EFFECT OF THE TEMPORARY THERMIC TREATMENT OF HONEY ON VARIATION OF THE QUALITY OF THE SAME DURING STORAGE

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Abstract

Bee honey is one of the main export produces of the Yucatan Peninsula. Nevertheless, its international trade becomes more and more difficult, because of the competition of other countries. Heating of honey could accelerate certain chemical reactions that lessen its quality during storage. The purpose of this study consists in assessing the effect of temporary heating the honey on the variation of its main quality characteristics during storage. For the study, Tahonal honey was used (Viguiera dentata var. helianthoides), as well as Dzidzilché honey (Gymnopodium antigonoides, Blake). Samples of each honey were heated at 55°C during 3, 6, 9, and 15 minutes, after which they were left to cool at the room temperature (26±2°C); they were stored at that temperature and, during three months and a half, there were taken samples in order to be assessed. The changes in the diastase activity were observed, as well as in color, total acidity, and the HMF. The temporary thermic treatment to which the samples were submitted exerted no significant influence on the examined quality characteristics, except the diastase activity in the Dzidzilché honey, which has diminished. During the storage, the average monthly growth of HMF was higher in the Tahonal honey than the Dzidzilché honey, without the initial heating to influence the variation. The temporary heating during 9 and 15 minutes, respectively, has significantly influenced only the growing of the acidity during the storage of the Tahonal honey. Also, the Tahonal honey grew darker in color more rapidly than the Dzidzilché honey, without heating to influence this difference.

Generally, there was concluded the initial thermic treatment has influenced changing certain quality parameters, and the behavior of both sorts of honey during storage was different, probably owing to their different composition.

Key words: *bee honey / heating / quality / storage / Tahonal / Dzidzilché / HMF / dynamics*

Introduction

Bee honey is a nourishment that is consumed since the most remote times. It is a complex mixture, mainly composed of water, sugars (glucose, fructose, saccharose, maltose, higher sugars), gluconic acid, lactone, nitrogenous compounds, minerals, and some vitamins.

It is a natural product, that presents high variations in composition and characteristics, mainly due to its geographical and botanical origin (MATEU, 1993), its main features depending on the floral origin of the nectar foraged by bees. In this way, the different sorts of honey are defined according to their main organolep-tic characteristics, such as color, flavor, taste, to their consistency, and the higher or lesser facility of crystallizing during their manipulation and storage. Also, the different sorts of honey more or less differ, as concerns their chemical composition, mainly the pH, the acidity, the content and the proportion of carbon hydrates, organic acids, minerals, and nitrogenous compounds.

The main quality factors that are used in the honey international trade are, besides its sensorial characteristics (that is, flavor, color and taste), humidity, HMF content, and the diastase index as well, the latter two being strongly influenced by heating and storage duration of this produce (ANÓNIMO, 1984). The one that had the bigger importance during recent years in the international trade was the HMF content.

HMF is a cyclic aldehyde (C6H6O3), which is produced by degradation of sugars, mainly starting from dehydration of fructose and glucose in an acid medium, especially when temperature is raising (BADUI,1986; ESPINOZA-MANSILLA et al., 1993). There was found thermogeneration of HMF in honey pursues a first degree dynamics (JUÁREZ-SALOMO and VALLE-VEGA), and it seems its formation is self-catalytic (GHLOSHDASTIDAR, CHAKRABARTI, 1992).

Sometimes, during its manipulating and packaging, honey is submitted to a temporary controlled heating in heat exchangers, with different purposes, such as diminishing the viscosity, dissolving the large crystallized particles, or destroying the yeasts (DETROY, 1979; SKOWRONEK et al., 1994; CRANE, 1985). However, this kind of heating, as well as the raising of its temperature due to its bad manipulation during transport and storage, could produce small raisings of the HMF content (SINGH et al., 1948; WHITE, 1980).

Different studies were achieved, regarding HMF formation during storage of bee honey, and modifying the main quality characteristics of the same, and, nevertheless, in the consulted literature there were found no references concerning the influence of the honey sort on the kinetics of the HMF formation.

Applying a proper method during honey extraction in the field helps obtaining a good quality produce (ROOT, 1976), while a faulty manipulation is able to lessen that quality. However, some studies demonstrate the main parameter to be controlled for maintaining the optimum quality of honey should be the temperature (WINKLER, 1955). It is also important to take into account in tropical countries the average ambient temperatures are significantly higher than those in the temperate climate countries. During harvesting,

manipulating and storing honey in tropical countries, the vessels in which honey is collected are sometimes being left for long hours in the sun, thus suffering an excessive heating (ROOT, 1976).

