

DETERMINATION OF QUALITY CHEMICAL PARAMETERS OF HONEY FROM CHUBUT (ARGENTINEAN PATAGONIA)

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ABSTRACT

This study was intended to evaluate the quality chemical parameters of 62 *Apis mellifera* L. honey samples, from the Province of Chubut, Argentina. Samples were obtained from the three melliferous areas of this province: Andean region, lower Chubut River valley and plains of Senguerr River. The average values obtained for electrical conductivity (0.33 mS cm^{-1}) and pH (4.17) indicate that the analyzed honeys came mainly from nectar. Electrical conductivity was higher in honeys from the Andean region than in honeys from the other two regions. Moisture (water content) was low, with an average value of 14.67%. The hydroxymethylfurfural (HMF) content was very low and ranged between 0.0 and 14.70 mg kg^{-1} . Moisture, HMF and free acidity values show good maturity and absence of undesirable fermentation in all the samples. Diastase activity had a mean value of 13.50 units on the Gothe scale. Color parameter presented variations between honeys from different areas. The analytical values for the samples from the Andean region, the lower Chubut River valley and the plains of the Senguerr River respectively were: 67.73, 40.33 and 23.26 mm Pfund. Results obtained in this study, indicate that honeys produced in Chubut present excellent quality properties according to international standards.

Key words: Honey characterization, Argentinean honeys, Patagonian honeys, quality parameters.

INTRODUCTION

Honey is a natural substance produced by bees, mainly *Apis mellifera* L., and is a nutritious food of economic importance worldwide. In the last years, production of honey in Argentina has been increased notoriously, setting the country among the first producers of honey, which in 2007 exported about 80 341 t (FAO, 2005; DNA, 2008). Argentinean honeys are recognized throughout the world due to their quality. Their chemical and microbiological characteristics and their attractive flavor have positioned these honeys at the top of world preferences (Finola *et al.*, 2007). Recently, the growing demand for contaminant-free honey products has increased the interest in Argentinean regions with little human impact. Because of the abundance of native and endemic plant species and the lack of human intervention, areas such as Patagonia offer possibilities for a diverse and contamination free apiculture industry (Forcone, 2008).

Chubut with an area of 224 686 km² is the second largest province in Argentinean Patagonia and the third largest administrative province in Argentina. It extends south from 42° to 46° S lat, and it is situated between the mountain range of Andes and the Atlantic Ocean (Figure 1). The apiculture industry in Chubut is still in its development stage with 6500 producing beehives in three melliferous areas: the Andean region, the lower Chubut River valley (both with 3000 hives) and the plains of the Senguerr River with 500 beehives.

In Chubut province melissopalynological studies have been reported from the three melliferous areas (Forcone *et al.*, 2003; 2005; 2006; Forcone, 2008). These studies have revealed that 48% of the production is unifloral, with 13 types of honeys, six of them corresponding to the native flora (Forcone, 2008). Although these works, a lack of information has been found concerning quality characteristics of Chubut honeys. The aim of the present work was to analyze the quality parameters, to find out whether they meet compositional standards of honey specifications and give information of honeys from the different production areas of this Argentinean province.

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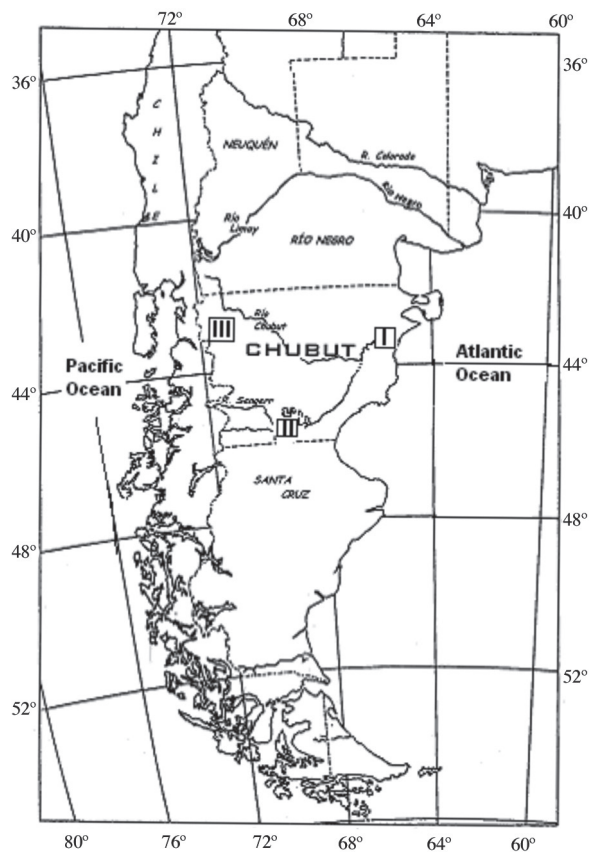


