Food Bioscience 15 (2016) 49–54

Contents lists available at ScienceDirect

Food Bioscience

journal homepage: www.elsevier.com/locate/fbio

Multivariate classification of honeys from Corrientes (Argentina) according to geographical origin based on physicochemical properties

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ARTICLE INFO

Article history:
Received 29 September 2015
Received in revised form
9 May 2016
Accepted 13 May 2016
Available online 14 May 2016

Keywords:
Honey
Geographical origin
Chemometrics
PCA
LDA

ABSTRACT

Honey is the natural sweet substance produced by *Apis mellifera* bees and is studied in different countries and zones because of the interest of consumers in origin and quality of food. The Corrientes Province (Argentina) produces and exports honey from different rural zones; therefore, the aim of this paper was to study the physico-chemical parameters of honeys using multivariate methods in order to classify honeys according to the geographical origin. Nine standard physico-chemical parameters were determined according to the international legislation. The results obtained were in agreement with international regulations. Then, the results obtained were analyzed by principal component analysis and linear discriminant analysis applying forward selection. The chemometric analysis allowed grouping samples according to their geographical origin by using only five parameters.

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1. Introduction

Honey is the natural sweet substance produced by *Apis mellifera* bees from the nectar of plants or from secretions of living parts of plants or excretions of plant-sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in honeycombs to ripen and mature (Communities, 2002). Honey is a complex product composed majority by monosaccharides and minority by components such as amino acids, enzymes, vitamins and minerals. The composition is influenced principally by the plant species that bees visit; and furthermore by geographic area, soil, weather conditions, and contribution of the beekeeping practices.

Argentina is among the main five producers of honey in the world, it is after China, Turkey, USA and Ukraine. According to FAO (Food and Agriculture Organization of the United Nations), Argentina produced 60,000 t of honey in 2011. Corrientes is one of the 12 provinces of Argentina that export honey. Because of a wide rural area as well as significant planted forests areas (Elizondo & Mestres, 2009), Corrientes Province produces mainly honey of native forest, citrus, eucalyptus, and esters and islands. The natural resource and the optimum utilization allow the production of honey without antibiotics, and a minimum stress for the bees (Haberle, 2013). In recent years, there has been a significant increase in honey production due to an increasing demand and interest by consumers in natural products, good climatic conditions and governmental action promoting beekeeping.

Producers, consumers, the food industry and regulatory authorities are interested in correct labeling of origin, traceability, and quality of honeys. For honey, quality is a multi-factorial parameter linked to botanical and geographical origin, which affects its commercial value; and Protection Denomination Origin (PDO) register is an added value that promotes and protects name of quality honeys. The geographical origin criterion is 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 (Silvano, Varela, Palacio, Ruffinengo, & Yamul, 2014). In this context, although there are powerful methods to prove honey adulteration, concerning the botanical origin of honey quality, rapid, reliable, and cheap analytical approaches applicable for the authentication of honey should be developed (de la Guardia & Illueca, 2013). Focusing in this aspect, researches have been proposed for authentications of honey the chemometric evaluation of classical physico-chemical parameters (Arvanitoyannis, Chalhoub, Gotsiou, Lydakis-Simantiris, & Kefalas, 2005; Jandrić et al., 2015; Yücel & Sultanoğlu,

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http://dx.doi.org/10.1016/j.fbio.2016.05.002
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2013).

Currently, numerous studies about honey produced in different countries, also mentioning Argentina have been published (Baroni et al., 2009; Belay, Solomon, Bultossa, Adgaba, & Melaku, 2013, 2015; Can et al., 2015; Chua, Abdul-Rahaman, Sarmidi, & Aziz, 2012; Conti et al., 2014; Conti, Stripeikis, Campanella, Cucina, & Tudino, 2007; Feás, Pires, Estevinho, Iglesias, & De Araujo, 2010; Karabagias, Badeka, Kontakos, Karabournioti, & Kontominas, 2014a, 2014b; Pellerano, Uñates, Cantarelli, Camiña, & Marchevsky, 2012). But only few studies have shown physico-chemical characteristics of honeys from Northeast of Argentina (Acquarone, Buera, & Elizalde, 2007; Lancelle, Fechner, Moresi, Armua, & Badan, 2013; Salgado & Maidana, 2014). However, at the moment no information is available concerning classification of honeys from Corrientes Province. In this context, this work explores the possibility to implement a protected geographical indication of origin system in order to promote and protect the reliability of international market of Argentinean honeys. The aim of this paper was to study the physico-chemical parameters of honeys using multivariate methods in order to classify honeys according to the geographical origin. In addition, to validate the proposed model, we included honey samples from a neighbor production region that were not considered for the training step.

