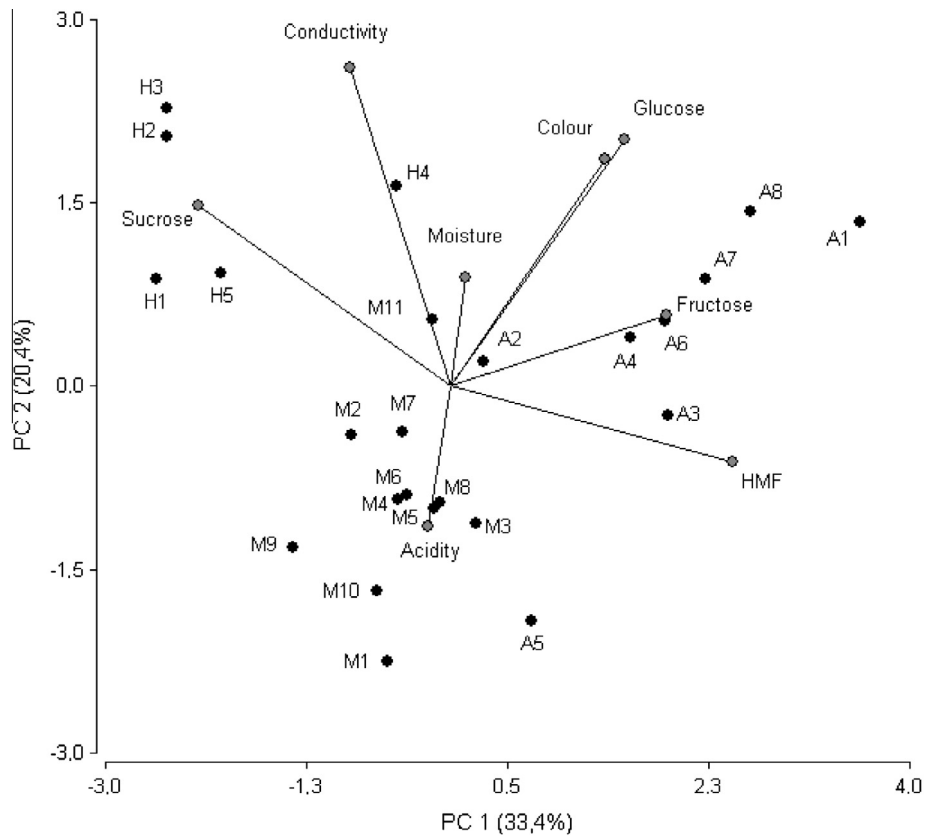


Fig. 3. Biplot of the principal component analysis of honey samples from different regions. A: agricultural zone, H: hills zone; M: meadow zone.

Table 2
Results of the principal component (PC) analysis on the physicochemical parameters.

	PC1	PC2	PC3
Eigenvalues	2.67	1.63	1.26
Variance (%)	33.4	20.4	16.2
Cumulative variance (%)	33.4	53.8	70.0
Moisture	0.03	0.20	0.60
Electrical conductivity	-0.20	0.59	-0.40
Free acidity	-0.04	-0.26	-0.48
HMF	0.56	-0.14	-0.09
Fructose	0.43	0.13	0.26
Glucose	0.31	0.42	0.12
Sucrose	-0.50	0.34	0.17
Colour	0.34	0.46	-0.36

CA was performed on the standardized data to classify samples on the basis of the similarities of their physicochemical and sensory parameters. Clusters were calculated using the Euclidian distance and the Ward technique as a hierarchical linkage criterion of amalgamation which is based on the minimum variance (Johnson, 2000). This technique allowed a better discrimination of the clusters.

The physicochemical and sensory parameters (independent variable) were subjected to linear LDA in order to evaluate the potential of these parameters for classification of the samples according to the geographical origin (grouping variable). LDA was performed on the standardized data. The statistical significance of each discriminant function (DF) was evaluated on the basis of the Wilks' Lambda factor which is a measurement of how well each function separate objects into groups. This parameter ranges from 1.0 (no discriminatory power) to 0.0 (perfect discriminatory power). The separation among groups in the discriminant space was checked by plotting the first and the second DF using 95% confidence ellipses around the means (group centroid) of each group. The leave one out method was used as cross validation procedure to evaluate the classification performance.

