

Impact of Microwave Heating on Chemical Properties of Romanian Honeys

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Abstract

In this work, the influence of microwave heating on the chemical proprieties of Romanian honeys (sun flower honey, tilia honey, polyfloral honey) was investigated. The chemical parameters determined were total acidity, hydroxymethylfurfural and ascorbic acid (vitamin C) content. Hydroxymethylfurfural content, as primarily indicator of heating, was determined by spectrophotometric method, while vitamin C level was measured with a liquid chromatograph equipped with US/VIS detector. Vitamin C and hydroxymethylfurfural turned out to be reliable indicators of microwave heating, displaying gradual decrease and increase, respectively. The variation of total acidity on the other hand could not be correlated with changes in the exposure time.

Keywords: honey, microwave heating, hydroxymethylfurfural, vitamin C, total acidity

1. Introduction

Microwaves have found many applications not only in the food industry, but also in agriculture, chemical engineering and mineral processing industry. The first major microwave applications in thermal food processing included finish drying of potato chips, tempering of frozen food and drying of pasta [1,2]. Since then microwave ovens became a common kitchen appliance. As the name suggests, this device uses for the heat treatment of food microwaves that are radio waves with frequencies between 3 and 300 GHz [3].

Microwaves are reflected, transmitted and absorbed in a similar way to light. Therefore, metallic materials totally reflect microwaves while non-metallic materials such as glass and some plastics are mostly transparent to microwaves [4].

When materials containing water, for e.g. foods or fluids are exposed to microwave heating the

microwave field causes the friction of these molecules which leads to the heating of the product.

As it contains about 20% water [5] honey can be heated in a microwave oven. Microwave heating can be applied especially for crystallized honey and represents one of the liquefying methods of honey outside the processing unit. Honey crystallization depends primarily on its moisture and glucose content. Other contributing parameters are temperature and processing level, used to distinct unprocessed honey from the liquefied and pasteurized one.

The purpose of this study is to observe the influence of microwave heating on honey composition by measuring the changes that occur in the hydroxymethylfurfural content as primarily indicator of thermal processing, honey total acidity, and vitamin C content which although is very low it is very important from a nutritional point of view.

2. Materials and Methods

Honey samples. In this study were investigated 3 honey samples (tilia honey, sun flower honey and polyfloral) from Romanian honey producers. All samples were purchased in an already crystallized form, and before being studied they were stored at 14°C for six weeks.

Microwave heating. From each honey variety were measured three equal volumes of honey that are put into beakers marked according to the floral source and heating time. The samples were individually heated at the selected power of 270 W for 60, 120 and 180 s, and then left to cool at 25°C.

Methods

Water content. The water content of the samples was determined by measuring the refractive index at 20°C according to the Harmonized Method for Honey developed by the International Honey Commission, IHC [6,7]. All measurements were performed with an Abbé Leica Mark II Plus refractometer.

Sugar content (°Brix). The sugar content of the honey samples, expressed in Brix degrees, was measured with an Abbé Leica Mark II Plus refractometer.

pH. The method used for the determination of pH was described by Bogdanov [6], and requires 10 g of honey dissolved in 75 ml of carbon dioxide-free water. After the mixture was homogenized with a magnetic stirrer, the pH electrodes were immersed in the solution, and then recorded the pH. For this determination it was used a Hach HQ11D pH meter (Hach Company, Colorado, USA).

Electrical conductivity. Electrical conductivity was measured with a Hach HQ14D conductivity meter after checking the cell constant of a 20% (w/w) honey solution at 20°C, according to the IHC method for honey [6].

Total acidity. Total acidity was determined by titration with 0.1N NaOH as follows: 10 g of honey were dissolved in 50 ml of water heated to 40-50°C, and then added two drops of phenolphthalein. The mixture was titrated with NaOH until a pink color that persisted for 30 seconds was produced [8].

The amount of sodium hydroxide used corresponds to honey sample's free acidity, expressed in acidity degrees (°A).

Determination of hydroxymethylfurfural. For the hydroxymethylfurfural (HMF) analysis was used the White method [6,9], based on the determination of UV absorbance of HMF at 284 nm. The samples were prepared by accurately weighting approximately 5 g of honey dissolved then in 25 ml of water and quantitatively transferred into a 50 ml volumetric flask. It was added 0.5 ml of Carrez solution I and mixed and 0.5 ml of Carrez solution II and mixed again, and made up to the flask's mark with water. The mixture was filtered through paper; the first 10 ml of the filtrate were rejected. 5.0 ml of filtrate were pipetted in each of two test tubes. In one test tube was added 5.0 ml of water (the sample solution), and in the other an equal volume of sodium bisulphite solution 0.2% (the reference solution).

