PHYSICAL-CHEMICAL CHARACTERISTICS OF HONEY ON BRAZIL

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ABSTRACT

The physicochemical characteristics of honey depend on many factors such as bee species, climatic aspects, physiological state of the hive and the vegetable species that serve the necessary nectar and pollen. The description of the physicochemical aspects of honey in Brazil becomes relevant to define the quality of Brazilian products, as well as regional aspects and species of bees influence the physical and chemical composition of honey. The objective of this paper is to describe the physicochemical quality of Brazilian honey, relating to the species of bees and the regional production and to highlight the importance of these elements to determine the quality of honey. In order to provide the standard research on the physicochemical characterization of honey, the following keywords have been set: honey and physicochemical quality. The physic-chemical characteristics are defined by the normative instruction MAPA No. 11/2000 and by the values, there were determined averages, standard deviation and analysis of the main components of honey from different Brazilian states and honey from different species of bees. Stingless bees produce honey with distinguished physical-chemical quality, depending on the species. The *Apis mellifera* honey has good physicochemical conditions, and most of the honey analyzed in the country has data within the standards established by law. The lack of characterization of honey from native bees leaves a gap on the Brazilian legislation when determining the limits of physical and chemical qualities of honey produced by beekeeping.

KEYWORDS: stingless bees, beekeeping, edaphoclimatic conditions, meliponiculture.

RESUMO

As características físico-químicas dos méis dependem de muitos fatores como espécies de abelha, aspectos climáticos, estado fisiológico da colmeia e espécies de vegetais que lhe servem o néctar e pólen. A caracterização dos aspectos físico-químicos do mel no Brasil torna se relevante para definir a qualidade do produto brasileiro, além de como os aspectos regionais e espécies de abelhas influenciam na composição físico-química do mel. Assim, o objetivo deste trabalho é a caracterização físico-química dos méis brasileiros, relacionando com as espécies de abelhas e a região de produção e destaque da importância destas características para a qualidade do mel. Para a busca padronizada sobre a caracterização físico-química nos méis, foram definidas as seguintes palavras-chave: mel e

caracterização físico-química. As características físico-químicas são definidas pela Instrução Normativa MAPA n° 11/2000 e com as caract erísticas dos méis foram realizadas médias, desvio padrão e análises dos componentes principais entre méis de diferentes estados brasileiros e méis de diferentes espécies de abelhas. As abelhas sem ferrão produzem méis com características físico-químicas particulares, dependendo da espécie. Os méis brasileiros de *Apis mellifera* apresentam boas condições físico-químicas, sendo que a maioria dos méis analisados no país apresentam valores dentro dos padrões estabelecidos pela legislação. A falta de caracterização dos méis de abelhas nativas deixa vago na legislação brasileira quanto aos limites das características físico-químicas dos méis produzidos pela meliponicultura.
PALAVRAS-CHAVE: abelhas sem ferrão, apicultura, condições edafoclimáticas meliponicultura.

CARACTERIZAÇÃO FISICO-QUÍMICA DOS MÉIS NO BRASIL

INTRODUCTION

Honey is defined as viscous and sugary liquid product, considered food, produced by bees (which may be *Apis mellifera* and other species of genus *Melipona*, *Friesomellita* and *Trigona*) (FREUND, 1998; SOUZA et al., 2012). Honeys are produced from the nectar and pollen of flowers collected and processed by your digestive enzymes or from secretions of living parts of plants. The physicochemical characteristic of honey depends on many factors such as bee species, climatic aspects, physiological state of the hive and plant species that serve as nectar and pollen. The bees collect, transform, combine with their own specific substances, store and leave to mature in honeycombs (BRASIL, 2000; ANACLETO et al., 2009; WITTER & NUNES-SILVA, 2014).

Honey is formed mostly of hydrocarbons (75%) as sugars, maltose, sucrose, glucose and fructose; water (20%); minerals such as copper, magnesium, calcium, phosphorus, potassium, among others. Half of the existing amino acids consists of organic acids such as acetic acid and citric acid, as well as B vitamins, vitamin C, D, and E; there is still a considerable amount of antioxidants (phenolic and flavonoids) (BARTH et al., 2005; GOIS et al., 2013).

