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EFFECT OF SONICATION ON THE CRYSTALLIZATION OF HONEYS

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Key words: sonication, crystallization, sugar, honey

Investigations were carried out into the effect of sonication of bee honeys on the course of their crystallization during storage. Use was made of ultrasounds with a frequency of 40 kHz and intensity of *ca*. 2 W/cm^2. Analyses were carried out for physicochemical characteristics of honeys, including: viscosity, texture, conductance and crystallization degree. After 30-min sonication, an increase in viscosity by *ca*. 30 mPa.s and a reduction in conductance by 0.6 mS/cm were observed in the solution examined. Analyses of the texture (hardness) of honey subjected to the sonication process demonstrated an initial increase of hardness and then its stabilization and even a slight decrease, as compared to the control samples. The degree of crystallization was proportional to the exposure time to ultrasound treatment. The biggest crystals were observed in the non-sonicated samples. Sonication modified the crystallization process of the examined sugar solutions to a significant extent. Observations of the solutions after the sonication demonstrated the formation of a high number of crystals in the whole volume of the sample, whereas the non-sonicated solutions were observed to crystallize unevenly forming large crystals. It was shown that the ultrasound treatment modified the course of recrystallization and, as a result, texture of the recrystallized honeys by decreasing their hardness.

INTRODUCTION

Quality honeys, *e.g.* rapeseed, buckwheat, are produced from nectar of specified species of plants and are characterized by specific sensory properties. Apart from monosaccharides solubilized in water, honey contains also enzymes, organic acids, minerals, proteins, vitamins, amino acids, pigments and essential oils [Rybak-Chmielewska & Szczęsna 1996]. Crystallization, namely granulation and formation of a hard structure, is a natural process proceeding with various rates in all Polish honeys. It does not change honey's composition, nor its nutritional or therapeutic properties. As demonstrated by investigations of, among other, Bakier [2002a] and D'Arcy [2006], in honey sugar crystals may attain various sizes and its consistency is determined by the size of crystals and is a typical trait of a given honey quality. Granulated honey may be liquidized by heating in *e.g.* warm water (*ca*. 40°C). Recrystallization of honeys proceeds with a higher rate than the primary crystallization. The recrystallized honey has a coarse-grained cyrstalline structure, and thus is sparingly spreadable. Usually, consumers prefer liquid or "creamy" honeys that possess fine-grained crystals, *i.e.* are easily spreadable. Liquid honey may flow off a course, whereas granulated honey is sometimes hard and cannot be spread.

Phenomena of matter exchange in supersaturated solutions of sugars may be controlled by conditions of exposure, *i.e.* frequency, intensity and period of ultrasound waves action. The effect of ultrasounds on the course of the crystallization process has already been confirmed in ample studies [Povey& Mason, 1998; Bund & Pandit, 2007]. Nevertheless, a number of issues referring to *e.g.* crystallization in multicomponent solutions (like honeys), still need to be elucidated [Bakier, 2002ab], especially in the aspect of ultrasound treatment [D'Arcy, 2006]. A correlation between parameters of sonication and primary and secondary effects induced in substances is the key objective of investigations carried out in a number of laboratories.

This study was undertaken to determine the effect of ultrasound treatment at low frequency and medium intensity on the course of recrystallization of honeys: polyfloral, lime and rapeseed, and consequently on achieving an easily spreadable crystalline structure of honey.

MATERIAL AND METHODS

Experimental material used in the study included: (a) an aqueous solution of saccharose – 720 g/L (white commercial sugar, colourization according to ICUMSA – 27, ash – 0.03% m/m); and naturally-crystallized honeys of commercial quality: (b) summer bright polyfloral nectar honey – PN (reducing sugars – 76.3%, saccharose – 1.98%, water – 18.2%, total acidity – 2); (c) bright lime nectar honey – LN (reducing sugars – 75.0%, saccharose – 4.21%, water – 18.3%, total acidity – 1.7); and (d) dark buckwheat nectar honey – BN (reducing sugars – 73.4%, saccharose – 3.74%, water – 17.9%, total acidity – 2.3).