In the Yucatán Peninsula, Mexico, mainly two sorts of honey are produced, with different characteristics, known as Tahonal (Viguiera dentata var. helianthoides) and, respectively, Dzidzilché (Gymnopodium antigonoides, Blake) honeys, very asked for on the international market.

On the other hand, according to the opinion of many beekeepers in the Yucatán Peninsula, temporarily heating the honey can accelerate some chemical reactions, able to entail lessening the quality of the same during storage, what could be a result of the catalytic activity of its main acids on the present sugars (CRANE, 1985), thus producing an undesirable growing of the content in certain compounds, such is that of HMF, and at the same time giving birth to forming some dark color pigments, which would be responsible for changing the color. The general purpose of this study is to assess the effect of momentarily heating the Tahonal and Dzidzilché honeys on the variation of the main commercial quality characteristics during storage.

Material and Methods

General Methodology

Samples of Tahonal and Dzidzilché honeys were used, taken from the Yucatán State, Mexico, during the harvesting season. A batch was used, of each honey sort, filtrated in cold for separating the particles in suspension. Honey of each sort was divided into four portions, each of those being then submitted to one of the treatments under study: heating at 55 ^{o}C (a moderate temperature, which is not able to sensibly modify the honey characteristics), during 3, 6, 9, and 15 minutes, respectively. The applied thermic treatments were made in a water bath with controlled temperature, directly measuring the honey temperature. The heated samples were then left to cool at the room temperature (26±2 C), and then stored at the same temperature. Periodically, that is once every 15 days, small samples were taken for analysis, for three months and a half. The effect was assessed, of heating on changing the main quality characteristics during storage: the diastase activity, the color, the total acidity, and the HMF. The study was effected in duplicate.

Analytical methods

For analyses, the methods recommended by the Mexican Quality Standard and the Codex Alimentarius were used.

The humidity percentage was determined by means of a laboratory refractometer of Abbe type, operating the proper correction of readings at 20 ^{o}C.

The diastase activity was quantified by the spectrophotometric method of SCHADE et al. (1961), as modified by HADORN (1962), which is based on measuring the necessary time for the diastase, which is naturally present in honey, to hydrolyze a known quantity of starch, added to the diluted sample of honey, whose pH is adjusted at 5.1 to a buffer solution in the presence of iodine (MILLO,1976).

The color was determined visually, using a Pfund comparator.

The total acidity was quantified by volumetry, titrating a honey sample with a solution of 0.1 N sodium hydroxide, up to a pH of 8.3, and expressing the result in milliequivalents of acid at 100 g of honey.

The HMF content was determined by applying the spectrophotometric method suggested by WINKLER (1955), which is based on its reaction with the tiobarbituric acid and p-toluidine.

Data Analysis

In order to quantify the global variation of the HMF content during storage, two factors were calculated (PAREDES,1983), known as Monthly Apparent Growing Coefficient (CI), and Growing Factor (FI). The first was calculated for having an average value able to relate to the monthly variation of HMF, and the second as a factor allowing to assess the HMF content after a certain time of storage, starting from its initial concentration.

These factors were calculated according to the following ratios:

$$CC = \frac{HMF}{t} \quad \text{et} \quad FC = \frac{\text{Final HMF}}{\text{Initial HMF}}$$

where:

- HMF is the difference between the final HMF concentration and the initial concentration, after the storage time t;
- The final HMF is the HMF concentration after a certain time, and the initial HMF is the content of HMF at the beginning of the storage.

The obtained results were analyzed statistically, by using the statistical package Statgraphics®.

Results and Discussion

General Initial Characteristics of Honey

Samples of the two sorts of honey were studied (see Table I); they were similar and fulfilled the quality standard, attracting the attention on the fact the HMF content was low, which shows honey was recently collected and it was not heated.

