

Hydroxymethylfurfural in honey: a public health problem

Hidroximetilfurfural no mel: Um problema de saúde pública

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Abstract

Honey is a sweet and natural product of high nutritional value, produced by honey bees (*Apis mellifera*) composed mainly of water and carbohydrates, nitrogen compounds, enzymes, organic acids, amino acids, phenolic compounds, flavonoids, vitamins, minerals and other phytochemical substances. For cultural reasons, it is widely used for therapeutic purposes for various. However, despite this factor, it is the most fraudulent food in Brazil. On the other hand, it is also marketed in many places without any control, with the appeal of "natural product". Due to its composition can form a compound called 5-hydroxymethylfurfural or HMF (a furanic ring with functional groups of aldehyde and alcohol), classified as an organic molecule produced from the degradation of sugar after the Maillard reaction that has harmful effects on consumer's healthy. The main objective of this study was to monitor the quality of honey, a product consumed broadly and increasingly by the population as food and/or medicine. We analyzed 34 honey samples without labeling and/or any type of inspection (US - unregistered samples) obtained in commercial establishments and from

unlegalized vendors in the region between the cities of Itatiaia, Resende, Penedo and Visconde de Mauá, all in the Rio de Janeiro State; and 20 samples that had label and identification (RS - registered samples). Aiming to compare the two groups, relevant analyses were performed: pH, Lugol test, Lund test, color and especially 5-HMF. It was concluded that low-cost physicochemical analyses can be used to ensure a fraud-free and quality product that there is no presence of HMF at high concentrations.

Keywords: Fraud. HMF. Physicist-chemical. Quality.

Resumo

O mel é um produto doce e natural, de alto valor nutricional, produzido por abelhas melíferas (*Apis mellifera*) composto principalmente por água e carboidratos, compostos nitrogenados, enzimas, ácidos orgânicos, aminoácidos, compostos fenólicos, flavonoides, vitaminas, minerais e outras substâncias fitoquímicas. Por razões de cunho cultural, é muito utilizado com fins terapêuticos para diversas finalidades. Entretanto, a despeito desse fator, constitui o alimento mais fraudado no Brasil. Por outro lado, também é comercializado em muitos locais sem nenhum controle, com apelo de “produto natural”. Em função de sua composição, pode formar um composto denominado 5-hidroxi-metilfurfural ou HMF (um anel furânico com grupos funcionais de aldeído e álcool), classificado como uma molécula orgânica produzida a partir da degradação do açúcar após a reação de Maillard que possui efeitos prejudiciais à saúde dos consumidores. O principal objetivo deste estudo foi monitorar a qualidade do mel, um produto consumido de forma ampla e crescente pela população como alimento e/ou medicamento. Foram analisadas 34 amostras de mel sem rotulagem e/ou nenhum tipo de fiscalização (ANR – amostras não registradas) obtidas em estabelecimentos comerciais e de vendedores não legalizados na região entre as cidades de Itatiaia, Resende, Penedo e Visconde de Mauá, todas no Estado do Rio de Janeiro; e 20 amostras que apresentavam rótulo e identificação (AR – amostras registradas), obtidas na cidade de Nova Friburgo, também estado do Rio de Janeiro. Objetivando comparar os dois grupos realizaram-se análises pertinentes como: pH, prova de Lugol, prova de Lund, cor e principalmente o HMF. Concluiu-se que análises físico-químicas de baixo custo podem ser utilizadas para garantir um produto livre de fraude e com qualidade e que não haja presença de HMF em concentrações elevadas.

Palavras-chave: Físico-químico. Fraude. HMF. Qualidade.

1. Introduction

Honey is a sweet and natural product of high nutritional value, produced by honey bees (*Apis mellifera*), from the nectar collected from flowers, secretions of living parts of plants, transformed and combined with specific substances specific to them. It is composed mainly of water and carbohydrates, besides containing nitrogen compounds, enzymes, organic acids, amino acids, phenolic compounds, flavonoids, vitamins, minerals and other phytochemical substances. Composition may vary due to various factors such as botanical and entomological origin, geographic and seasonal conditions. Technological processing, storage conditions and storage time affect the composition and may compromise the quality and food safety of honey due to the presence of Hydroxymethylfurfural - HMF (Shapla et al., 2018).

The HMF, also called 5-hydroxymethylfurfural (a furanic ring with functional groups of aldehyde and alcohol), is an organic compound produced from the degradation of sugar after the Maillard reaction. In honey, the presence of simple sugars such as glucose and fructose, acids such as gluconic acid, water and minerals contribute to the formation of this compound. The increase in HMF can occur due to aging of honey, inadequate storage or inadequate processing, when the binomial time x temperature is not complied with as provided by the legislation (Brazil, 1985). Every extra 10 °C applied to honey, the formation of HMF increases by 4 to 5 times, making this parameter a heating indicator and, when this occurs, the honey moisture will be low and the HMF high (Crane, 1987). In prolonged storage with exposure to sunlight or high temperatures, the increase in HMF occurs due to the degradation of monosaccharides in acidic medium and, in this case, the moisture of honey with high concentrations of HMF will be high, since for every one

molecule of HMF will have two water molecules. High concentrations of HMF may also indicate fraud by adulteration of the product with invert sugar syrup, which can be evaluated with physicochemical analyses of sugars, since these syrups are rich in sucrose, of which the limit is 6% (Food Safety Brazil, 2015).