The absorbance of the sample solution against the reference solution was measured at 284 and 336 nm in 10 mm quartz cells with a T70 UV/VIS spectrophotometer (PG Instruments Ltd., United Kingdom).

Calculation of the results was made according to the following equation:

$$HMF \text{ in mg/kg} = (A_{284} - A_{336}) \times 149.7 \times 5 \times D/W$$

Where:

A_{284} = absorbance at 284 nm

A_{336} = absorbance at 336 nm

149.7 = $126 \times 1000 \times 1000 / 16830 \times 10 \times 5$ = Constant

126 = molecular weight of HMF

16830 = molar absorptivity ϵ of HMF at $\lambda = 284$ nm

1000 = conversion g into mg

10 = conversion 5 into 50 ml

1000 = conversion g of honey into kg

5 = theoretical nominal sample weight

D = dilution factor, in case dilution is necessary

W = Weight in g of the honey sample

Determination of vitamin C content. Vitamin C content of the honey samples was determined by HPLC method using a liquid chromatograph equipped with an auto injector along with a UV/VIS detector (DAD) and 4.6 x 250 mm, 5 μ m column. The mobile phase was a 100% solution of phosphate and the flow rate was maintained at 0.6 ml/min.

The calibration curve of the standard sample is presented in Figure 1.

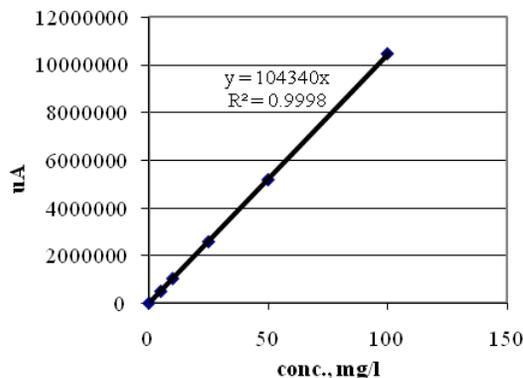


Figure 1. Calibration curve for vitamin C by HPLC

The samples were prepared as follows: 4 g of honey were mixed with 12 ml of acid solution (10% perchloric acid and 1% ortho-phosphoric acid) and quantitatively transferred into a 50 ml volumetric flask. The mixture was stirred and added up mobile phase (0.02 mol/L monopotassium phosphate acidified to pH=3.5 with 10% ortho-phosphoric acid) until the flask's mark was reached. After it was stirred again, the resulted solution was filtered through paper. 1 ml of filtrate was analyzed.

3. Results and discussion

Physicochemical properties. Moisture content, °Brix concentration, pH and conductivity of the unheated honey samples are presented in Table 1. As the results show, the moisture content varies from a floral source to another, displaying the lowest value for tilia honey sample (13.76 g/100 g), and the highest one for unheated sun flower honey (14.16 g/100 g). The moisture content of polyfloral honey sample was 14.03 g/100g. These values were much lower than other obtained for the same samples of Romanian honey by other authors [10], who reported a minimum moisture content of 17.80±0.06 g/100 g and a maximum of 19.70±0.12/100 g for crystallized sun flower honey, and a 16.80±0.01/100 g moisture content for tilia honey. However, honey samples used in this study did not exceed the maximum moisture content of 20% defined by the Codex Alimentarius [11] and established by the European legislation through Council Directive 2001/110/EC [12].

Regarding the pH of the analyzed honey samples, the lowest value was measured for polyfloral honey (4.10), while tilia honey displayed the highest one (4.42).

Electrical conductivity depends on the ash and acid contents of honey: the higher their content, the higher the resulting conductivity [6,13]. The measured electrical conductivity varied between 307 µS/cm (tilia honey) and 362 µS/cm (polyfloral honey).

Table 1. Physicochemical properties of the unheated honey samples

	Moisture content (g/100 g)	°Brix	pH	Conductivity (µS/cm)
Sun flower	14.16	83.9	4.33	322
Tilia	13.76	84.9	4.42	307
Polyfloral	14.03	84.0	4.10	362

Total acidity of honey. The variation in total acidity of honey before and after microwave heating is presented in Figure 2. Total acidity depends on the product content in acids and their salts. The highest acidity of the unheated sample was determined for polyfloral honey, 2.5°A, while the other samples were less acidic: 1.3°A for tilia honey and 1°A for sun flower honey.

As Figure 2b shows, tilia honey had the major increase in total acidity by heating treatment; after a 60 s exposure time the measured value was 2.4°A, and continued to increase until it reached 2.9°A (180 s). Therefore, it was noted that after the longest exposure to microwaves total acidity of the honey sample had doubled. This could be a result of fructose decomposition at high temperature in formic and levulinic acid, which leads to an increase in honey's acidity. Similar to tilia honey, total acidity of polyfloral honey showed a polynomial increase with the length of exposure, and the highest value was reached as expected after a heating of 180 s. Variation of total acidity for sun flower honey was different from the other two samples: the only increase of this parameter was noted after the shortest heating treatment (60 s), from 1°A to 1.8°A, while longer heating did not lead to any changes in the previously measured value.