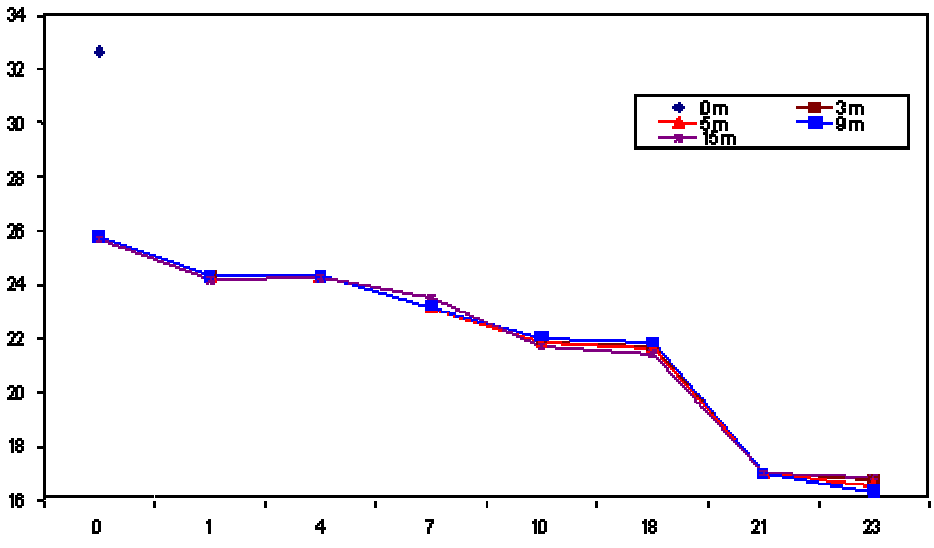
Table I

Sensorial, Physical and Chemical Characteristics of the Tahonal and Dzidzilché Honeys

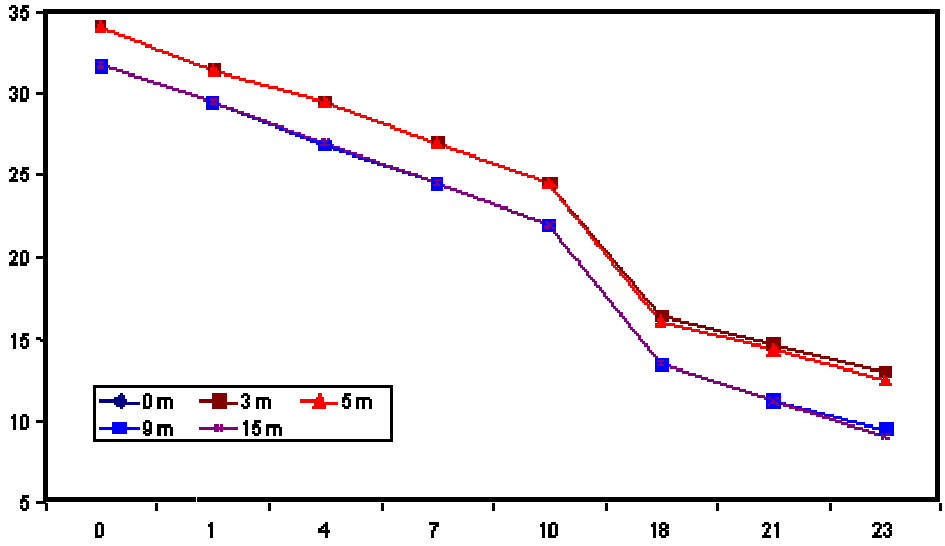
Flavor & taste	typical	typical
Humidity (%)	20.0	18.48
Diastatic activity (° Schade)	32.5	34.17
HMF (mg/kg)	2.85	2.63
Color, degrees Pfund	42.0	45.0
Total Acidity, meq /kg	28.2	29.0
pH	3.55	3.70

Variation of the Diastatic Index, ID

The initial diastatic activity was similar in both sorts of honey (Fig.1); nevertheless, the initial heating had different effects. In the Tahonal honey it diminished significantly and in the same ratio in all the four treatments (from 32.6 to 25.8 degrees Schade), while in the Dzidzilché honey only the initial heating, of 9, and, respectively, 15 minutes, caused a significant diminution (from 34.2 to 31.7 degrees Schade) of the diastatic index as compared to the honeys heated for 3 and 5 minutes; the difference was maintained during the storage (Fig. 1).