2. Materials and methods

2.1. Samples

One hundred forty one honey samples were directly provided by the beekeepers. Honey samples were collected during the 2010, 2011 and 2012 harvest from the most important production areas in Corrientes Province (Argentina), which include different botanical origins and soil characteristics. We selected four honey production areas: Corrientes (CT, $n=29$), Bella Vista (BV, $n=29$), Goya (GY, $n=23$) and Monte Caseros (MC, $n=60$) (Fig. 1). All samples were unheated and were analyzed no later than 4 weeks after extraction from the hives by the beekeepers. In addition, 19 honey samples were collected from Formosa Province (Argentina) to validate the chemometric classification model proposed in this work. Even though the Northeast region of Argentina is formed by four provinces, in this work, we select East region of Formosa to obtain samples for validation, because this region has similar climate characteristics as Corrientes Province: subtropical, wet, with hot summers and without dry season. In addition, this province shares with Corrientes the international boundary with the Southwest region of Paraguay, which is another significant producer of honey from South America.

Bee flora from Corrientes Province and from Formosa Province is different. In one hand, principal bee flora from Corrientes is *Eucalyptus spp., Citrus aurantium, C. limon, Eryngium elegans, E. horridun, Cordia sp., Baccharis punctulata, Mikania sp., Senecio grisebachii, Trixis antimenorrhoea, Thyreus praestans, Persea americana, Fragaria x annanasa, Acicarpha tribuloides, Acacia caven, Clematis montevidensis, Elephantopus mollis, Cirsium vulgare, Chorisia speciosa, Oenothera spp*., (Salgado & Pire, 1998). In other hand, principal bee flora from Formosa is *Bulnesia sarmientoi* Lorentz ex. Griseb., *Geoffroea decorticans, Copernicia alba, Eugenia uniflora, Prosopis alba*, *Schinopsis balansae, Schinus* spp.*and Ziziphus mistol* (C. Salgado & Cabrera, 2006).

2.2. Methods

The samples were kept in the dark at room temperature 20–25 °C in plastic flask before physical and chemical analysis. These analyses were performed following international recommendations.

2.2.1. Moisture

Water content was determined by using a digital ABBE WYA-1S refractometer (ICSA, China) according to AOAC Official Method 969.38B (AOAC, 1996). The honey samples that were crystalized at the moment of analysis were previously heated until 40 °C. The measurement was done for three times and the results (refractive index) were displayed on the instrument. The refractive index values were converted to moisture contents from the Chataway table.

2.2.2. Electrical conductivity (EC)

Electrical conductivity (EC) was measured at 20 °C using an ORION 3 STAR (Thermo Scientific, Beverly, USA) conductivity meter according to IRAM 15945, 1996. EC was measured in a 20% (w/v) solution of honey in CO_2-free deionized water. The results were expressed as mS/cm. All measurements were performed in