In Brazil, the productive chain of beekeepers is formed by more than 300 thousand beekeepers, processing well over 100.000 of honey units and employing about five hundred thousand people. In 2004 beekeeping was responsible for producing 32.000 tonnes of honey and 1.600 tonnes of beeswax, becoming prominent with US$42 million of exports. In the same year the world honey production reached 1.3 million tonnes, confirming the steady growth of 1.9% per year over the past decade (BRASIL, 2007). According BÖHLKE & PALMEIRA (2006) Brazil is the eleventh of the world's largest producer of honey.

The characteristic honey indicators are still largely unknown, especially in tropical regions, due to the high temperature and humidity rates, which are also the highly diversified bee flora (ABADIO-FINCO et al., 2010; MOURA et al., 2014). In addition to the high diversity of bee flora in Brazil, which made it necessary to standardize the creations of bees and then increase the quality of honey. So the environmental, phytophysiognomic and edaphic factors becomes relevant to characteristics of honeys (OLIVEIRA & SANTOS, 2011; VIT et al., 2013).

Bee products in Brazil are required to obtain registration with the Ministry of Agriculture, Livestock and Supply (MAPA) and also submit this information on the

label. This means that the quality standards were supervised by the Federal Inspection Service (SIF) (PREZOTTO, 2013). The characterization of the physicochemical aspects of honey in Brazil becomes relevant to define the quality of Brazilian products, as well as regional aspects and species of bees influence the physical and chemical composition of honey. Different species of honey bees naturally produce differentiated, along with environmental factors such as precipitation, temperature, flowering in the environment among others (CAMPOS et al., 2003; VIT et al., 2013). The aim of this work is the physicochemical characterization of Brazilian honey, relating to the species of bees and the production region and highlights the importance of these features to the quality of honey.

MATERIAL AND METHODS

Standard search

For the standardized search on the physicochemical characterization in honeys, the following keywords have been defined: Honey (honey) and physicochemical characterization. The keywords were searched in Google Scholar (www.googlescholar.com). Articles found were checked the results of physicochemical characteristics of honey, which were noted in a spreadsheet (adapted de NABOUT et al., 2010).

Characteristcs of honeys

The relevant physicochemical characteristics are: moisture (%), acidity (milliequivalent), pH, ash (%), reducing sugars (%), insoluble sugars (%) Hydroxymethylfurfural (HMF - mg / kg), diastase or amilica activity. The relevant characteristics were defined based on the criteria established by the Normative Instruction of the Ministry of Agriculture, Livestock and Supply (MAPA) nº 11/2000 (BRASIL, 2000). Besides these features established by normative instruction, when studies showed the values evaluated for apparent sucrose and hydrogenic potential (pH), were considered for analysis.

TABLE 01. Characteristics of honeys with limit values for *Apis mellifera* established by the Instruction of the Ministry of Agriculture, Livestock and Supply (MAPA) n°11/2000.

Characteristic	Limit
Moisture	≤ 20%
Acidity	≤ 40 milequivalentes
Ashes	≤ 0,6%
Reducing sugars glucose	≥72%
Insoluble sugars	≤1%
Hydroxymethylfurfural (HMF)	≤ 40 mg/kg
Diastase or amilica activity (amylase)	≥8 (3 if HMF ≥15 mg/kg)

Statistical analysis

For definition of each variable values for each Brazilian state (for the honeys from *Apis mellifera*) and comparison of honeys of each bee species were carried out means and standard deviations. For analysis of the variables of different Brazilian regions and different species of bees combined was performed principal components analysis (PCA) at a significance level of 95% (GONZALEZ-MIRET et al., 2005).

RESULTS AND DISCUSSION

Honeys of different species of bees

The honeys of *Apis mellifera* present the least moisture from the honey (values below 17.88%) of all other species of bees (Table 02). This moisture

characteristic reflects both the intrinsic characteristics of the honey of this species, as different management practices and the creation of bees with stinger and stingless bees (meliponiculture) (DE CARVALHO, 2005; DE CARVALHO, 2009; SOUSA et al., 2013). These average values for the country are below the limit set by law. As for species of stingless bees, all moisture values have been on average above 20% established. RIBEIRO et al., (2012) analyzed 14 samples of honey bee species *Melipona fasciculata* and founded values between 21.44 to 27.51%. The high rates found in these honeys are due to the low nectar dehydration rate during the honey transformation process (RIBEIRO et al., 2012). This reinforces the necessity to create private parameters of the legislation to these groups of bees, once naturally the honeys are higher than the established. (DE CARVALHO, 2005; OLIVEIRA & SANTOS, 2011).