The characteristics of raw material was carried out in a laboratory of the Apiculture Co-operative "APIS" in Lublin. Honeys were stored in tightly closed glass vessels without the access of light, at a temperature of 18±2°C. Decrystallization of honeys directly before sonication was conducted in a water

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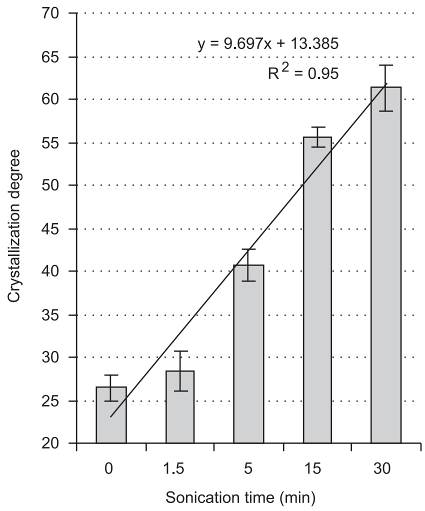

FIGURE 1. Crystallization degree of a saccharose solution.

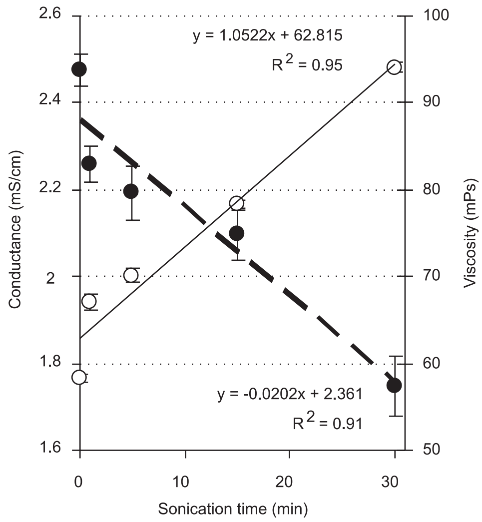

FIGURE 2. Changes in viscosity (○–) and conductance (●--) of saccharose solutions during sonication.

bath at a temperature of 40°C. Sonication was carried out with an ultrasound apparatus equipped with a working chamber with a 40 kHz ultrasound converter generating a field with an average intensity of 2 W/cm^2. Initial temperature of the honeys during sonication reached 20°C. Temperature measurement was carried out with the accuracy of ±1°C. Viscosity of solutions was analysed with the use of a DV-II+ Pro viscosimeter (Brookfield) with an SSA unit and a spindle No. 21 (n = 1 s^{-1}). Texture of granulated honey was measured by means of a TA.XTplus texture analyser equipped with a cylindrical mandrel 15 mm in diameter operating with a working speed of 0.17 mm/s. Conductance of the solutions was measured with an CPC-501 pH-conductometer (Elmetron) with temperature compensation and a CD-2 electrode (Hydromet). A degree of crystallization was determined based on the mass of separated saccharose crystals. Experiments were carried out 3 times in 3 replications. Results were analysed statistically (statistics in a sample and analysis of regression).

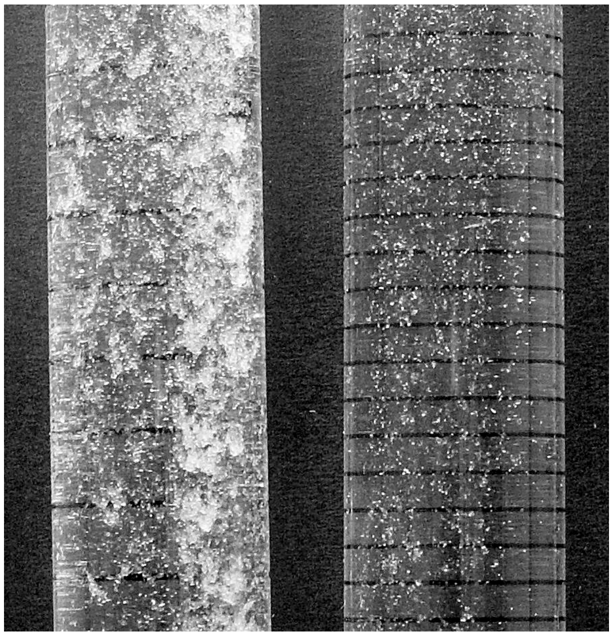

FIGURE 3. Sugar crystals in solutions treated with ultrasounds for 15 min (on the left) and in a control solution after 3 days.

RESULTS AND DISCUSSION

Results obtained in the study demonstrated that the number of crystals in an ultrasound-treated sugar solution was significantly higher as compared to the control sample not subjected to the sonication (Figures 1 and 3). The degree of crystallization was increasing proportionally to the time of solution exposure to ultrasounds. After 30 min of sonication, the total increase in the crystallization degree of the sugar solution reached 34.9% (Figure 1). The solution was also characterized by smaller sizes of the separated crystals (Figure 3).