Brazilian legislation establishes a maximum limit of HMF in honey of 60 mg.kg^{-1} (Brazil, 2000). The *Codex Alimentarius* and the European Union have established for honey a maximum limit of HMF of 40 mg.kg^{-1} , and for honeys from tropical countries and for honeys with low enzyme levels, the maximum limits set respectively are 80 mg.kg^{-1} and 15 mg.kg^{-1} (Codex standard for honey, 1981). The consumption of products with high levels of HMF exposes the population to the risk of toxicity to the organism, with cytotoxic, organotoxic, genotoxic and mutagenic effects (Spano et al., 2009).

The main objective of this study was to monitor the quality of honey, a product consumed broadly and increasingly by the population as food and/or medicine, because by quantitatively analyzing the HMF in line with the analyses established by the Technical Regulation of Quality and Honey Identity (HONEY RTQI), it becomes feasible to diagnose the traceability and quality of this animal product.

2. Methodology

We analyzed 34 honey samples without labeling and/or any type of inspection (US - unregistered samples) obtained in commercial establishments and from unlegalized vendors in the region between the cities of Itatiaia, Resende, Penedo and Visconde de Mauá, all in the Rio de Janeiro State; and 20 samples that presented label and identification (RS - registered samples), obtained in honey houses, in Nova Friburgo city, Rio de Janeiro, totaling 54 samples. It is noteworthy that the samples were collected in their original packaging and transported in boxes protected from sunlight and humidity, at room temperature.

To evaluate possible storage, aging and high temperature failures, the production of HMF was evaluated in all samples obtained after 6 months of storage at room temperature. In order to evaluate possible fraud by adding commercial glucose, the Lugol test and Lund test were performed. The pH and water activity (a_w) of the samples were also evaluated. Visual color observation was performed to infer about a possible correlation with the presence of HMF in the samples, since the darkening rates may vary depending on the composition of the honey and may also be directly and/or indirectly related to the production of this molecule.

The identification of proteins made through Lund's reaction is based on the reaction of the tannic acid that precipitates albuminoid substances (proteins such as proline and hydroxyproline) that are present in this matrix. Thus, in the presence of fraud by the addition of commercial glucose, precipitation is minimal. While lugol's evidence proves the presence of fraud, since the Lugol reacts with the starch present in the sample analyzed. In the pH test, considering that honey is a product of animal origin classified as acidic, the values can vary between 3.5 and 5.5 by the presence of organic acids. Finally, the water activity (a_w) also corresponds to an important analysis to be performed on honey to ensure the sanitary hygienic quality of this product.

3. Results and Discussion

From the samples obtained, the most expressive results stand out according to each analysis performed, being pH, Lugol test, Lund test, color and especially HMF. The pH values, which may indicate the formation of gluconic acid in honey, ranged from 3.72 to 4.3 ($\Delta=0.58$). Regarding the Lugol test, for unregistered samples (US), we obtained a positive result in 4 of the 34 samples analyzed, which corresponds to 11.77% of fraud. In the registered samples (RS), none of them showed a positive result.

3.1 Lund's Test

The results obtained in Lund's test that indirectly allows the evaluating of fraud by adding commercial glucose, found precipitate in all registered samples, being in accordance with the results

obtained in the Lugol test. It is noteworthy that some samples presented a higher amount of albuminoids than others, however, all presented a significant amount. For samples without inspection record, the result corroborates those obtained in the Lugol test for the 4 positive samples, where precipitate was observed below 0.3 mL, which allows us to affirm that the Lugol test, easy to apply, speed and low cost, is effective for evaluating fraud.

3.2 Colorimeter

Regarding honey color, the 20 samples recorded presented amber coloration. Regarding the unregistered samples, different results were observed: 23 samples classified as amber (~ 69.7%); 5 samples as caramel (~ 15.15%); 2 samples as dark amber (~ 6.06%) and 1 sample classified as dark caramel (~3.03%). A finding of relevance was the fact that 100% of the samples classified as caramel and dark amber coincided with samples with high HMF content.

3.3 Hidroximetilfurfural

For the HMF, in the unregistered samples stored for 6 months, the results obtained were: 19 ND samples (not detectable), equivalent to (~55.88%); 7 samples with values ~20 mg.kg⁻¹ (~20.58%); 4 samples ~10 mg.kg⁻¹ (~8.82%); 3 samples ~30 mg.kg⁻¹ (~8.82%) and 1 sample ~50 mg.kg⁻¹ (~2.94%). Regarding registered samples, 22 were classified as ND (~91.66%) and two presented results like 10 mg.kg⁻¹ (~8.33%).

Interestingly, the samples acquired in Nova Friburgo (n=14), which are registered samples, showed positive results, with values ~70 mg.kg⁻¹, indicating greater deterioration of the product. It is also worth mentioning that the Bianchi color table was used as a parameter, which has a colorimetric classification graded into five categories, being: 0 - 10 mg.kg⁻¹; 11-20 mg.kg⁻¹; 21-40 mg.kg⁻¹; More than 40 mg.kg⁻¹; More than 70 mg.kg⁻¹.

4. Conclusion

From the results obtained, it was possible to conclude that low-cost physicochemical analyses can be used to ensure a product free of fraud and quality; there is a direct relationship between product staining and presence of 5-HMF; samples are not always free from problems arising from loss of quality. And as honey is considered one of the most defrauded foods in the country and in the world, it can be speculated that with minimal efforts cases of fraud and illegal trade of this product can be controlled.

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