Among the characteristics that may reveal contamination of honey, are a hydroxymethylfurfural, the percentage of ash and the amount of insoluble solids (Figure 01). For these characteristics, the bees showed honeys with higher values are *Apis mellifera*, *Scatotrigona bipunctata*, *S. depilis* and *Tetragonisca anguscula*. This higher standard of contaminants indicators in honey, not necessarily evidence of higher contamination of honey species. The characteristic of honey may reflect the general behavior collection of food resources that these species are, for example, visitors from these bees are many food sources and can also collect non-floral sources resources (DA LUZ et al., 2007; FERREIRA et al., 2010; OLIVEIRA-ABREU et al., 2014).

In relation to the acidity, the *A. mellifera*, *Melipona mandacaia*, *S. bipuncatata* and *S. depilis* honey's are the most acids, with this feature reflecting in lower values of pH. Already *M. scutellaris* and *Tetragonisca anguscula* honey's are the most basic honeys, with values higher than the established in the legislation. The insoluble solids and the hydroxymethylfurfural are related to the total acidity of the honeys, may indicate higher waste honeys have, the higher total acidity (SILVA et al., 2004; STRAMM, 2011).

The *Melipona fasciculata*, *M. scutellaris* and *Scaptotrigona bipunctada* honey's showed, among the species of meliponiculture, the most similar to *Apis mellifera* honey's. Even so, there are various differences between the characteristics of natural honeys; each species has a honey with particularity which makes the individual characterization of honey by species relevant to the establishment of new parameters specific for these groups of bees (WITTER & NUNES-SILVA, 2014).

Apis mellifera honey from different regions of Brazil

The main honey components are water together with sugar represent 80% of monosaccharides, fructose and glucose, with 10% of the disaccharides including maltose and sucrose, with these different types of sugars end causing physical changes in viscosity, crystallization, density and other physical aspects of honey (MOREIRA & MARIA, 2001). In Ceará State was obtained value of 78.16% in the analyzes in reducing sugars (Table 03) already in São Paulo State was found the value of 72.83% in honey with propolis, getting then to 67.90% São Paulo with analysis of honeys without propolis, the states of Maranhão, Mato Grosso do Sul, Paraná and Rio Grande do Sul had variation between 66.58 to 67.58% not being in agreement with Brazilian law. Already SODRÉ (2005) obtained a maximum of 88.38% of recuding sugars, and these values are outside the standards specified by legislation, may indicate mature honey or adulteration.

TABLE 02. Physical-chemical characterization of honeys by species of bees in Brazil (moisture - %, apparent sucrose -%; hydroxymethilfurfurol - HMF - mg/g; ashes -%, total acidity - mill equivalent; insoluble solids in water -%; diastase activity and pH - scale; reducing sugars -% N – number of sample studies).

Especie	N	Moisture	Apparent sucrose	HMF	Ashes	Total acidity	Insoluble Solid in water	Diastase activity	pH	Reducing sugars
Apis mellifera	121	17.88 ± 2.98	1.52 ± 2.30	52.47 ± 79.33	0.41 ±0.50	32.71 ± 13.68	0.23 ± 035	7.18 ± 2.59	3.80 ± 0.47	68.84 ± 5.52
Melipona fasciulata	14	23.79 ± 1.89	2.65 ±1.29	27.38 ±19.31	0.204 ±0.15	31.88 ±7.10	0.02±0.02	1.43 ±0.77	3.58±0.45	60.68 ± 42.1
Melipona mandacaia	1	28.78	-	5.79	-	43.48	-	-	3.27	74.82
Melipona scutellaris	1	25.26	-	18.92	0.17	28.33	0.01	-	4.66	-
Scaptotrigona bipunctata	1	24.71	4.65	4.85	0.83	38.57	0.27	-	3.97	60.01
Scaptotrigona depilis	3	25	-	27.75±4.35	0.18±0.04	98.43 ± 5.51	1.96 ±0.22	-	3.36 ±0.05	65.3 ±5.96
Tetragonisca anguscula	1	25	0	55.63	0.36	69.06	2.86	-	4.2	53

- - There is no result because the authors did not perform the analysis.