3. Results and discussion

3.1. Physicochemical variables and sensory analysis

Fig. 2 shows the mean values of the physicochemical parameters of honeys from different zones of the south east region of BA province.

Moisture, which is parameter related to the climatic conditions, handling of honey by the producer and the degree of maturity, showed (Fig. 2a) mean values around 17%. None of the samples exceeds the 20% allowed by the Codex Alimentarius (2013), although, seven samples were barely above the limit of 18% allowed by Argentinean regulations (CAA, 2010). These results were slightly lower than those obtained by Fangio et al. (2010) in monofloral honeys of the phytogeographic region of the province pampeana (BA province, Argentina). Corbella and Cozzolino (2006) found similar values of moisture in multifloral honeys from Uruguay, a country located entirely within a climatic region quite similar to the south east of BA.

In fresh honeys the content of HMF is often very low, however, the storage and overheating of the product favors the increase of the HMF levels. Results in Fig. 2b depicts that the content of HMF in all honeys analyzed were below the 40 mg kg⁻¹. This result complies with national regulations (CAA, 2010), international trade guidelines (European Economic Community, 2002) and some European bee federations who consider as a "quality honey" when the HMF content is lower than 15 mg kg⁻¹. Values of the HMF content of the meadow and agricultural zones coincides with results reported by Corbella and Cozzolino (2006).