Analyses of apparent viscosity of a saccharose solution demonstrated that it increased from 58.2 mPa.s before sonication to 94.12 mPa.s after 30-min ultrasound treatment (Figure 2). Ultrasound-induced acceleration of graining and formation of sugar crystals in the ultrasound-treated solution affected a decrease in conductance by 0.73 mS/cm after 30-min sonication, as compared to the control solution.

During sonication of a saccharose solution carried out in a laboratory ultrasound apparatus, there was observed an effect of acoustic pressure in the form a local change in the height of liquid column reaching 5 mm. Dissipation of acoustic energy was demonstrated in a linear increase of solutions temperature by *ca*. 0.7°C/min/L, in the range from 20°C (ambient temp.) to 30°C. During sonication of the saccharose solution, periodical occurrence of dynamic areas of cavitation in which aluminum foil sheets were subject to perforation was observed directly above the ultrasound transducer. Such a phenomenon was not observed during sonication of honeys.

Honeys subjected to analyses originated from various flows, which affected their composition [Rybak-Chmielewska & Szczęsna, 1996]. The examined recrystallized nectar honeys were characterized by a lower initial hardness both before and immediately after sonication. During storage, hardness of the honeys was observed to differ as affected by ultrasounds. The lowest hardness (despite the fastest crystallization) was reported for polyfloral honey, slightly higher hardness for lime honey, and the highest – for buckwheat honey (the longest time of crystallization), (Figure 4).

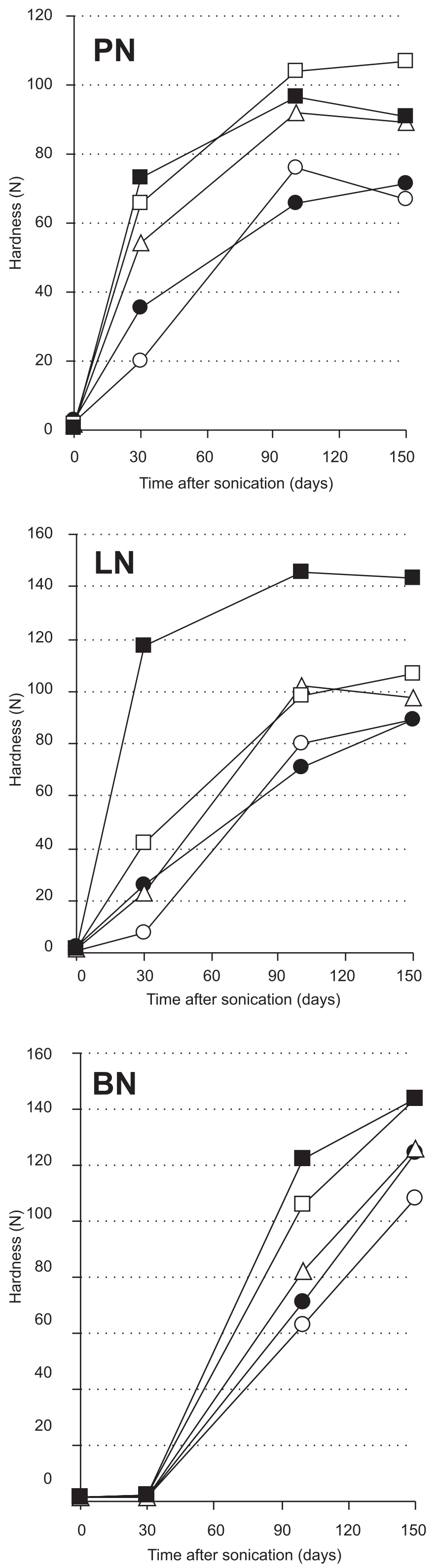

FIGURE 4. Hardness of granulated polyfloral (PN), lime (LN) and buckwheat (BN) honeys after sonication for 0 min (○–○), 3 min (●–●), 5 min (Δ–Δ), 10 min (■–■) and 15 min (□–□).

Buckwheat honey kept the liquid consistency for the longest period of time. The control sample (not treated with ultrasounds) of honey formed coarse-grained granulated honey. As a result of recrystallization of polyfloral and lime honeys after sonication, after 100 days the hardness of granulated honey obtained reached *ca*. 100 N, whereas hardness of buckwheat honey was increasing for 150 days reaching the maximum value of *ca*. 140 N. The higher mechanical resistance of buckwheat granulated honey has already been confirmed by *e.g.* Bakier [2002a].