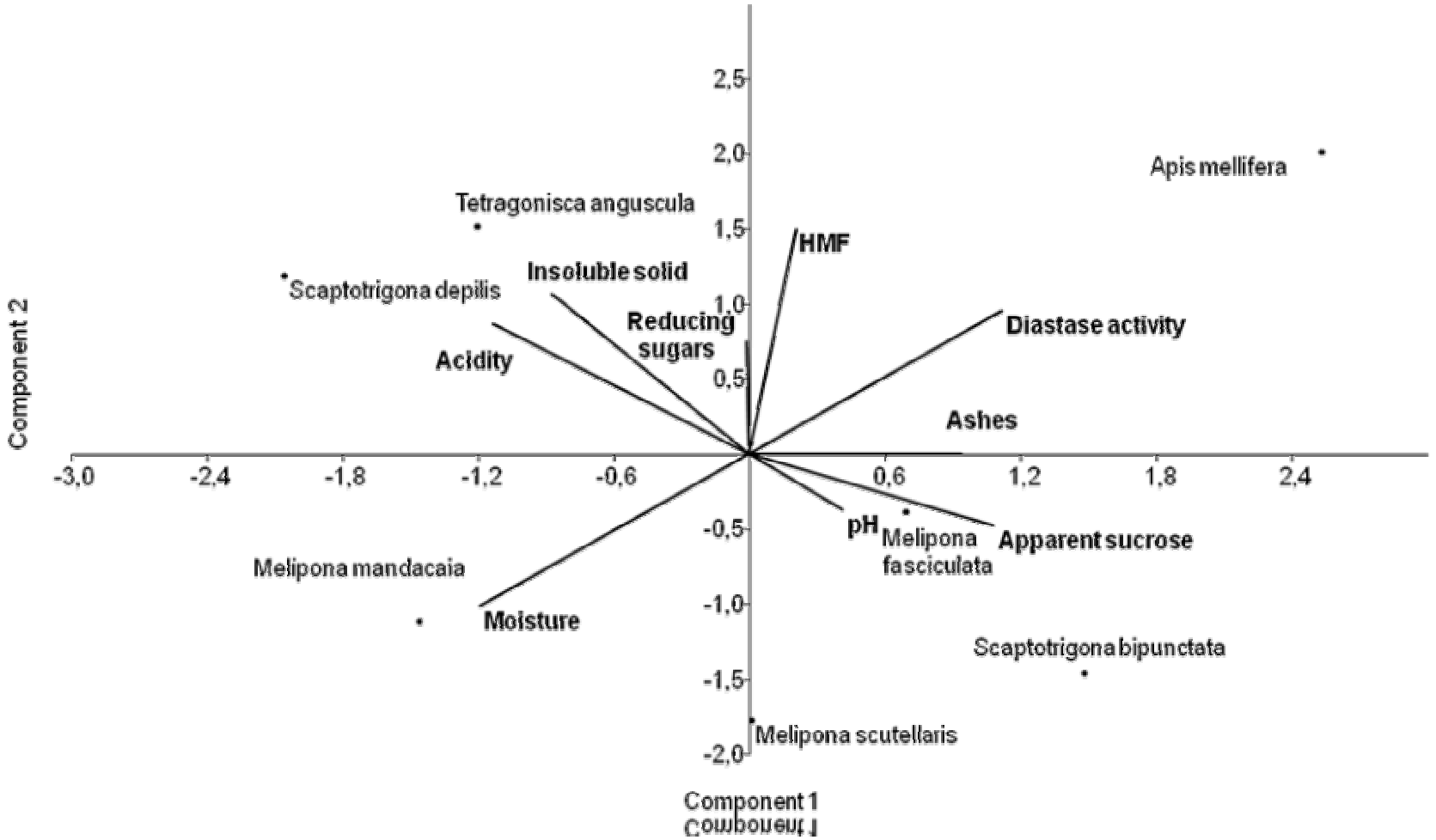

FIGURE 01. Principal component analysis (PCA) of honeys of different species of bees (moisture - 35.83%; apparent sucrose - 27.65%; hydroxymethilfurfurol - 18.14%; ashes -12.75%; total acidity - 3.79% and 1.83% insoluble solids in water).