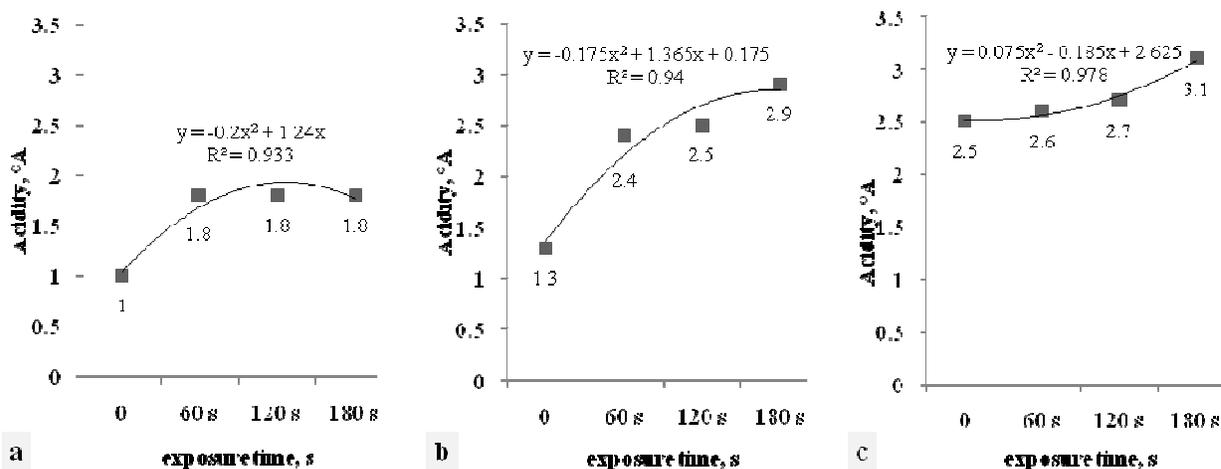


Figure 2. Total acidity of honey in function of microwave heating: a - sun flower honey, b – tilia honey, c – polyfloral honey

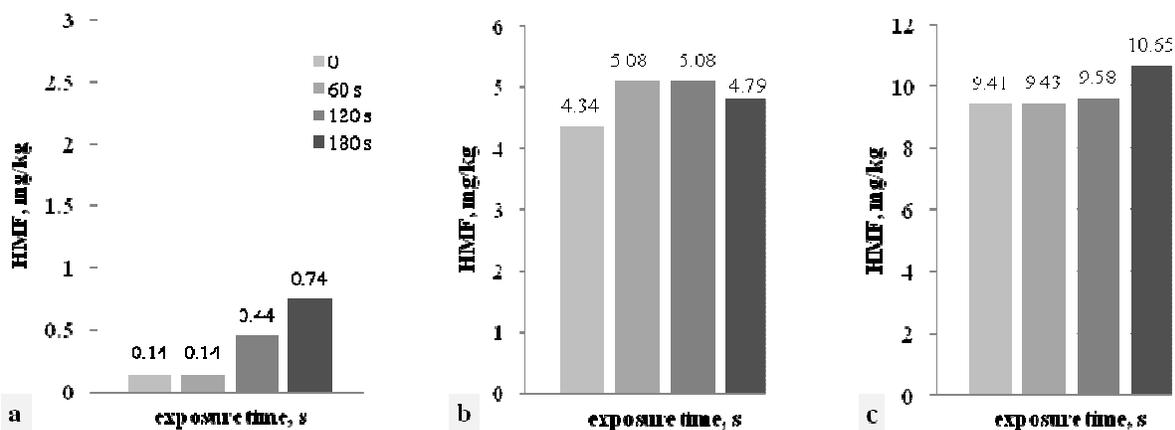


Figure 3. HMF content of honey in function of microwave heating: a - sun flower honey, b – tilia honey, c – polyfloral honey