Figure 1. Geographic location of the melliferous areas of the Chubut Province. I. Lower Chubut River valley, II. Plains of Senguerr River, III. Andean Region.

MATERIAL AND METHODS

Sixty two *Apis mellifera* L. honey samples were characterized through physico-chemical analysis. The samples were provided by local producers at the end of 2005, 2006 and 2007 apicultural periods. Thirty two samples came from the lower Chubut River valley, 13 from the plains of Senguerr River and 17 from the Andean region.

The physico-chemical analyses conducted included color, moisture (water content), hydroxymethylfurfural (HMF), pH, free acidity, ashes, electrical conductivity and diastase activity. Color was determined by optical comparison with the tintometer (Lovibond™ Series 52; The Tintometer Ltd., Wiltshire, UK). Approximately 5 g of sample was loaded into the measuring tube and the color compared with standards. The results were expressed in the Pfund scale (mm Pfund) (Aubert and Gonnet, 1983; AOAC, 1999). Moisture was determined based on the refractometric method. The refractive index of honey samples was measured with a refractometer (Abbe™ 2 WAJ; Shangai Optical Instrument Co. Ltd., Shangai,

China) and the reading were further corrected for a standard temperature of 20 °C, by adding the correction factor of 0.00023/°C. The moisture values corresponding to the corrected refractive indices values were calculated using the Chataway Table (AOAC, 1999). Free acidity was determined by titrimetric method. The addition of 0.10 N sodium hydroxide (NaOH) was stopped at pH 8.3 (AOAC, 1999). The pH was measured in a pH-meter (Ultrabasic; Denver Instrument, Colorado, USA) from a solution containing 10 g honey in 75 mL of CO₂-free distilled water (AOAC, 1999). HMF was determined after clarifying samples with potassium hexacyanoferrate (Carrez I) and zinc sulfate -7- hydrate (Carrez II) and the addition of sodium bisulphate. Absorbance was determined at 284 nm and 336 nm in a spectrophotometer (SP-300 Plus Uv-vis; Optima, Tokio, Japan) (AOAC, 1999). Electrical conductivity of a honey solution at 20% (dry matter basis) in CO₂-free deionized distilled water was measured at 20 °C (Bogdanov *et al.*, 1997). Ash percentage was calculated on the basis of the results of electrical conductivity (Bogdanov *et al.*, 1999). The method of Schade modified by White was used to determine the diastase activity. A buffered solution of soluble starch and honey was incubated in a thermostatic bath until the end-point was determined photometrically. Its result was expressed in Gothe unit, as mL of 1% starch hydrolyzed by the enzyme in 1 g of honey in 1 h (AOAC, 1999).

Physico-chemical results were compared with International Regulatory Standards (Bogdanov *et al.*, 1999). Means and standard deviations were calculated by using the software Microsoft® Excel 2007.

RESULTS

Honey from all melliferous areas of Chubut province were studied in terms of physicochemical properties. Moisture for all the samples was low, with an average value of 14.67% (Table 1). The lowest moisture value came out at 5.40% for honeys from lower Chubut River valley (Table 2).