tahonal honeys



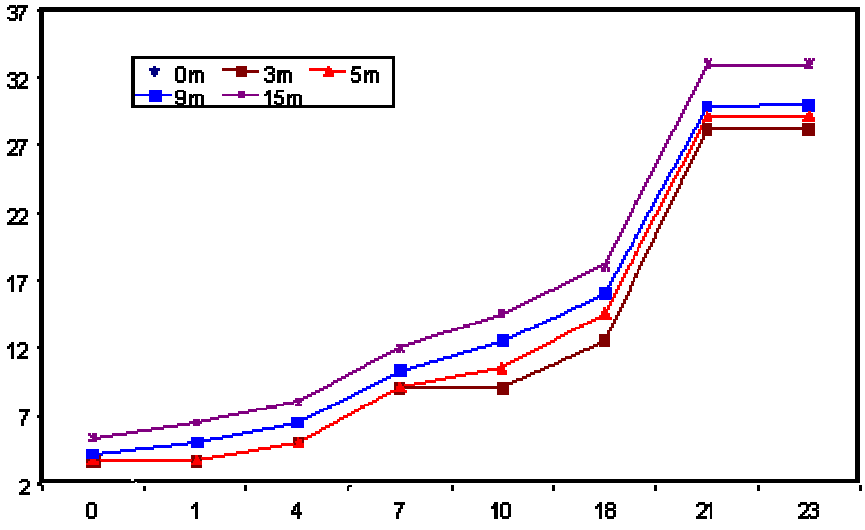
dzidzilché honeys

Fig. 1 - Variation of the diastatic index. Time of storage (weeks).

During the storage, the changes of the diastatic index (ID) in the honey samples, according to the four treatments applied to each of the two sorts of honey, that is, Tahonal and Dzidzilché, had similar behaviors, as in both cases the ID diminished continuously. By the end of 23 weeks of storage, the Tahonal honey had lost about 35% of its activity, while the Dzidzilché honey had lost from 61 to 71% of its activity, according to the heating time. This general behavior was noticed in different studies (WHITE, 1964; IMÁN, 1990). The initial heating, to which the samples of both honeys were submitted, had no significant catalytic influence on the speed of that activity diminution during storage. From these results, the conclusion can be drawn, the honey sort significantly influenced the ID diminution during storage, what could be interpreted as an effect of the differences presented by honeys as concerns their chemical composition.

Variation of the HMF content

The initial content of HMF was low in both types of honey, that is, about 3 mg/kg (Fig. 2), and the heating to which the honey samples were subjected only produced a slight growth in both cases, which practically did not depend on the time of treatment, as that grown up to concentrations of around 5 mg/kg.



tahonal honeys

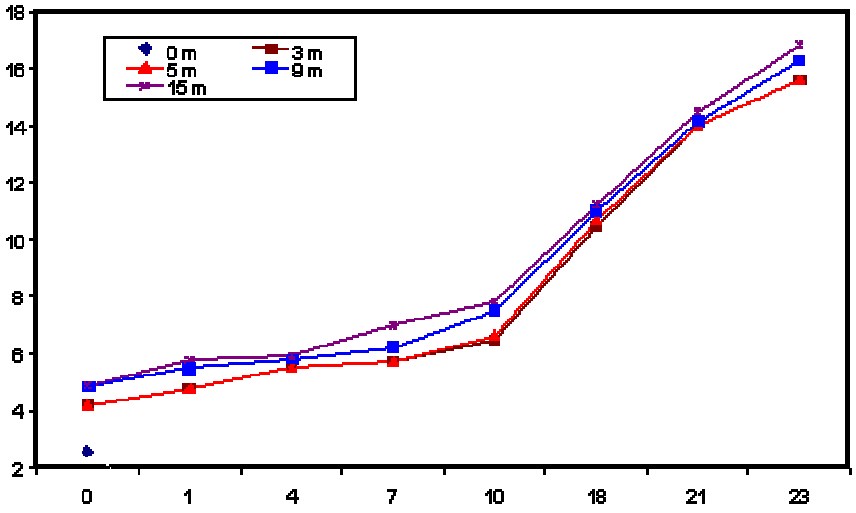


Fig. 2 - Variation of the HMF content. Storage time (weeks).

As regards the initial heating, in this study there was found no significant difference among the 4 treatments of each honey sort, which shows the initial heating to which the honey samples were submitted did not cause a catalytic effect upon the HMF growth during storage.

