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DESCRIPTION OF PHENOMENA OCCURRING DURING THE HEATING OF CRYSTALLIZED HONEY

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A b s t r a c t. This paper describes processes that occur in the structure of crystallized honey exposed to heat treatment. Shearing-type refractometry in reflected light and a heating table were used to directly view the changes occurring when honey crystals were undergoing melting. As a result of the study it was found that the fastest rate of honey melting occurred between 40 and 50°C. This notwithstanding, at high temperatures in excess of 83°C crystalline structures do occur, the crystals having been termed fibrous crystals. A quantitative description of those structures was made, together with a detailed determination of quantitative characteristics using imaging software. The results of that analysis allow the choice of a filtration medium for the removal of all crystalline structures from liquid honey.

K e y w o r d s: bee honey crystals, birefringence, fibrous crystals

INTRODUCTION

Heating is the basic processing treatment of bee honey. The principal objective of heating is to change the state of the product from solid to liquid. Additionally, when properly combined with filtration, it prolongs the re-crystallization of honey [11]. The effect of heating and filtration on honey re-crystallization has been generally recognized for all long time. Based on those two treatments, a number of methods were developed which are devised to maximize the duration of the liquid state of the product. For instance, there is a method that consists in the filtration of honey through a quartz deposit while it undergoes heating [6]. It allows the separation of alien intrusions and air bubbles. Another method recommends heating honey up to 77°C for 5 min. and, subsequently, filtering it carefully and cooling down rapidly to room temperature [4]. There is yet another approach to honey processing that makes honey stay liquid for a long time, a method that additionally makes use of small quantities of water being added at the initial heating stage to facilitate the dissolution of crystals [8]. The above examples show that in liquid honey (even that heated up to 77°C) there are inclusions that have to be removed because they make honey crystallize rapidly. It is often remarked that among those inclusions are external additions such as pollen grains and air bubbles, or alien intrusions such as dust grains [11]. Other reports comment on undissolved glucose crystals [1] that provide nuclei of crystallization. It is borne out by the observations of the remains left on the membrane after filtration. Their main portion always consists of viscous and stringy precipitation, usually light in colour, with all the other remains on top of it. If filtration is omitted, those substances come to the surface and form white foam once honey has been cooled down [2]. Similar structures were identified in different food products, for example in condensed apple juice [3] and milk [12].

The study was an attempt to investigate the phenomena that occur during the heat-processing of honey through direct observation of the changes in honey crystalline structure. Crystalline objects that fail to melt at high temperatures were identified. Their qualitative and quantitative characterization was performed.

MATERIAL AND METHODS

Granulated forms of the following honey varieties were used in the study: rapeseed honey, linden honey, conifer honeydew honey, buckwheat honey, multifloral honey and heather honey. It must be stressed that the honey had not been heated prior to the study. The water content of honey was measured by means of the refraction coefficient as determined using an Abbe refractometer.

To obtain images of the crystalline structure of honey, birefringent interferometry was used as described in detail by Pluta [10]. The method makes use of the interference effect occurring in the polarizer-birefringent plate-analyzer system. The role of the birefringent plate was performed by honey crystals present in a thin layer between two cover slips. Honey structures were viewed in white light with the polarizer and the analyzer positioned crosswise. The investigations were performed using an NU optical microscope equipped with a heater stage of a special design. It permitted samples to be heated to a temperature above 90°C. The study consisted in direct viewing of a heat-processed granulated honey sample contained between two microscopic slides. The distance between the slides was defined by a thermocouple that measured temperature changes in the layer of melting honey. The temperature measurements were taken using a NiCr-NiAl thermocouple 0.5 mm in diameter. The second thermocouple was placed in a thermos bottle with ice-water mixture and it provided the reference temperature.

The investigations were run over a wide range of temperatures from 18.5°C to 83°C. Heat treatment for the study was performed using two methods:

- the first method, that can be described as dynamic, consisted in placing the sample on a heated surface and examining the changes of the structure during rapid heating
- the second approach, that can be termed static, was effected by exposing a sample placed on the heated table to a constant temperature for 30 minutes.

The idea behind the second method was to offset the effect of time on the amount of the solid phase at a given temperature. The heating time of 30 min was adopted, based on the results of an additional experiment. Samples of the same honey were placed in tightly sealed jars weighing 0.5 kg each and heated in a laboratory incubator for 24 hrs. Heat treatment was carried out in the respective temperatures of 40, 50, 60, 70, 80°C. Once heated, the samples were collected from the jars and placed on microscope slides, and their structure was viewed at the same temperature as that used in the incubator. When the images were compared, the samples heated for 30 min. were found not to differ in structure from those heated for 24 hr in the incubator.

The observations of high temperature-exposed honey allowed the identification of peculiar elongated crystalline structures. Quantitative geometrical analysis of those structures was performed using the image processing software Microscan v. 5 for detailed quantitative description of the objects observed. The following geometric parameters of identified crystals were used in the analysis: surface area, perimeter, thickness (measured at 5 positions), equivalent diameter (diameter of the circle the area of which is equal to the area of the crystal).