The average free acidity values obtained were 23.40, 19.70 and 24.23 meq kg⁻¹, for honeys from the lower Chubut River valley, plains of Senguerr River and Andean region, respectively (Table 2). The highest pH values were obtained for honeys from Andean region, while the lowest values were registered in honeys from lower Chubut River valley (Table 2). All the samples had very low ash values, ranged from 0.00 to 0.54%. Electrical conductivity values ranged from 0.14 to 1.08 mS cm⁻¹ (Table 1). The highest records for ash and electrical conductivity were found in honeys from Andean region, as it was expected because these two characteristics are positively correlated (Table 2). The average amount of HMF was very low for all the

Table 1. Physicochemical parameters of *Apis mellifera* L. honey samples from Chubut, Argentina.

| Parameters | Mean | SD | Maximum | Minimum |
|--|-------|-------|---------|---------|
| Moisture, % | 14.67 | 2.21 | 18.40 | 5.40 |
| HMF, mg kg ⁻¹ | 2.42 | 3.44 | 14.70 | 0.00 |
| Free acidity, meq kg ⁻¹ | 22.85 | 7.13 | 40.00 | 11.00 |
| pH | 4.17 | 0.52 | 5.70 | 3.20 |
| Electrical conductivity, mS cm ⁻¹ | 0.33 | 0.17 | 1.08 | 0.14 |
| Ash, % (w/w) | 0.11 | 0.09 | 0.54 | 0.00 |
| Diastase activity (Gothe units) | 13.50 | 7.56 | 39.28 | 3.90 |
| Color, mm Pfund | 43.72 | 23.35 | 114.00 | 5.00 |

Number of analyzed samples = 62; SD: standard deviation.

HMF: hydroxymethylfurfural.

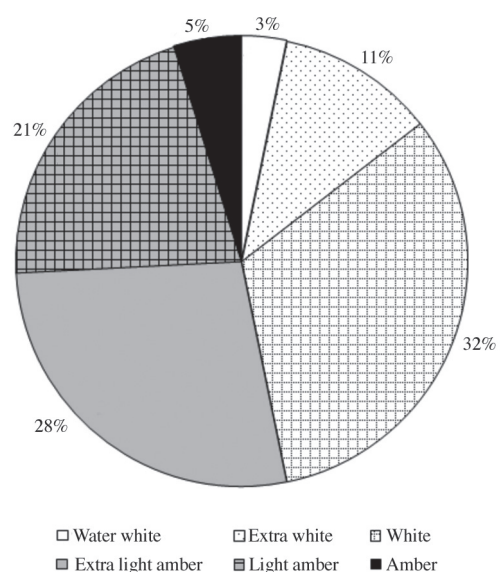
Table 2. Physicochemical characteristics of *Apis mellifera* L. honeys samples from the three melliferous areas of Chubut Province.

| Parameters | Lower Chubut River Valley | | | | Plains of Senguerr River | | | | Andean Region | | | |
|------------------------------------|---------------------------|-------|-------|-------|--------------------------|-------|-------|-------|---------------|-------|--------|-------|
| | Mean | SD | Max | Min | Mean | SD | Max | Min | Mean | SD | Max | Min |
| Moisture, % | 14.16 | 2.64 | 18.40 | 5.40 | 14.30 | 1.23 | 16.00 | 12.00 | 15.95 | 1.24 | 18.40 | 13.00 |
| HMF, mg kg ⁻¹ | 3.54 | 4.30 | 14.70 | 0.00 | 1.57 | 1.69 | 5.60 | 0.00 | 0.95 | 1.35 | 4.43 | 0.00 |
| Free acidity, meq kg ⁻¹ | 23.40 | 7.07 | 40.00 | 14.00 | 19.70 | 5.22 | 28.00 | 12.00 | 24.23 | 8.60 | 38.00 | 11.00 |
| pH | 3.88 | 0.39 | 4.90 | 3.20 | 4.56 | 0.41 | 5.10 | 4.00 | 4.41 | 0.51 | 5.70 | 3.30 |
| EC, mS cm ⁻¹ | 0.28 | 0.10 | 0.58 | 0.14 | 0.29 | 0.12 | 0.61 | 0.16 | 0.46 | 0.24 | 1.08 | 0.17 |
| Ash, % | 0.08 | 0.06 | 0.25 | 0.00 | 0.08 | 0.07 | 0.27 | 0.01 | 0.19 | 0.14 | 0.54 | 0.00 |
| Diastase activity, Gothe units | 13.77 | 5.60 | 34.30 | 4.90 | 8.84 | 4.70 | 21.00 | 3.90 | 16.53 | 10.70 | 39.30 | 5.50 |
| Color, mm Pfund | 40.33 | 23.90 | 80.00 | 7.70 | 23.26 | 14.74 | 45.00 | 5.00 | 67.73 | 25.60 | 114.00 | 29.00 |

SD: standard deviation; HMF: hydroxymethylfurfural; EC: electrical conductivity.

samples (Table 2). The diastase activity was between 3.90 and 39.28 units on the Gothe scale (Table 1), with a mean value of 13.77 for honey from the lower Chubut River valley, 8.84 for plains of Senguerr River and 16.53 for the Andean region.