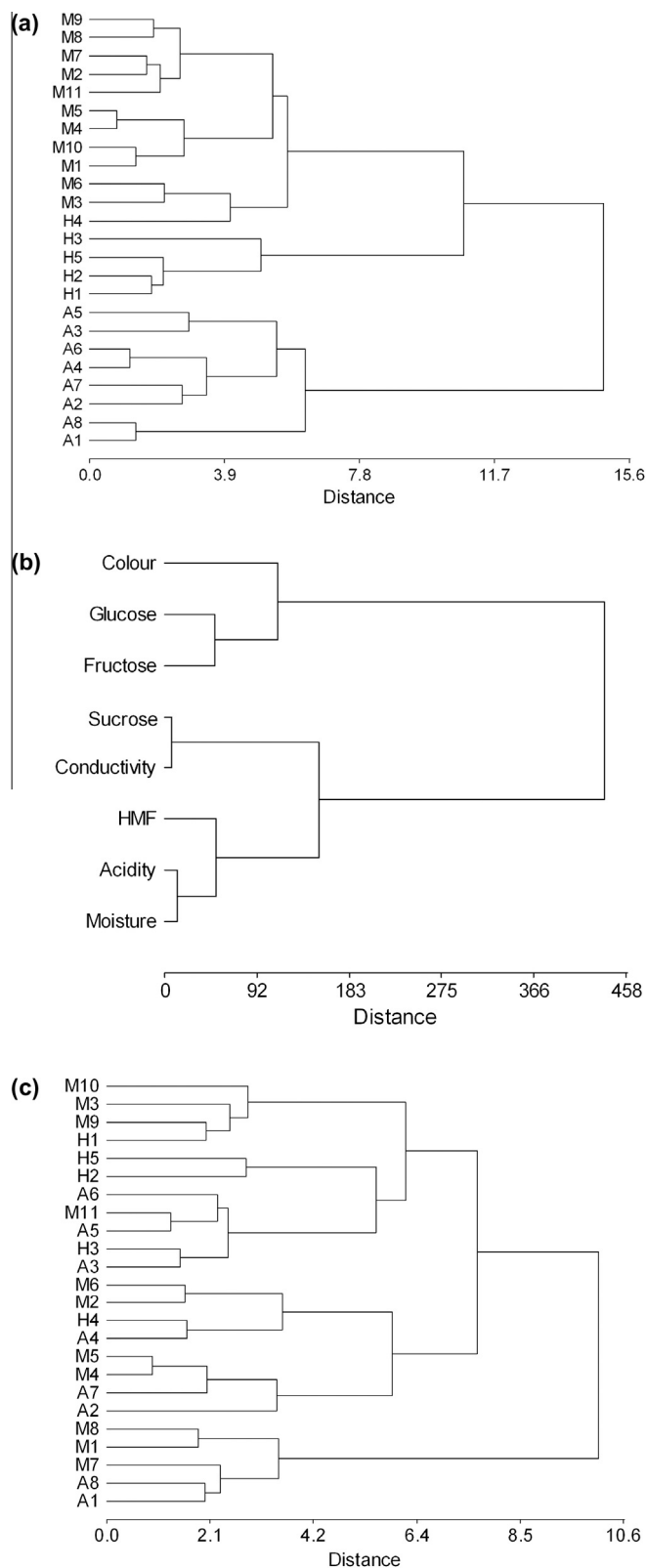


Fig. 4. Dendrogram of cluster analysis. (a) Regions based on physicochemical properties, (b) variables based on physicochemical properties, (c) regions based on the sensory analysis. A: agricultural zone, H: hills zone; M: meadow zone

The honeys studied in the present work depicted values of color between 29 and 71 mm in the Pfund classifier which corresponds to white, extra light amber and light amber honeys. These honeys

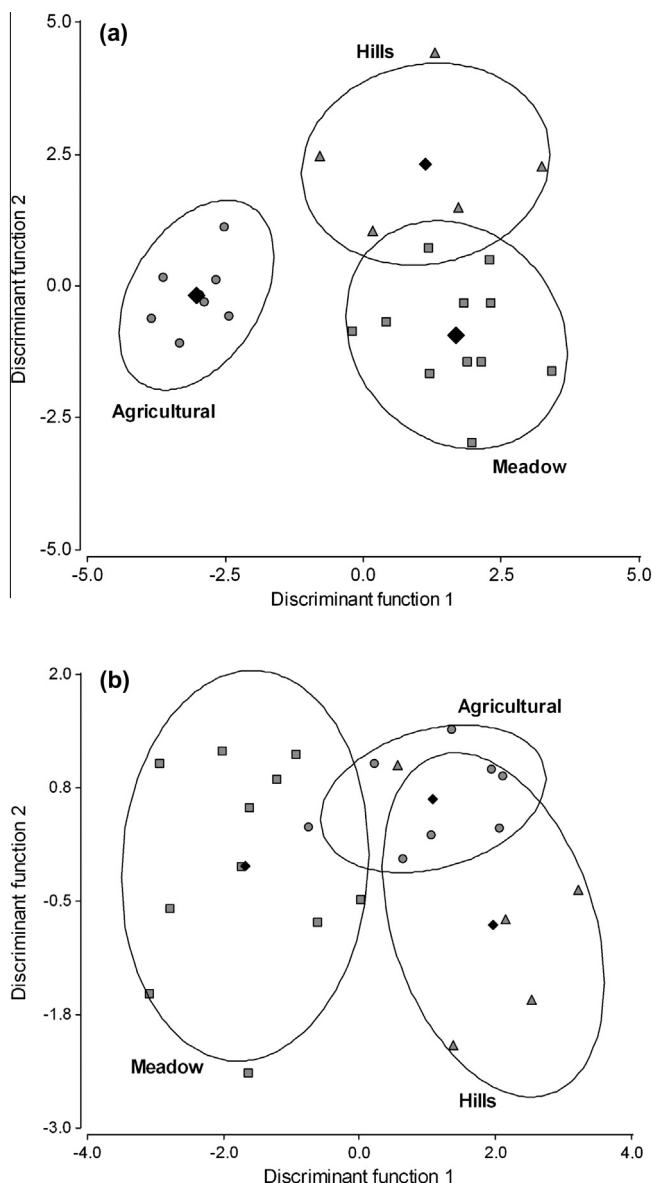


Fig. 5. Geographic origin based discriminant analysis on (a) physicochemical parameters and sugar composition (b) sensory analysis. (♦) Group centroid.

fall within the international classification as clear honeys, which is a competitive advantage since they are preferred in the international market. It was observed in Fig. 2c that the meadow zone had the clearest honeys (54.5% of extra light amber and 18.2% of white), whereas the 80% of the samples from the hills zones were light amber. Also, all (100%) the honeys analyzed from the agricultural zones were light amber. The colour of honeys reported by Corbella and Cozzolino (2006) was darker than the honey samples analysed in the present work.