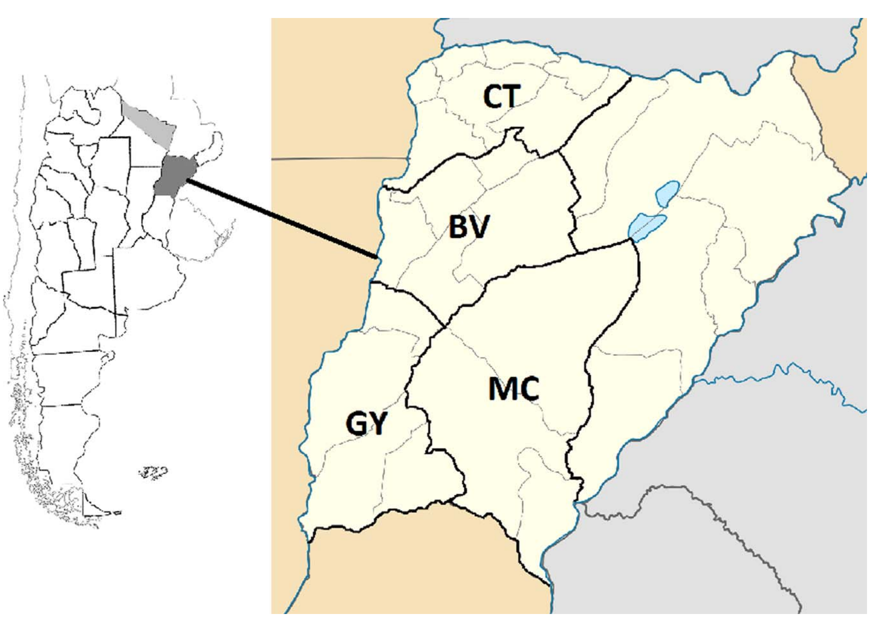

Fig. 1. Geographical origins of the honey samples from basins of Corrientes Province: BV (Bella Vista), CT (Corrientes), GY (Goya), and MC (Monte Caseros).

Table 1
Mean ± Standard Deviation for physico-chemical contents of honey samples produced in basins BV (Bella Vista), CT (Corrientes), GY (Goya), and MC (Monte Caseros).

Parameter	BV	CT	GY	MC
Moisture (%)	17.8 ± 0.8	18.0 ± 0.9	17.7 ± 1.1	16.8 ± 0.8
Color (mm Pfund)	71 ± 24.2	68 ± 21.4	76 ± 18.5	71 ± 15.8
pH	4.45 ± 0.25	4.59 ± 0.46	4.54 ± 0.34	4.68 ± 0.34
Acidity (meq/kg)	25.2 ± 6.5	26.1 ± 9.9	30.4 ± 8.6	21.5 ± 6.9
EC (mS/cm)	0.640 ± 0.150	0.470 ± 0.140	0.750 ± 0.330	0.790 ± 0.160
RedSug (g/100 g)	75.0 ± 3.9	74.7 ± 2.7	76.3 ± 2.9	77.7 ± 3.9
HMF (mg/kg)	10 ± 8.3	6 ± 6.2	4 ± 2.8	5 ± 4.4
Proline (mg/kg)	573 ± 361	687 ± 390	648 ± 423	666 ± 243
ApSuc (g/100 g)	1.8 ± 1.1	1.6 ± 1.1	2.1 ± 1.9	1.3 ± 0.9
Diastase (ºGhote)	14 ± 4.2	15 ± 7.5	18 ± 7.6	16 ± 7.1

EC, electrical conductivity; RedSug, reducing sugar; HMF, hydroxymethylfurfural; ApSuc, aparent sucrose.

triplicate.

2.2.3. pH

pH was measured by a HANNA HI 98129 pH-meter (HANNA Instruments-Woonsocket, Rhode Island, USA) in a 10% w/v solution of honey prepared with CO_2-free deionized water, according to AOAC Official Method 962.19 (AOAC, 1996).

2.2.4. Hydroxymethylfurfural (HMF)

Hydroxymethylfurfural (HMF) was determined by the standard method AOAC Official Method 980.23 (AOAC, 1996). In brief, 5 g of each honey sample were transferred to a 50 ml volumetric flask with a total of 25 ml of deionized water. After clarifying samples with 500 µL of Carrez reagents (I and II), samples were diluted to 50 ml with water. If necessary, alcohol may be added to suppress surface foam. With a clarified honey solution containing 0.2% (m/v) sodium bisulfite as a reference and a similar solution without bisulfite as a sample, a difference spectrum was obtained which represented only the HMF in the sample, without the interfering absorption of the honey. Absorbance was determined at 284 and 336 nm in a 1 cm quartz cuvette in a spectrophotometer Metrolab 1700 (Metrolab, Buenos Aires, Argentina). HMF contents, expressed as mg/kg, were calculated after subtracting background absorbance at 336 nm.

2.2.5. Color value

Color value was determined using glycerol as standard in a digital C221 honey color analyzer (HANNA instruments-Italy, Hungary, Europe) reading in millimeter Pfund scale, according to IRAM 15941-2 (IRAM, 1997). The honey samples were heated until 40 °C before read to prevent crystals and bubbles.

2.2.6. Free acidity

Free acidity were determined by a titrimetric method AOAC 962.19 (AOAC, 1996) by addition of 0.1 M NaOH to a 10% w/v solution of honey prepared with CO_2 free distilled water up to pH 8.3.