RESULTS

The pattern of changes in honey structure is shown in photo 1 as a sequence of several photographs of granulated rapeseed honey. The structure of the same honey, heat-treated at constant temperatures of 40 and 50°C for 30 min., is shown in photo 2. The photographs of honey samples following a 24-hour heat treatment in the incubator are shown in photo 3. Subsequently, an extensive account was given of the observations made during the heating of honey. In the further part of photo 4, several photographs of crystalline objects fibrous in structure are shown, viewed at a high temperature. The results of the detailed computer analysis of such 20 objects are listed in table 1.

The process of “dynamic” heat treatment of granulated rapeseed honey is shown in photo 1, at the top. The photographs are accompanied by temperature information. The heating was dynamic (method 1), so the exposure of honey to a given temperature was short. As the treatment temperature increased, there was a growth of the dark field area in the images.

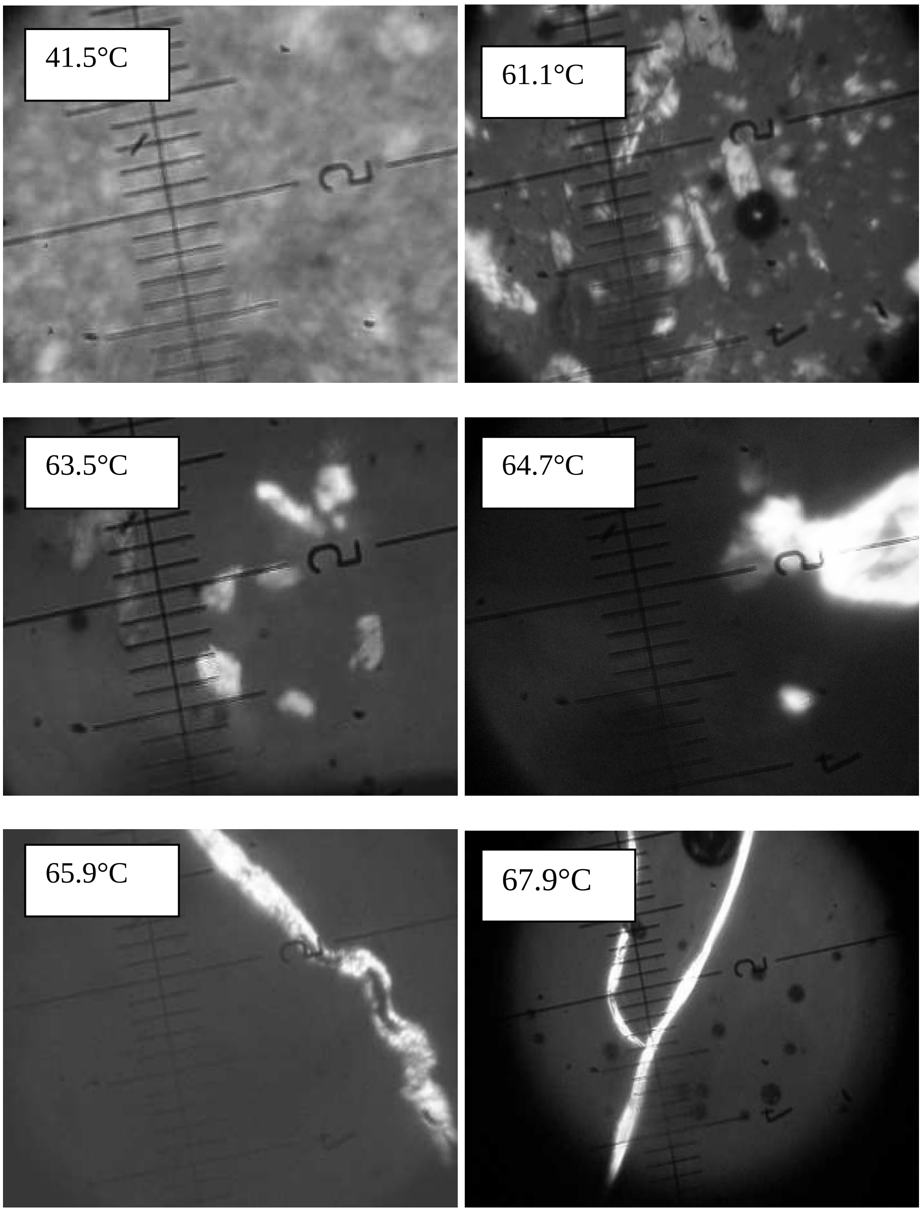

Photo 1. Changes in the structure of granulated rapeseed honey during heat treatment

It reflects the transition from crystalline structure – characterized by optical birefringence – to isotropic liquid state. At a temperature of 41.5°C there is no appreciable loss of the solid state yet. It is only at temperatures above 50°C that considerable melting occurred. At a temperature of 61.1°C there still remained a large number of flaky crystals. At 64.7°C those crystals occurred but sporadically. The crystalline structure was not eliminated completely by further heating. Novel formations emerged which could be termed fibrous crystals. In the last two photographs there are examples of such a structure. Frequently, they took on the shape of twisted or ramified fibers that made up a small percentage of the total heat-processed product. Analogous measurements carried out for other honey samples confirmed the occurrence of such structures.