Electrical conductivity is a good criterion of the botanical origin of honey, and today it is determined in routine honey control instead of the ash content (Bogdanov et al., 1999). Results in Fig. 2d depicts that the electrical conductivity of honeys from the hills zone is higher than that of honeys from the meadow and agricultural zones. Probably due to differences in the flora of the region. On the other hand, Corbella and Cozzolino (2006) obtained a higher electrical conductivity for Uruguayan multifloral honeys.

Free acidity is a quality parameter of honey related with honey fermentation. National regulations (CAA, 2010) establish a

maximum of 40 meq kg⁻¹ of total free acidity. Fig. 2e showed values ranging from 10 to 20 meq kg⁻¹, below the tolerance limit. Similar values were reported by Mendes, BrojoProença, Ferreira, and Ferreira (1998) in Portuguese honey and lower values were obtained by Fangio et al. (2010) in monofloral Argentinian honeys. On the other hand, our results were higher than those reported by Sporns, Plhak, and Friedrich (1992) in Alberta honeys.

The HMF content and electrical conductivity of the hills zones, moisture and free acidity coincides with results obtained by Malacalza, Mouteira, Baldi, and Lupano (2007). On the other hand, our honeys were darker than those reported by the same authors.

The sugar profile is depicted in Fig. 2e–g. Fructose and glucose represents the largest portion of honey composition but a small quantity of sucrose was also found. The monosaccharide content was within the limits of Argentinean regulations (CAA, 2010), European and Codex standards of 65% minimum for glucose and fructose, confirming that all samples were genuine honeys. Values of glucose and fructose reported in this work were higher than those reported by Baroni et al. (2009) but similar to those reported by Ouchemoukh et al. (2010). Molan (1996) reported that the proportions of fructose and glucose are determined by the composition of the plant secretion. The ratio of fructose to glucose was between 1.14 and 1.36 (results not shown), indicating the variety of floral sources from which the honey samples originated. Bentabol Manzanares et al. (2011) reported a fructose/glucose average ratio around 1.2 for blossom honey and around 1.3 for honeydew honey coinciding, the latter, with our results (1.31). Results of the sucrose content is agreement with that obtained by Ouchemoukh et al. (2010) in multifloral honey from Algeria and a little higher than the results obtained by Bentabol Manzanares et al. (2011) in blossom and honeydew honeys from Tenerife. Sucrose is present in all the samples analysed, ranging between 0.60 and 3.14%. According to Da Costa Leite et al. (2000), the reason for the variable levels of sucrose could be due to a transglucosylation reaction initiated by transference of the α -D-glucopyranosyl unit from sucrose to an acceptor molecule. None of the samples exceeded the highest limit (8%) set by the Argentinean regulations (CAA, 2010). Results of the sensory analysis are shown in Table 1. Only the flowery sensory attribute of honeys from the meadow zone was significantly different ($p < 0.05$) from the others.

3.2. Principal component analysis

Fig. 3 is the biplot and shows the effect of variables on the principal components. Sucrose can be associated to the hills zone and free acidity to the meadow zone. On the other hand, fructose and HMF are associated to the agricultural zone. The physicochemical parameters of honey with its major contribution to PC1 were HMF and fructose together with sucrose which were opposite to the aforementioned. PC2 was strongly associated to conductivity, colour and glucose. PC1, which explains the 33.4% of the variance, separates sucrose from fructose and HMF thus; most of the variability on the physicochemical properties of honey from different zones can be explained with these variables. On the other hand, PC2, which explains the 20.4% of the variance, separated conductivity, glucose, colour and moisture from the free acidity, thus, the rest of the variability not accounted by the PC1 was explained by these variables.