2.2.7. Reducing sugar content

Reducing sugar content was determined by the method of Fehling-Causse-Bonnans, IRAM 15934 (IRAM, 1997). Apparent sucrose was calculated as the difference between total reducing sugars and reducing sugars. Honey samples were treated with HCl concentrated and then neutralized with 6 M NaOH for total reducing sugars determination.

2.2.8. Diastase activity

Diastase activity was measured according to AOAC Official Method 958.09 (AOAC, 1996). We used a buffered solution of soluble starch and honey, which was incubated in thermostatic bath until the endpoint was determined photometrically in a spectrophotometer Metrolab 1700 (Metrolab, Buenos Aires, Argentina).

2.2.9. Proline

Proline was determined by the method AOAC Official Method 979.20 (AOAC, 1996). The resulting product of the reaction of the amino acid with ninhydrin in an acidic medium was measured at 517 nm in a spectrophotometer Metrolab 1700 (Metrolab, Buenos Aires, Argentina).

All the analyses were done in triplicate and the mean values were used for the multivariate analysis.

2.3. Statistical and multivariate analysis

Principal component analysis (PCA) and linear discriminant analysis (LDA) were performed on the physico-chemical variables after auto-scaling the variables. All statistical data analysis was performed using R software version 3.1.2 (R Development Core Team, 2011).

3. Results and discussion

3.1. Physico-chemical parameters

Table 1 summarizes the results obtained in this work. In general, the results obtained agree with previous studies from Argentinian honey (Isla et al., 2011; Silvano et al., 2014). All the variables presented a wide variability, as evidenced by large standard deviations, due to environmental and maturational differences among samples of honey.

3.1.1. Moisture

The highest and lowest levels of water contents were determined in samples from CT basin (19.6%) and GY basin (15.0%), respectively. All samples show lower values than the limit of the MERCOSUR and Codex Alimentarius (20%) (Codex, 2001); however, 45 samples exceed 18% that is the maximum allowed by local regulations Código Alimentario Argentino, CAA (CAA, 1997). In general, the results obtained agree with previous studies from Argentinian honey samples (Baroni et al., 2009; Conti et al., 2014).

Water content is a parameter that is related to the climatic conditions, the degree of maturity, conditions during extraction and storage. Besides, moisture content affects honey color, viscosity flavor, density and reflective index. And it is relevant to note that high level of this parameter stimulates fermentation process in honey; consequently the quality decreases rapidly.

3.1.2. Electrical conductivity (EC)

The EC ranged from 0.16 mS/cm to 1.79 mS/cm in samples produced from CT basin and GY basin, respectively. In addition, 30% of samples from GY basin showed higher values than the limit established by the CAA for floral honeys (0.8 mS/cm). These high levels of EC together with dark color may suggest that the mentioned honeys can correspond to honeydew honey (honey that honeybees produce from secretions from the living parts of plants or excretions of plant-sucking insects on the living parts of plants). The other samples show similar values to previous reports from honeys produced in the world (Belay et al., 2013; Bentabol Manzanares, Hernández García, Rodríguez Galdón, Rodríguez Rodríguez, & Díaz Romero, 2014; Corbella & Cozzolino, 2006; Yücel & Sultanoğlu, 2013).

The electrical conductivity of honey is a parameter closely related to the ash and acid content of honey, which reflects the presence of ions, organic acids and proteins.

3.1.3. pH

All samples were in the range of 3.67–5.40. The average of pH (4.56) was higher than previous studies published on the literature (Baroni et al., 2009; Bentabol Manzanares et al., 2014; Conti et al., 2014; Isla et al., 2011).

The pH of honey is affected by conditions during extraction and storage, and it influences the texture, stability and shelf life of honey (Terrab, Recamales, Hernanz, & Heredia, 2004).

3.1.4. HMF

A honey sample from BV basin showed the highest value of HMF (31 mg/Kg), the lowest value of HMF (1 mg/Kg) were found in samples from all basins. The honey samples exhibit low values of HMF, showing that beekeepers carried out the extraction of honeys following good practices of harvest and storage. HMF is a compound derived from dehydration of fructose that is formed slowly and naturally during the storage of honey but more quickly when honey is heated (de la Guardia et al., 2013). Because of this, the HMF content is widely recognized as a parameter of freshness and unheated treatments in honey samples because several factors influence the formation of HMF, such as temperature, time of heating, storage conditions and floral source (Fallico, Zappalà, Arena, & Verzera, 2004; Guler, Bakan, Nisbet, & Yavuz, 2007).