During storage, the changes of the HMF content in the honey samples ac-cording to the four treatments of each type of the two sorts of honey, Tahonal and Dzidzilché, followed similar global behaviors, as in both cases HMF raised continuously during storage, although according to different ratios (Fig. 2). Also, in both cases this growth was not linear. After 23 weeks of storage, the HMF raised up to concentrations around 30 mg/kg (900%) in the Tahonal honey, while in the Dzidzilché one it reached around 16 mg/kg (433%). This general qualitative behavior (signaling a significant growth) is similar to that found in other studies (WHITE, 1964; SKOWRONEK et al., 1994; GHOSHDASTIDAR, 1992; IMÁN, 1900; HADORN, 1962).

We can however notice that, from a quantitative point of view, the growth of the HMF concentration during storage was significantly higher in the Tahonal honey, than in the Dzidzilché one, which was rendered evident by the values that were reached after 23 weeks of storage (that is, around 32 and 16 mg/kg in the Tahonal and the Dzidzilché honeys, respectively) and by the average monthly apparent growth coefficients (CI) and the average apparent growth, 4.4 and 7.3 for the Tahonal, and 2 and 3.5 for the Dzidzilché one. The identified growth coefficients (CI) are significantly higher than those obtained by GONNET (1979), who studied honeys from cold and warm climates - 1.1 mg/kg and 2.1 mg/kg, respectively, although the honey sorts are not specified.

Besides, when analyzing the growing dynamics of the HMF concentration during storage, a first degree dynamics could be established, taking into account a ratio of the type:

$$\ln C/Co = Kt,$$

where C, is the concentration in HMF (in mg/kg), after the storage time t, in weeks;
Co, is the initial HMF concentration, at the beginning of the storage;
K, is the constant of first degree.

According to the obtained K constants (Table II) in the two assessed sorts of honey, there is confirmed the pattern is a good assessment, through the high correlation coefficients obtained, and the different speed of its formation in both sorts of honey - as values of the K constant.

Table II

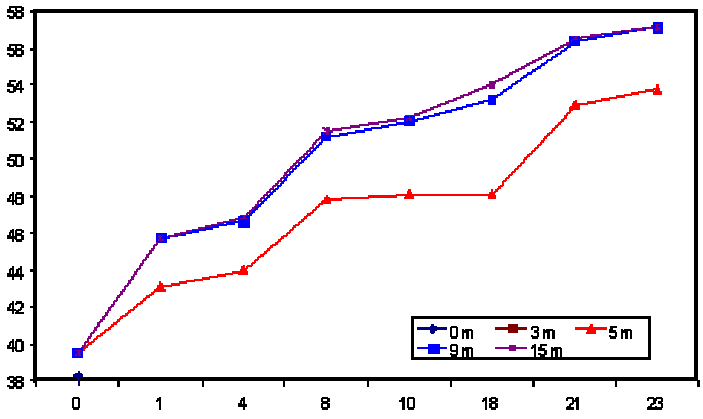
Correlation coefficients and constants (of the first degree) of HMF forming during honey storage

Heating time (min)	Tahonal		Dzidzilché	
	Correlation coefficient	Dynamic constant, K	Correlation coefficient	Dynamic constant, K
3	0,973	0,0380	0,983	0,0248
5	0,980	0,0393	0,986	0,0247
9	0,979	0,0355	0,989	0,0226
15	0,979	0,0324	0,994	0,0225

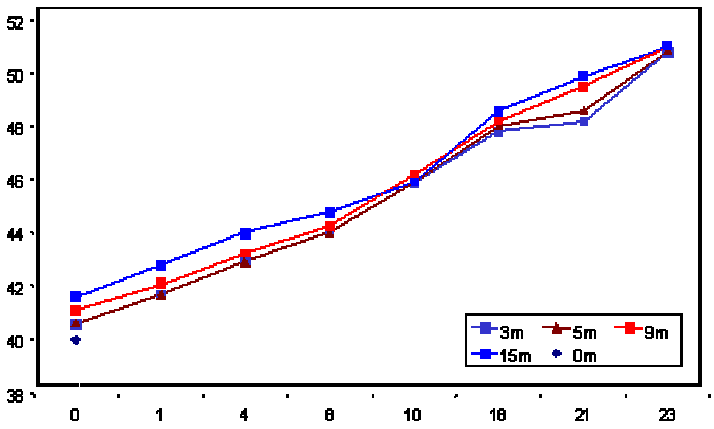
The so different behaviour of both honey sorts towards this parameter could be interpreted as an effect of the differences as regards their chemical composition according to their floral origin, especially the reductive sugars. The increase of the HMF concentration was connected to the diminution of the fructose content (HADORN, 1962). This result allows us to draw the conclusion the speed of HMF increasing during storage should be calculated for each honey sort separately.