With regard to color, honeys from the Chubut Province were from water white (5 mm Pfund) to amber (114 mm Pfund) with an average value of 43.72 mm Pfund (Table 1). The most frequent colors present in studied honeys, were white, extra light amber and light amber (Figure 2). Honey samples from the lower Chubut River valley varied from water white to light amber. Forty-four percent were white and 28% extra light amber (Figure 3). In the plains of Senguerr River 77% of the samples presented variations of white color (5-30 mm Pfund), most of them were white and extra white. Only one sample was water white, the rest of the samples were extra light amber. Honeys from the Andean region were predominantly amber extra light amber and light amber. Only two samples were white (Figure 3).

**Figure 2. Frequency of colors of *Apis mellifera* L. honey samples produced in Chubut province.**

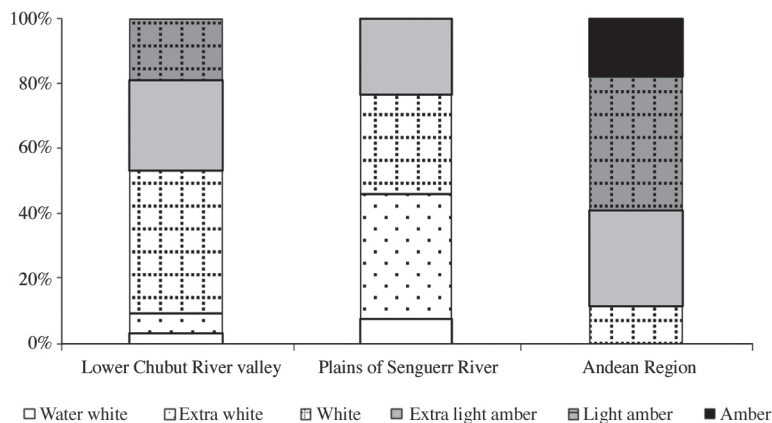


Figure 3. Color variation in *Apis mellifera* L. honey samples from three production areas of Chubut province.

DISCUSSION

The quality parameters evaluated in this study showed values in agreement with international requirements (Bogdanov *et al.*, 1999). The moisture content of honeys of different origins show varietal differences and it may range from 13% to 29% (Saxena *et al.*, 2010). The average moisture content of Chubut honeys was low (14.67%) and indicated a proper degree of maturity. According to the results obtained for free acidity, none of the samples analyzed exceeded the limit of 40 meq kg⁻¹ established by the international regulations (Bogdanov *et al.*, 1999), all samples were in accordance with the standards. The lowest acidity value was found in honeys from Andean region.

The mean acidity value observed for Chubut honeys (22.85 meq kg⁻¹) was higher than that obtained for honeys from Buenos Aires province (Valle *et al.*, 2001), but similar results were found by Baldi *et al.* (1993) and Naab *et al.* (2008) for honeys from Argentinean provinces Entre Ríos and La Pampa, respectively. Variation in free acidity among different honeys could be due to floral origin or variation in harvest season (El-Sherbiny and Riszsk, 1979; Pérez- Arquillué *et al.*, 1994).

Most of the analyzed honeys showed a pH values characteristic of floral honeys (< 4.5) (Piazza *et al.*, 1986). Samples from the plains of Senguerr River had the highest records. The values obtained for Chubut River valley were slightly lower than the results obtained for honeys from the other studied regions of Argentina (Baldi *et al.*, 1993; Naab *et al.*, 2008).

Almost all of the samples presented electrical conductivity values characteristic of nectar honey (≤ 0.8 mS cm⁻¹) (Bogdanov *et al.*, 1999) with the highest records obtained in honeys from Andean region. Only one sample presented an electrical conductivity value higher than 0.8

mS cm⁻¹. These results were consistent with data obtained in the microscopic analysis of honey from Chubut which had revealed scarce or absent honeydew indicators (Forcone, 2008).