TABLE 03. Physical and chemical characterization of honeys from *Apis mellifera* in different Brazilian states (moisture -%, apparent sucrose -%; hydroxymethilfurfurol - mg/g; Ashes -%, total acidity - milliequivalent; insoluble solids in water -%; diastase activity and pH - scale; reducing sugars -%; N – number of sample studies).

Locality	N	Moisture	Apparent sucrose	HMF	Ashes	Total acidity	Insoluble Solid in water	Diastase activity	pH	Reducing sugars
Ceará	32	18.65±1.59	1.13±2.62	85.61±108.15	0.59±0.87	38.34±13.56	0.40±0.43	7.18±2.59	3.44±0.28	78.16±2.44
Maranhão	7	9.42±4.26	-	66.9	0.14±0.04	48.05±14.21	-	-	3.74±0.12	67.58±2.26
Mato Grosso do Sul	16	18.34±2.01	-	-	0.12±0.04	32.69±19.87	-	-	-	65.15±4.40
Minas Gerais	17	19.91±0.57	-	-	0.21±0.11	27.01±9.56	0.05±0.07	-	3.92±0.42	-
Paraíba	2	18.41±0.49	-	22.3±2.26	0.18±0.02	38.33±4.7	0.01±0	-	4.23±0.53	-
Paraná	2	13.15±6.29	-	-	-	-	-	-	4.05±0.77	60
Rio Grande do Sul	19	18.45±1.53	0.82±0.58	21.21±16.37	0.45±0.23	28.76±7.9	-	-	-	66.58±3.57
São Paulo (mel com própolis)	11	18.85±1.07	3.10±2.65	39.43±20.22	-	-	-	-	-	72.83±2.99
São Paulo	10	17.39±1.24	1.74±1.00	12.46±14.18	0.50±0.33	29.64±10.91	0.73		4.33±0.46	67.90±3.49
Tocantins	5	14.84±0.49	-	-	1.25±0.17	28.3±5.79	-	-	3.57±0.1	-
Média		18.84	1.76	46.36	0.38	34.73	0.31	7.18	3.76	67.29

- - There is no result because the authors did not perform the analysis.

Among the physicochemical aspects of Brazilian honeys, moisture proved quite variable among states in the country. Moisture is a relevant variable in physical and chemical analysis, it presents strong relationship the amount of water present in the honey. The water content in honey may influence the viscosity, specific weight, maturity, crystallization, flavor and conservation, honeycomb, or improper storage after extraction (MELO et al., 2003; MARCHINI et al., 2004; MENDES et al., 2009).

The average moisture was found to be 18.84% which is considered within the established by Brazilian law. The Maranhão State had the lowest average moisture of honey with 9.42%, already Minas Gerais presented honeys with higher moisture values of 19.91% and these values higher than those found for honey with propolis in the São Paulo State. Usually propolis mixing honey increases the proportion of water, thus making honey with higher moisture (BERA et al., 2007; PIRES, 2011).

The apparent sucrose found in Brazil was 1.76g per 100g of honey. According to the legislation sucrose should contain no more than 6g/100g of honey (representing 6%). The high levels of sucrose may indicate an apparent premature collecting honey because honey present in the sucrose tends to be converted into fructose and glucose by the action of the enzyme invertase, but this reaction requires a specific time, this called Honey maturation (AZEREDO et al., 1999; MENDES et al., 2009). In the Sao Paulo State the highest value of apparent sucrose was 1.74%this value is below honey with propolis with a value of 3.10%. The lowest value found for apparent sucrose was 0.82% in Rio Grande do Sul.

Already for hydroxymethilfurfurol (HMF) the average for the country was 46.36 mg/g, below 60 mg/g defined by law. The Ceará State presented the highest value with 85.61 mg/g, followed by the State of Paraiba, Rio Grande do Sul. Already in the State of Paulo honey with propolis, showed the highest amount of HMF in relation to honey without propolis. It is considered that the HMF is used as a quality indicator, as has origin in the degradation enzymes present in mature honeys (SILVA et al., 2004). However, honeys with high fructose rates can form high hydroxymethilfurfurol rates for storage processes. Since newly collected honey having small amounts of HMF. So these values can indicate significant changes caused by prolonged storage at ambient temperature or overheating (VILHENA & ALMEIDA-MURADIAN, 1999; MELO et al., 2003).