Results in Table 2 suggest that the analysis explains the 70% of the variance among samples with the first three PC which are related to most of the physicochemical parameters of honey and can be informative for cluster samples in a two-dimensional space. It is observed that for PC1, HMF and fructose were the most important variables that explain the separation of the honey samples according to the geographical origin. Other authors (Corbella & Cozzolino, 2006; Serrano, Villarejo, Espejo, & Jodral, 2004; Terrab,

Table 3
Results of the linear discriminant analysis (LDA)

(a) Results of the statistical evaluation				
Discriminant function	Eigenvalues	Variance (%)	Cumulative variance (%)	Wilk's Lambda
<i>Physicochemical parameters</i>				
1	5.28	75.32	75.32	0.06
2	1.73	24.68	100	0.36
<i>Sensory analysis</i>				
1	2.85	90.64	90.64	0.20
2	0.29	9.36	100	0.31
(b) Results of prediction ability for LDA model				
<i>Physicochemical parameters</i>				
Geographical area	Meadow	Agricultural	Predicted group Hills	Error (%)
Meadow	10	0	1	9.09
Agricultural	0	8	0	0
Hills	0	0	5	0
<i>Sensory analysis</i>				
Geographical area	Meadow	Predicted group Agricultural	Hills	Error (%)
Meadow	11	1	0	9.09
Agricultural	1	7	0	12.50
Hills	0	1	4	20.0

Gonzalez, Diez, & Heredia, 2003) also found that electrical conductivity could be associated to the floral origin whereas moisture had been reported as a variable that rarely described the floral origin (Serrano et al., 2004). The loading in PC2 and PC3 (16.2%) shows that the electrical conductivity, glucose and colour and moisture and free acidity respectively were the most important variables that explain the separation between honey samples. The number of significant PCs usually relates to the number of pre-defined groups (Yücel & Sultanoglu, 2012). This fact can be confirmed by the results shown in Table 2, in which three significant PCs were needed to describe the 70% of the variance among samples. Fig. 3 depict that honeys were clustered into three groups, which correspond to the different zones, suggesting that these zones have honeys with unique characteristics in relation to the physicochemical parameters analysed.

The further away the variable from the origin point, the larger the contribution of that variable to PC model (Rohman, Triyana, Sismindari, & Erwanto, 2012). Sucrose, electrical conductivity, glucose and HMF have the same contribution towards the PC separation (Fig. 3), since they depict the same distance from the origin point. The results suggest that these variables contribute to the model with the same weight. On the other hand, moisture colour, and free acidity depicted a shorter distance from the origin point.

The angle between the vectors that represents the variables can be understood as the correlation between the variables. Those vectors with an angle of 90° indicate that both variables are not correlated. On the other hand, values lower or higher than 90° suggest a positive or negative correlation between the variables, respectively. Moisture had a positive correlation with electrical conductivity, colour and glucose whereas strong negative correlation was observed with sucrose and HMF and free acidity and moisture. Negative correlations were also observed between electrical conductivity and free acidity or colour/glucose and free acidity. No correlations were observed between HMF and moisture or free acidity.

3.3. Cluster analysis

Fig. 4a shows unrandom samples arrangement and three clusters were observed at the middle point of the whole range distance (7.8). The first group of samples corresponds to the meadow zone; the second and third groups include the hill and agricultural zone

respectively. These groups, although they are separated at the considered linkage distance, are close together in the dendrogram. From 24 samples, only sample H4 was misclassified using CA. The results showed both the importance of the selected variables as well as the association and linkage criterion, to obtain adequate grouping.

A multivariate CA of variables (Fig. 4b) showed the presence of two groups at the considered linkage distance of 183. The first cluster composed by moisture, free acidity, electrical conductivity, sucrose, and HMF and the second group composed by colour, glucose and fructose. The monosaccharides were close together in the dendrogram suggesting that there is not a great difference between the levels of glucose and fructose. Similar results were obtained by Ouchemoukh et al. (2010) with the hierarchical cluster analysis of sugars from Algerian honeys.

Fig. 4c depicts the dendrogram of cluster analysis for zones based on the sensory analysis. Results show that three clusters were obtained at a linkage distance of 6.4. All the clusters depict a random arrangement of the samples suggesting that honeys from the three zones have similar sensory properties.