The ash percentage found in honey expresses its richness in mineral content and constitutes a quality parameter (Marchini *et al.*, 2007), therefore it can be seen that honey from all the studied regions showed mean ashes percentages below the allowable maximum and thus conform to the international regulatory standards for quality honey (Bogdanov *et al.*, 1999).

The HMF values ranged from 0 to 14.7 mg kg⁻¹, showing a HMF level very much lower than 40 mg kg⁻¹, maximum value proved satisfactory in international trade (Bogdanov *et al.*, 1999). Several samples presented no detectable HMF, suggesting freshness and good practices by beekeepers (Bogdanov *et al.*, 1999; Marchini *et al.*, 2007). Also these low values could be attributed to the climatic conditions of Chubut province, unlike honeys from subtropical countries which have naturally high content of HMF due to the high temperatures (White Junior, 1978).

Diastase activity is a quality factor influenced by honey storage and heating. Although there is a large natural variation of this parameter in honey, a standard of a minimum value of 8 on the Gothe scale, has proven to be useful (Bogdanov *et al.*, 1999). From this point of view the analyzed samples were fresh with a mean value of 13.50 Gothe units. Thirty-eight percent of the samples from the region of Senguerr River presented diastase activity lower than 6 but greater than 3 Gothe units, with very low or no detectable values of HMF, so the honey samples were in line with international standards. Further studies could be necessary to determine whether the differences in diastase activity of these honeys were mainly due to the botanical origin.

Although honeys from Chubut were predominantly light, the color varied according to the melliferous areas. Plains of Senguerr River presented the lightest honeys. In this region predominated white tones, particularly extra white. These results agree with the data previously obtained in the palynological analysis of honeys of this area, 45% of them come from *Melilotus* spp. (Forcone, 2008), taxa that originates white honey (Baldi Coronel, 1998; Forcone *et al.*, 2009). Honeys from lower Chubut River were distributed among white and amber tones, with predominance of white and light amber. Samples from the Andean region were mostly in the range of amber. The heterogeneity of colors in this last area was consistent with the diversity of nectar sources reported (seven unifloral types of honey) (Forcone *et al.*, 2005; Forcone, 2008).

CONCLUSIONS

The analytical result indicated that honeys produced in Chubut come mainly from nectar and presented excellent quality properties according to international standards.

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RESUMEN

Determinación de parámetros químicos de calidad de las mieles de Chubut (Patagonia Argentina). Este estudio se realizó para evaluar los parámetros químicos de calidad de 62 muestras de mieles de *Apis mellifera* L., provenientes de la Provincia de Chubut. Las muestras de mieles se obtuvieron de las tres regiones melíferas de esta provincia: la Región Andina, el valle inferior del Río Chubut y la llanura del Río Senguerr. Los valores promedio obtenidos para conductividad eléctrica ($0,33 \text{ mS cm}^{-1}$) y pH (4,17) indican que las mieles fueron principalmente de néctar. Los valores de conductividad eléctrica fueron mayores en las mieles de la Región Andina que en las mieles de las otras regiones. La humedad (contenido de agua) fue baja, con un valor medio de 14,67%. El contenido de hidroximetilfurfural (HMF) fue muy bajo y varió entre 0,0 y $14,70 \text{ meq kg}^{-1}$. Los valores obtenidos para humedad, HMF y acidez libre indican una buena maduración de las mieles y ausencia de fermentación indeseada en todas las muestras. La actividad diastásica presentó un valor medio de 3.50 unidades en la escala Gothe. Se registraron variaciones de color entre las muestras de las diferentes áreas, con valores medios obtenidos para las muestras de la región Andina, el valle inferior del Río Chubut y la llanura del Río Senguerr, de

67,49; 40,33 y 23,26 mm Pfund, respectivamente. Los resultados obtenidos en este estudio, indican que las mieles producidas en Chubut presentan propiedades de excelente calidad según las normas internacionales.

Palabras clave: caracterización de mieles, mieles argentinas, mieles patagónicas, parámetros de calidad.

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