Irregularities are found in honey determined by the method of ashes, as example not decantation, filtration and lack of hygiene in the final process of withdrawal of the honey, the beekeeper (EVANGELISTA-RODRIGUES et al., 2005). For the ashes were found on average 0.38%. Tocantins State samples originated from only gave values of 1.25% ash, thus being above the maximum allowed by Brazilian law. Samples of other states were within the established standards.

The variation of organic acids originates the acidity of the honey, caused by different sources of nectar, by the action of the enzyme glucose - oxidase on glucose yields gluconic acid, also observed by bacteria during maturation and minerals present in honey (MORAES et al., 2014). High acidity rates were found in Maranhão state with a value of 48.05 milleq/kg, being in the Ceara State obtaining a value of 38.34 milleq/kg being behind states: Paraíba, Mato Grosso do Sul, São Paulo, Rio Grande do Sul and Tocantins. In Minas Gerais it was observed the minimum value of 27.01 milleq/kg of acidity, considering that 50 milleq/kg is the maximum allowed by law.

The quality control of Brazilian honeys today is not mandatory potential analyzes the hydrogenionic (pH), but it would be very useful to define the quality of honey, because these values can be influenced by soil pH and nectar or plant

associations for the honey composition. Even the pH indicating the acidity of the honey, and the already existing total acidity parameter for honeys, the pH is an important parameter because it influences the rate of formation of HMF is a strong indicator of quality (SILVA et al., 2008). According to Souza et al. (2006) no reference values required by legislation for pH, however ideal for honey should be at least 3.5 and at most 4.6. Thus the values found for the honeys only for the Ceará State showed average values just below the limit suggested by Souza et al. (2006).

Already the insoluble solids analysis shows the impurities that exist in honey, a very important method for the safe and effective marketing honey, it will be checked if there are parts of bees and waste wax and other bee products (SILVA et al., 2006). Even with great variations among Brazilian states such as Paraíba with 0.01% and 0.73% in São Paulo, no studies showed results with average values above the standard set by legislation.

Different concentrations of insoluble solids in honey may be strongly related to the environment in the surroundings of the apiaries in addition to the processing methods of honey for consumption. Apiaries near urban environments, sources of contamination or inappropriate places has a higher concentration of insoluble solids and contaminants as well as honey with inferior quality (WOFF et al., 2006; LOPES et al., 2011; PÉRICO et al., 2011), the same way as to honey post harvest handling may contribute to the increased amount of insoluble solids (CAMARGO et al., 2003; PAULINO & MARCUCCI, 2009).

As the honey is a product non-toxic and can be consumed without restriction, one should take some care when purchasing that product for consumption, valuing the knowledge of the source with quality control and inspection by competent bodies (PÉRICO et al., 2011). Brazil presents diversity of soil and climatic conditions that can affect the production of honey differently (CAMPOS et al., 2003; ABADIO et al., 2010; SOUSA et al., 2013). As well as each region has similarities and differences in conditions, bees creations are also affected by this, generating honeys with different characteristics and qualities (DE CARVALHO, 2005). Is worth emphasizing that these differences can be harnessed to produce honeys qualities and values, but also pay attention to the difficulties of standardization of the Brazilian product.

It is essential for producers of Brazilian honey to carry out an adequate management of apiaries and meliponicultures seeking qualified technical assistance to assist in the activities, besides searching improvements in harvesting and processing of honey (FREITAS et al., 2004; DE CARVALHO, 2005). These actions aim at improving the characteristics of honeys using the full diversity of honeys that the country has (different regions with honey of *Apis mellifera* and different species of stingless bees) and thus produce honeys with better quality. Many future studies (sanity, bee management, artificial feeding, harvesting techniques, post-harvest techniques and honey storage) are needed for beekeeping in different weather conditions in Brazil, and stingless species, encouraging production in meliponiculture.

CONCLUSIONS

Brazilian honeys have good physicochemical conditions, and most of the analyzed honeys in the country have values within the standards established by law. The lack of study for species of stingless bees, and characterization of these honeys, left vacant by Brazilian law as to the limits of physical and chemical characteristics of honeys produced by meliponiculture.

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