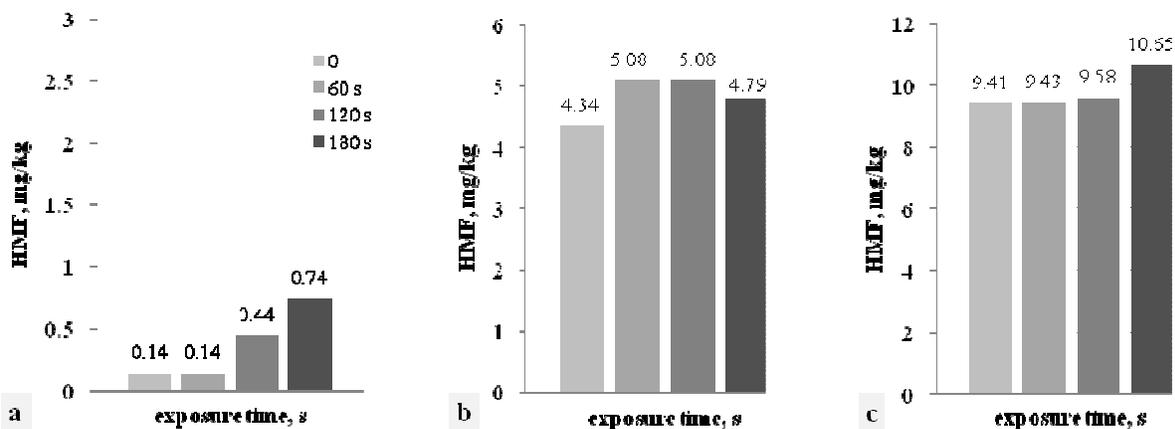


Figure 3. HMF content of honey in function of microwave heating: a - sun flower honey, b – tilia honey, c – polyfloral honey

Hydroxymethylfurfural content. HMF formation in the analyzed honey samples due to microwave heating is presented in Figure 3. As these graphics show, no gradual increase in HMF content occurred as the heating interval was lengthened. On the contrary, for some samples the HMF content was identical after two distinct heating intervals, and then slowly increased or even dropped.

The lowest HMF content in crystallized honey was measured for sun flower variety, 0.14 mg/kg, while polyfloral honey had the highest level of this compound, 9.41 mg/kg. Hydroxymethylfurfural content of crystallized tilia honey was 4.34 mg/kg. All these values are lower than 40 mg/kg, the maximum HMF content admitted in honey by the European legislation.

Although it was very low in the unheated sample, the HMF content of sun flower honey increased significantly after heating intervals of 120 and 180 s, respectively.

A 60 s exposure to microwaves did not lead to any change in hydroxymethylfurfural content compared to the value obtained for the unheated sample of honey. A similar variation pattern also resulted for polyfloral honey, as Figure 3c shows. An interesting variation was observed in HMF content of tilia honey, which is equal, 5.08 mg/kg, for samples heated for 60 and 120 s, but then drops at 4.79 mg/kg after the longest heating. A similar behavior was noted by other authors [14] from a microwave exposure of 30 s to a 45 s one at the selected power of 500 W.

Vitamin C content. Honey may be considered a vitamin C source, that unlike other vitamins it doesn't derive from pollen, but has its origin in nectar. Vitamin C is also an important compound of honey because of its antioxidant character. It is known that a drop in vitamin C content marks a long exposure of the product to light or a heating treatment. This instability towards heating is the reason why vitamin C content was one of the analyzed parameters in this study.

The vitamin C values obtained for the three honey varieties before and after microwave heating by chromatographic determination are presented in Figure 4. The highest level of vitamin C in the

unheated sample was measured for tilia honey, 18.79 mg/kg, followed by polyfloral honey, 15.77 mg/kg, and sun flower honey, with a content of 12.72 mg/kg. The most significant drop of this parameter was observed for sun flower honey; after the shortest microwave exposure (60 s) vitamin C content reduced to 92.25%, and after 180 s dropped to 26.01% of its initial value. Similarly, a 180 s heating in the microwave oven of tilia and polyfloral honey led to a polynomial decrease of vitamin C level to 31.54% and 34.77%, respectively.

It was concluded that for all honey varieties vitamin C level dropped at a third of its initial value after the longest heating. This can occur due to decomposition of ascorbic acid in dehydroascorbic acid, reported by other authors [15], but this wasn't an aspect followed by the current study. It was also noted that vitamin C level had a polynomial decrease as the heating interval was lengthened. Although its content is significantly lowered, vitamin C isn't completely destroyed by a 180 s exposure time to microwaves. It was assumed that heating treatments longer than 180 s can lead to a total decomposition of this natural antioxidant.

4. Conclusions

In order to assess the influence of microwave heating on honey's composition the following parameters were studied: total acidity, HMF and vitamin C content. The samples used in this study were sun flower honey, tilia honey and polyfloral honey, all of Romanian origin.

An increase in total acidity due to microwave exposure was determined for all samples apart from sun flower honey, whose acidity did not change after exposures longer than 60s. HMF content also increased for all honey samples, but not too far from the level measured in the unheated sample. Vitamin C content on the other hand reduced gradually as the heating time was lengthened; this behavior was expected, since researches show that ascorbic acid is thermosensitive. Among the studied parameters, vitamin C and HMF content turned out to be reliable indicators of microwave heating.

Compliance with Ethics Requirements: Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human and/or animal subjects (if exists) respect the specific regulations and standards.

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