3.1.5. Color

The highest value of color (150 mm Pfund) was determined in a honey sample from basin BV, and the lowest (29 mm Pfund) in a honey sample from both MC basin and CT basins. Contrarily, most of the samples from MC show darkest color; five of these samples showed Dark Ambar color. The others samples of total showed lighter colors, which is an advantage for sale because of consumers preferences. The range was wider than the results reported by Silvano et al. (2014), and at similar levels than the results published by Isla et al. (2011).

The color intensity is related to pigments (carotenoids, flavonoids) that are also known to have antioxidant properties (Ozcan & Olmez, 2014). And it is an important commercial factor that determines its price in the world market. Honey can undergo darkening during shipping and storage, and parallel changes in its organoleptic properties (de la Guardia et al., 2013).

3.1.6. Free acidity

Free acidity was highest (50.4 meq/Kg) in a honey sample from GY basin, and was lowest (11.5 meq/Kg) in a honey sample from CT basin. Six samples exceed the limit of Codex; this indicates a beginning of fermentation.

Free acidity is useful for evaluation of honey fermentation, authentication of unifloral honeys and differentiating nectar from honeydew honeys. In addition, this quality indicator can be affected by various factors such as floral origin or harvest season.

3.1.7. Reducing sugar

The highest (82.6 g/100 g) and lowest (67.6 g/100 g) levels of reducing sugars were determined in samples from MC and BV basin, respectively. The monosaccharide content was within the limits of European regulations and CAA. Values reported in this work were higher than those reported by (Belay et al., 2013; Habib, Al Meqbali, Kamal, Souka, & Ibrahim, 2014; Sajid et al., 2013); however, the levels measured in this work were lower than those reported by Conti et al. (2014).

Sugars are the major component of honey, and determine the physical properties of honey: viscosity, density, granulation, tendency to absorb humidity.

3.1.8. Diastase activity

The results showed the highest value (45 °G) in a honey sample from MC basin, and the lowest value (5 °G) in honey samples from CT basin. One sample was out of limit of Codex because it had 5 °G for diastase and 23 mg/L for HMF. On one hand, these results were similar to those obtained by Baroni et al. (2009), except for samples that are out of limits of CAA. On the other hand, the results determined in our research were in contrast with other studies. We found a mean of 15.83 °G for diastase, in difference to another study that published mean of 43.8 °G for a monofloral oregano honey (Bentabol Manzanares et al., 2014). Another report showed the highest value of 19 °G for diastase (Yücel & Sultanoğlu 2013; Ozcan et al., 2014; Santos, Moreira, & De Maria, 2015), while the 17% of results that we found were higher than 19 °G.

The diastase activity is commonly used as a measure of honey freshness, because their activity decreases in old or heated honey.

3.1.9. Proline

The proline values ranged from 110 mg/Kg to 1860 mg/Kg in honey samples from BV and GY basins, respectively. Only three samples were lower than 180 mg/Kg recommended for authentic honey. The majority of proline results published in this study were higher than other results published before (Baroni et al., 2009; Bentabol Manzanares et al., 2014; Kropf et al., 2010; Lancelle et al., 2013; Santos et al., 2015).

The proline content can be used to distinguish genuine honey samples from honey produced from non-floral sources. Minimum value of 180 mg/Kg is accepted for genuine honey, therefore is not regulated in any legislation. However there is considerable variation depending on the honey type (Bogdanov & Martin, 2002).