3.4. Linear discriminant analysis

Results in Fig. 5a illustrates the scatter plot of the first and second discriminant function. The results obtained in this assay showed a good differentiation on the basis of honey geographical origin considering the physicochemical parameters. However, the prediction ellipses of the hills and meadow zones overlap.

Table 3a shows the classification parameters and results of the LDA. The small values of the Wilk's Lambda showed a great discriminatory ability of the discriminant function. The first function explained 75.32% and second function 24.68% of the total variance. Table 3b shows the results of the LDA model applied to the complete data matrix. All the samples were in the training set. After the cross validation only one sample from the meadow zone was misclassified for the physicochemical parameters. The other samples were correctly classified (100%).

On the other hand, Fig. 5b shows the LDA based on the sensory properties of honeys. Results depict a good separation for honeys from meadow and hills zones; however, the prediction ellipse of honeys from the agricultural zones overlaps with the prediction ellipses from the meadow and hills zones. This fact suggests that

the discriminatory power based on the sensory characteristics of honeys is not as good as using the physicochemical parameters. Results in Table 3a confirm this fact as the Wilk's Lambda value of discriminant function 1 for the physicochemical parameters is lower than that of sensory analysis. Moreover, in Table 3b it can be observed a higher rate of misclassified samples for the sensory analysis. The poorest classification was obtained for the hills zones (20% error). On the other hand, the best classification was obtained for meadow zone (9.09% error) and agricultural zone (12.50% error). It might be possible that the skills of the assessors to differentiate between honeys of the different zones were not enough. Guler et al. (2008) concluded that not only the type of honey but also the ability of the assessor in discrimination of honey is important.

4. Conclusions

Some differences were observed in the physicochemical parameters between honeys from different zones. The sugars content profile showed that these honeys are nectar honeys and they are not adulterated.

The application of multivariate analysis is adequate to classify samples of natural honey from nearby areas within the south east region of BA province (Argentina) using the physicochemical parameters as predictors. However, the prediction of the geographical origin based on the sensory properties provided a lower percentage of predicted membership which means that the physicochemical variables were better predictors. The proposed method could be useful to define the designation of origin in regional natural honey contributing to the chemical traceability of the product.

Results also suggest that these honeys are of good quality as they are in agreement with standards of quality established by national and international regulations.

Acknowledgments

The authors would like to thank the sensory panel for their cooperation and for the beekeepers for providing the honey samples.