Variation of acidity

The initial acidity was slightly higher in the Dzidzilché honey (40 meq./kg.), as compared to the Tahonal one (38.3 meq./kg.), and the initial heating had no significant effect on these values. Nevertheless, during storage a significant in-crease was discovered, in direct ratio with time (Fig. 3), which coincides with the results obtained by HADORN (1962) and IMÁN (1990).



tahonal honeys



dzidzilché honeys

Fig. 3 - Variation of acidity. Time of storage (weeks).

However, while in the Dzidzilché honey there was encountered no significant difference in variation at the four heating times, in the Tahonal one higher, significant values were found in the samples heated for 9 and 15 minutes, as compared to those heated only for 3 and 5 minutes, which shows the initial heating, to what the samples were submitted, produced a catalytic effect on the acidity increase speed.

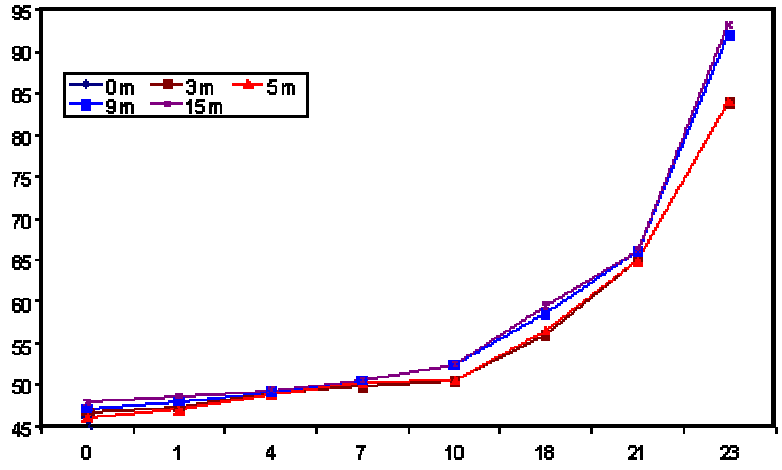
From the obtained results there can also be drawn the conclusion the honey type had no significant effect on the acidity increase speed during storage.

Variation of colour

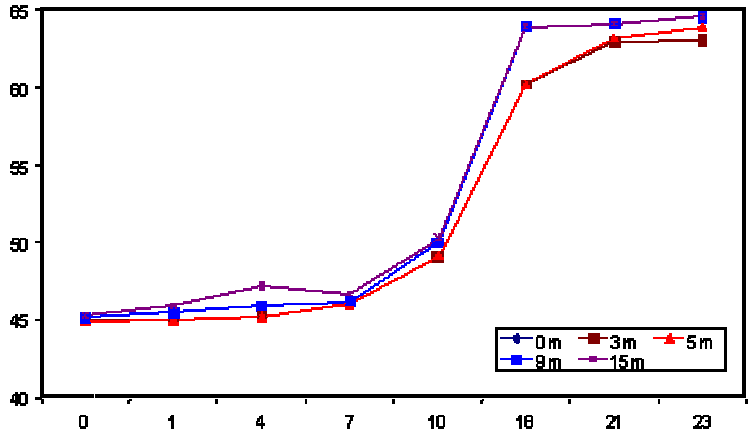
The initial heating exerted no considerable effect on the colour of the honey samples, which coincides with the results reported by ROOT (1976). In both sorts of honey, colour has intensified significantly during storage, although with different qualitative patterns of change with respect to the standard colour, what means to say they grew darker in color, but to a different extent.

During storage of the Tahonal honey (Fig. 4), an intensification of colour was noticed, following an exponential type curve, with the colour growing darker much faster, starting from the tenth week of storage. Nonetheless, the same effect was noticed in the Dzidzilché honey, but it happened earlier, starting from the seventh week.

When comparing the values reached by both sorts of honey, after the 23 weeks of storage, there is noticed the Dzidzilché honey grew much more darker (90 mm) than the Tahonal honey (65 mm). This shows the differences as concerns the composition of both sorts of honey exerted a significant effect on their colour. This growing darker in colour is mainly due to to some browning reactions of a chemical type, where sugars acquire a prevalent role.



tahonal honeys



dzidzilché honeys

Fig. 4 - Variation of colour. Time of storage (weeks).