3.2. Statistical and multivariate analysis

Univariate analysis was done for each parameter (Table 1). PCA was performed to explore experimental data, evaluate relevant variables and correlations, and produce bidimensional plots in which samples and variables are visualized in a particular plane that maximize the variance. So, in this plane, the quantity of useful analytical information is maximized. The first principal component (PC1) represented 24% of the total variance and the next principal components, 18%, 14%, and 11% respectively. Thus, the first four PCs accounted 66% of the total variance of the original result data matrix. The loadings plots on PC2 versus PC1 are shown in Fig. 2a. It allows visualizing the relationship of original variables with each PC. The first principal component (PC1) was strongly correlated with the values of acidity, HMF, color, pH and reducing sugars. For the second principal component (PC2), the dominant variables were EC, reducing sugar and color. Fig. 2b shows PC1 vs PC2 grouping the samples studied into four different groups, each corresponding to a honey production area (basin). BV and CT basins were majority characterized by negative values of PC2, corresponding to high contribution of moisture, HMF and apparent sucrose. In addition, both BV and CT basins showed positive and negative values of PC1. The MC basin was majority characterized by positive values of PC1 and PC2, corresponding to high contribution of EC, reducing sugar and pH. Moreover, 45% of the GY basin was characterized by positive values of PC1 and 55% by negative values of PC1; corresponding to higher values of conductivity, free acidity, proline and color. So, CT and MC basins were well separated, although BV and CT basins were overlapped. And the ellipsis of GY was partially overlapped between CT and MC ellipsis. Therefore, there is a gradual change from North to Southeast in the ambient conditions that modify gradually the physico-chemical parameters of honey samples. Thus, the neighbor basins (or the closest basins) were partially overlapped; in addition, BV and CT basins were similar within these PCs.

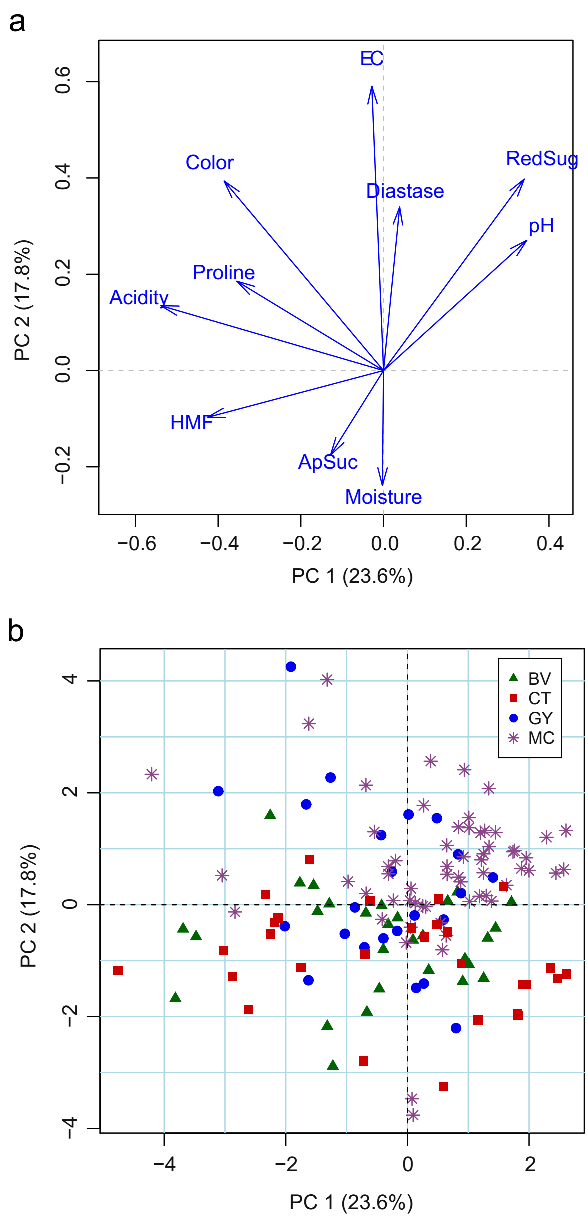

Fig. 2. (a) Loading plot of the variables for the two principal components. EC: electrical conductivity; RedSug: reducing sugar; HMF: hydroxymethylfurfural; ApSuc: aparent. Sucrose. (b) Principal component analysis, distribution of honey samples from Corrientes Province in score plots. (BV: Bella Vista, CT: Corrientes, GY: Goya, and MC: Monte Caseros).

After that, LDA was performed applying forward selection to classify honey according to basin groups only with relevant variables. The most important variables obtained were: moisture, EC, pH, acidity and HMF. The Fig. 3, LD1 versus LD2, shows ellipsis separate for CT and MC but overlap for BV and GY basins. This is confirmed by the apparent error: BV and GY show the major percentage, 44.8% and 47.8% respectively. In the total of samples, the percentage of cases correctly classified was 65.8%.