References

- Anupama, D., Bhat, K. K., & Sapna, V. K. (2003). Sensory and physico-chemical properties of commercial samples of honey. *Food Research International*, 36, 183–191.
- AOAC (1990). Association of Official Analytical Chemists.
- Baroni, M. V., Arrua, C., Nores, M. L., Fayé, P., Díaz, M., Chiabrand, G. A., et al. (2009). Composition of honey from Córdoba (Argentina): Assessment of North/South provenance by chemometrics. *Food Chemistry*, 114, 727–733.
- Bentabol Manzanares, A., Hernández García, Z., Rodríguez Galdón, B., Rodríguez Rodríguez, E., & Díaz Romero, C. (2011). Differentiation of blossom and honeydew honeys using multivariate analysis on the physicochemical parameters and sugar composition. *Food Chemistry*, 126, 664–672.
- Bogdanov, S., Lüllmann, C., Martin, P., Von der Ohe, W., Russmann, H., & Vorwohl, G. (1999). Honey quality and international regulatory standards: Review by the International Honey Commission. *Bee World*, 80, 61–69.
- CAA (2010). *Código Alimentario Argentino*. <http://www.anmat.gov.ar/alimentos/normativas_alimentos_caa.asp> [Accessed 24.06.13].
- Camiña, J. M., Cantarelli, M. A., Lozano, V. A., Boeris, M. S., Irimia, M. E., Gil, R. A., et al. (2008). Chemometric tools for the characterisation of honey produced in La Pampa, Argentina, from their elemental content, using inductively coupled plasma optical emission spectrometry (ICP-OES). *Journal of Apicultural Research and Bee World*, 47(2), 102–107.
- Codex Alimentarius (2013). <<http://www.codexalimentarius.org/>> [Accessed 24.06.13].
- Corbella, E., & Cozzolino, D. (2006). Classification of the floral origin of Uruguayan honeys by chemical and physical characteristics combined with chemometrics. *LWT—Food Science and Technology*, 39, 534–539.
- Da Costa Leite, J. M., Trugo, L. C., Costa, L. S. M., Quinteiro, L. M. C., Barth, O. M., & Dutra, V. M. L. (2000). Determination of oligosaccharides in Brazilian honeys of different botanical origin. *Food Chemistry*, 70, 93–98.
- Esti, M., Panfili, G., Marconi, E., & Trivisonno, M. C. (1997). Valorization of the honeys from the Molise region through physico-chemical, organoleptic and nutritional assessment. *Food Chemistry*, 58, 125–128.
- European Economic Community. (2002). EEC Council directive of 20 December 2001 relating to honey. *Official Journal of the European Communities*, 110, 47–50.
- Fangio, M. F., Iurlina, M. O., & Frotz, R. (2010). Characterization of Argentinean honeys and evaluation of its inhibitory action on *Escherichia coli* growth. *International Journal of Food Science & Technology*, 45, 520–529.
- Guler, A., Bek, Y., & Kement, V. (2008). Verification test of sensory analyses of comb and strained honeys produced as pure and feeding intensively with sucrose (*Saccharum officinarum* L.) syrup. *Food Chemistry*, 109, 891–898.
- Johnson, D. E. (2000). *Métodos multivariados aplicados al análisis de datos* (1st ed.). Mexico DF: International Thompson Ed.
- Malacalza, N. H., Mouteira, M. C., Baldi, B., & Lupano, C. E. (2007). Characterization of honey from different regions of the province of Buenos Aires, Argentina. *Journal of Apicultural Research and Bee World*, 46, 8–14.
- Mendes, E., Brojo Proença, E., Ferreira, I., & Ferreira, M. A. (1998). Quality evaluation of Portuguese honey. *Carbohydrate Polymers*, 37, 219–223.
- Molan, P. C. (1996). Authenticity of honey. In P. R. Ashurst & M. J. Dennis (Eds.), *Food authentication* (pp. 259–303). London: Blackie Academic and Professional.
- Montenegro, G., Gomez, M., Pizarro, R., Casaubon, G., & Peña, R. (2008). Implementation of a sensorial panel for Chilean honeys. *Ciencia e Investigación Agraria*, 35, 41–48.
- Norma IRAM 15937-2; 15938 (1995). Instituto Argentino de Normalización.
- Norma IRAM 15941-2; 15945 (1997). Instituto Argentino de Normalización.
- Normas IRAM 15931; 15932; 15933 (1994). Instituto Argentino de Normalización.
- Ouchemoukh, S., Schweitzer, P., Bachir Beya, M., Djoudad-Kadji, H., & Louaileche, H. (2010). HPLC sugar profiles of Algerian honeys. *Food Chemistry*, 121, 561–568.
- Rohman, A., Triyana, K., Sisindari, & Erwanto, Y. (2012). Differentiation of lard and other animal fats based on triacylglycerols composition and principal component analysis. *International Food Research Journal*, 19, 475–479.
- SAGPyA (2013). <<http://www.minagri.gov.ar>> [Accessed July 2013].
- Serrano, S., Villarejo, M., Espejo, R., & Jodral, M. (2004). Chemical and physical parameters of Andalusian honey: Classification of Citrus and Eucalyptus honeys by discriminant analysis. *Food Chemistry*, 87, 619–625.
- Sporns, P., Plhak, L., & Friedrich, J. (1992). Alberta honey composition. *Food Research International*, 25, 93–100.
- Terrab, A., Gonzalez, G. A., Diez, M. J., & Heredia, F. J. (2003). Mineral content and electrical conductivity of honeys produced in Northwest Morocco and their contribution to the characterization of unifloral honeys. *Journal of the Science of Food and Agriculture*, 83, 637–643.
- Yücel, Y., & Sultanoğlu, P. (2012). Determination of industrial pollution effects on citrus honey with chemometric approach. *Food Chemistry*, 135, 170–178.