There was found no significant difference as concerns the growing darker in colour, produced in both types of honey on the opportunity of the four treatments, which is showing there is no possibility of determining the initial heating would have catalysed the changing in colour. Nevertheless, the honey origin had exerted a significant effect.

Conclusions

a. Thermic treatment at 55 ^{o}C, during the four studied temporary heating times (that is, 3, 5, 9, and 15 minutes), applied to the Tahonal and Dzidzilché honeys exerted no significant effect on the main quality indexes of both sorts of honey, except the diastatic activity in the Dzidzilché honey, in the samples heated for 9 and 15 minutes, respectively.
b. Temporary heating for 9 and 15 minutes, respectively, at 55 ^{o}C, did significantly affect only the increase of acidity during the storage of Tahonal honey, which grew bigger.
c. In both sorts of honey, the increase of the HMF concentration during storage followed a first degree reaction.
d. Behaviour of the Tahonal and Dzidzilché honeys during storage, after they had been temporarily heated, was different.

LITERATURE

1. Anonyme, Comission du Codex Alimentarius/Norme Régionale Européenne Recommandée pour le miel. FAO/OMS, 1984
2. Badui D.S., Química de los alimentos. Ed. Alhambra, 1986
3. Crane Eva, "El libro de la miel". Marilus Coso. Ed. Breviarios del Fondo de Cultura Económica, 1985
4. Detroy, B.F., Elaboración, envase y distribución de la miel. En La Apicultura en los Estados Unidos, S.E. Mc Gregor, editor, 1979 Espinoza Mansilla A., Muñoz de la Peña, Salinas F., Semiautomatic determination of furanic aldehydes in food and pharmaceutical samples by a stopped-flow injection analysis method. J. of the AOAC International, 1993
5. Ghoshdastidar N., Chakrabarti J., Studies on hydroxymethylfurfural formation during storage of honey. J. of Food Science and Technologyy, 29 (6) (1992), 399
6. Gonnet M., Conservation du miel et principale modifications physiques, chimiques et biologiques subles par le produit pendant son stockage. Bull. Tech. Apic., 6 (4) (1979), 13
7. Hadorn, H., "Über Wärme und Lagerschädigungen von Bienenhonig". Trac. Chim. Alim. Hyg. (Berne). 53 (3) (1962), 191-192
8. Imán Morales C., "Evaluación de las principales características del envase ideal para la miel y la influencia del material de éste sobre sus propiedades durante su conservación". Tesis. UADY, 1990
9. Juárez-Salomo A., Valle-Vega P., Termogeneración de hidroximetilfurfural (HMF) en miel de abeja como parámetro de calidad. Tecnología de Alimentos, 30 (6) (1995), 13
10. Mateu Andres I., Burgaz Moreno M.E., Rosello Caselles J., La apicultura valenciana. Tradición y aprovechamiento. Generalitat Valenciana. Consellería D'Agricultura i Pesca. España, 1993
11. Millo L., Legislación Alimentaria Española. Ed. Revista de Derecho Privado, 1976, Madrid
12. Paredes O., Efectos de la temperatura y tiempos en la calidad de la miel de abeja. Rev. Tecnología de Alimentos, 2 (89) 1983
13. Schade B., Diastase activity and hydroximethylfurfural in honey and their usefulness in detecting heat alteration. Food Res., 23 1958, 446. Academic Press Inc. Publishers, New York
14. Root, A.I., ABC y XYZ de la Apicultura. Librería Hachette S.A., Buenos Aires, 1976
15. Singh B., Dean G.R., Cantor S.M., The role of 5-(hydroxymethyl)furfural in the discoloration of sugar solutions. J. Am. Chem. Soc., (1948), 70:507
16. Skowronek W., Rybak Chmielewska H., Szczesna T., Pidek A., et al., Study of optimum conditions for slowing down the crystalization of honey. Pszczelnicze Zeszyty Naukowe, 38 (1994), 75
17. White Jr., "Effect of storage and processing temperatures on honey quality", Food Technology 18 (1964), (40)
18. White J.W., Hydroxymethylfurfural content of honey as an indicator of its adulteration with inverted sugars. Bee World, 61 (1980) 29
19. Winkler, "Beitrag zum Nachweis und zur Bestimmung von Hydroximethylfurfural in Honig und Kunsthonig". Lebensm. Unters. und Forsch. 102 (1955) (3)