As compared to the control samples, sonication of all honeys examined caused an initial increase of their hardness which appeared to be proportional to the time of the ultrasound treatment. The hardest granulated honey was obtained as a result of crystallization of honey subjected to ultrasound treatment for 15 min. The increase in hardness resulted from ultrasound-induced formation of a higher number of crystal nuclei, and consequently the formation of more fine sugar crystals affecting the acceleration of honey granulation and reduction of the effect of its liquid phase (intercrystalline) on hardness. The control sample was characterize by a lower number of crystals, yet greater in size, thus forming coarsely-crystallized krupiec. A decrease in the size of crystals evoked by ultrasounds was also confirmed by visual observations. Irrespective of honey type, after 150 days of sonication the granulated honeys were more homogenous and, on average, by 40 N harder than the control samples. That effect results from finely-crystallized consistency of honeys. Thus, the study points to a significant thermal effect of ultrasounds treatment. Dissipation of wave energy did not result in the exceeding of the temperatures applied during decrystallization of honey. As demonstrated in research by Povey & Mason [1998], Bakier [2002a], and D'Arcy [2006], the effect of ultrasounds on sugar solutions is determined, among other things, by their concentration, viscosity, chemical composition, and affects the shape of crystals. Irrespective of differences in the effects of ultrasounds on saccharose and honey solutions, analogous modifications were observed in the course of crystallization. Uniform crystallization of sugars evoked by physical factors facilitated the formation of finely-crystallized structure typical of creamed honeys. A traditional technique of preparation of creamed honeys consists in long-term mechanical stirring of honey until the moment of crystallization. Sonication enables the initiation of the formation of a fine-grain crystalline structure in honey as a result of ultrasound treatment exclusively in the initial phase of the crystallization process.

Preservation of the biological activity of honey during its fluidization is an important issue from the technological and health-promoting point of view. Multiple fluidization of hard granulated honey (recrystallized honey) through its heating up poses a risk of its overheating and deterioration of its qualitative traits. The proposed parameters enable carrying out honey sonication at a low temperature and obtaining its finely-crystallized structure. It dose not affect the biological activity of honeys linked with rich chemical composition, of the so-called microelements in particular [Czaplicki, 2003; Niedźwiedzki, 2003].

SUMMARY

Based on the analyses carried out in the study it was demonstrated that ultrasounds with a frequency of 40 kHz and intensity of *ca*. 2 W/cm^2 modify the course of nucleation and crystallization in a standard solution of saccharose and in honeys. The structure of the forming liquid phase is determined by parameters of an ultrasound field. As demonstrated in the study, sonication of honeys with low-frequency ultrasounds modifies the course of monosaccharide crystallization and granulated honey formation. The ultrasound treatment results in - proportional to exposure time - a steady increase of its hardness linked with the increased number of fine crystals in the matter. In the case of polyfloral, lime and buckwheat honeys, the increase of hardness accounted for 30-40 N on average. Based on detailed results of analyses, it is possible to model honey crystallization so as to obtain its desired consistency by treatment with ultrasounds of low frequency and low or medium intensity without deteriorating the biological activity of honey. The finly-crystallized structure of honey obtained as a result of sonication should be claimed as desirable due to its appearance and spreadability.

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WPŁYW SONIKACJI NA KRYSTALIZACJĘ MIODÓW

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Przeprowadzono badania wpływu sonikacji miodu pszczelego na przebieg krystalizacji podczas przechowywania. Zastosowano ultradźwięki o częstotliwości 40 kHz i natężeniu ok. 2 W/cm^2. Zakres badań obejmował cechy fizykochemicznych takie jak: lepkość, tekstura, kondunktancja, stopień krystalizacji. W roztworze bezpośrednio po 30 min sonikacji obserwowano wzrost lepkości o ok. 30 mPa/s, obniżenie kondunktancji o 0,6 mS/cm. Badania tekstury (twardości) miodu poddanego sonikacji wykazały początkowo wzrost twardości, a następnie stabilizację lub wręcz lekkie jej obniżenie w porównaniu do prób kontrolnych. Stopień krystalizacji był proporcjonalny do czasu trwania sonikacji. Największe kryształy obserwowano w próbkach niesonikowanych. Sonikacja istotnie modyfikowała proces krystalizacji z badanych roztworów cukrów. Obserwacje roztworów po sonikacji wykazały powstawanie dużej liczby kryształów w całej objętości próbki, podczas gdy roztwory niesonikowane krystalizowały nierównomiernie z wytwarzaniem dużych kryształów. Stwierdzono, że obróbka ultradźwiękowa modyfikowała przebieg rekrystalizacji, a w efekcie – teksturę rekrystalizowanych miodów obniżając ich twardość.