Finally, as an external validation, we applied LDA to honey samples from Corrientes Province (as one group) and Formosa Province (as another group). In this instance, we used only the five parameters selected by the stepwise LDA applied to honey samples from Corrientes Province. The two groups were classified with 98.7% of cases correctly classified. In order to visualize, we show PC1 vs. PC2 (Fig. 4). It shows that the two groups of different

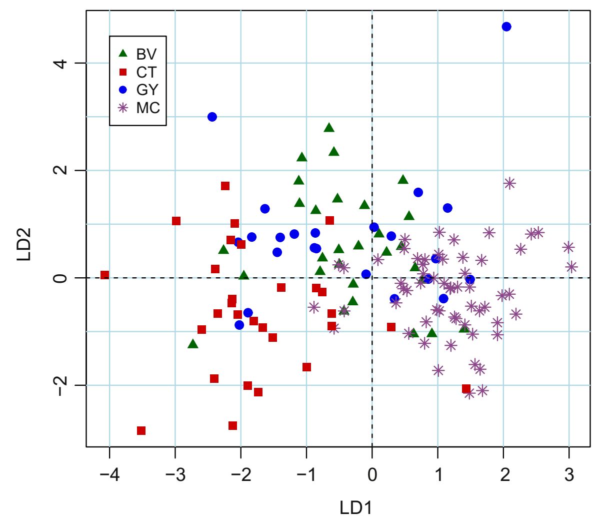

Fig. 3. Linear discriminant analysis: projections of honey samples from different basins of Corrientes Province in the space formed by the two discriminant functions. (BV: Bella Vista, CT: Corrientes, GY: Goya, and MC: Monte Caseros).

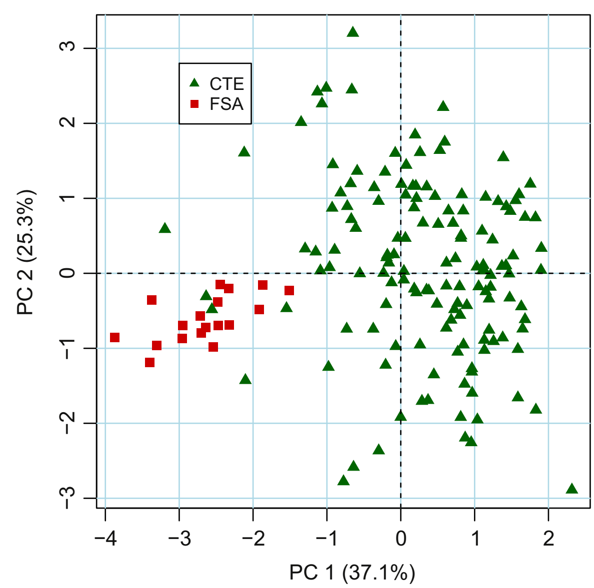

Fig. 4. Principal component analysis: distribution of honey samples from Corrientes (CTE) and Formosa (FSA) Provinces.

provinces were separated: honey samples from Formosa Province were in the left side and honey samples from Corrientes Province were in the right.

4. Conclusion

In this work 141 honey samples produced in the province of Corrientes (Argentina) were analyzed physico-chemically. Majority of results obtained were in agreement with regulatory limits established by Codex Alimentarius. Thus, our results indicate that honey produced in the Province of Corrientes has remarkable quality. Additionally, the evaluation of physico-chemical profile, coupled with chemometrics, represents a method to assess the provenance of honey from different basins of Corrientes, with percentage correctly classified of 65.8%. It is because the flora and climatic conditions of the geographic zone studied are similar. As a consequence, honey from Corrientes Province is differentiating in gradient manner from North to Southeast. We arrived to this conclusion because PCA and LDA applied to this samples show overlapping between samples from neighbor basins. Finally, in the validation step, PCA and LDA applied to honey from Corrientes and Formosa Provinces discriminate the two groups with a high correct classification rate (98.7%). Therefore, this work demonstrates that it is possible to confidently classify honey by region of origin, contributing to the knowledge of chemical traceability of this product.

Conflict of interest statement

There are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

Acknowledgment

The authors thank to Secretaria General de Ciencia y Técnica – Universidad Nacional del Nordeste (PI F001/2010), and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) Argentina for financial support.

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