In photo 2 there are two images of rapeseed honey heat-treated at temperatures of 41.5°C and 50.1°C for 30 min on the microscope stage. By judging them against those presented earlier, it can be clearly seen that the duration of heating has an appreciable effect on the amount of solid phase. It is particularly manifest when the image taken at 50.1°C (photo 2) is compared with that taken at 61.1°C shown in photo 1. Analogous observations made for other honey varieties confirmed the effect of the duration of heating on structural changes.

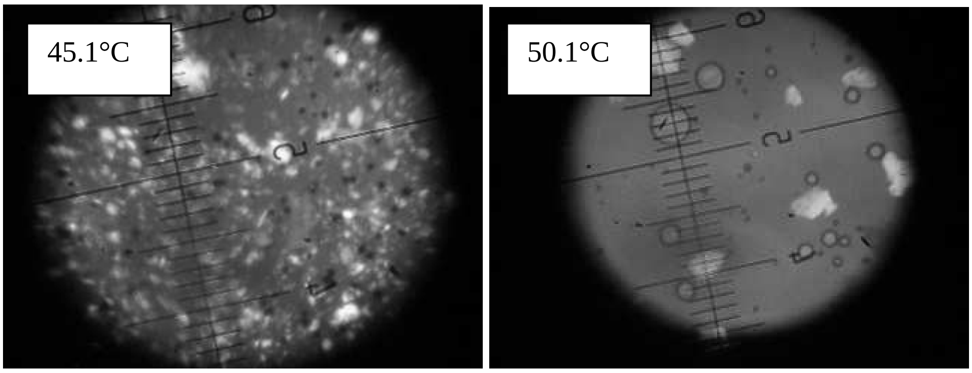

Photo 2. Images of rapeseed honey structure following heat treatment at 45.1°C and 50.1°C for 30 min

The structure of rapeseed honey obtained following heat treatment at 45°C and 50°C for 24 hr in the incubator is shown in the images of photo 3. When compared with the analogous images of honey heat-treated on the microscope stage for 30 min., those images were found not to differ qualitatively. Because of that, the main part of the study involved observations of honey samples heat-treated for 30 min. on the heater stage of the microscope.

The results of the study furnished evidence that intensive meltdown of honey crystals occurred between 40 and 50°C, which was in agreement with reports in literature [7,9]. Vestigial flaky crystals persisted in small amounts up to the temperature of 60°C, even with the heating process lasting for 24 hr. That fact gives rise to problems with the determination of the accurate temperature at which the crystal melting process is completed. The speed with which the structure of different honey varieties melts down is similar. It was found that small crystals melt faster, whereas the large ones lose weight at a much slower rate. The melting tests of different honey varieties showed that honey origin had little effect on the melting temperature. However, it was noticed that the melting rate was affected by the water content of honey. The crystals from samples with a higher water content were found to melt more rapidly. However, a more precise determination of the effect of water content on the melting rate requires some additional investigations. None-the-less, addition of water to speed up and to facilitate liquefaction of honey seems to be an effective approach to make the honey melt faster as is shown by the method of Kranz [8].

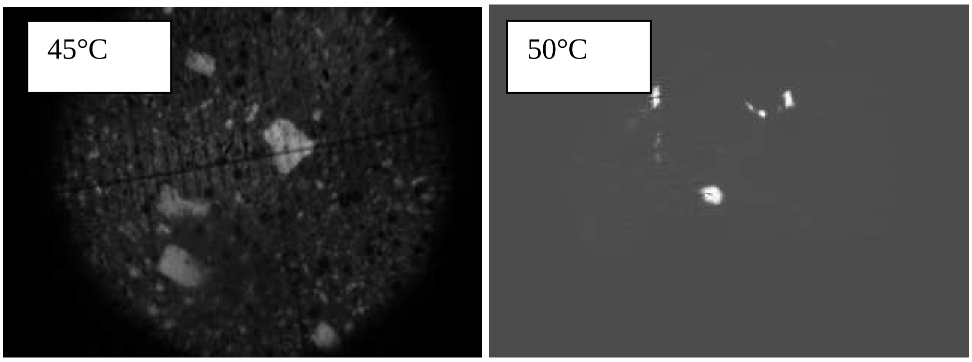

Photo 3. Images of rapeseed honey samples heat-treated in containers placed for 30 min in the incubator set at 45°C and 50°C

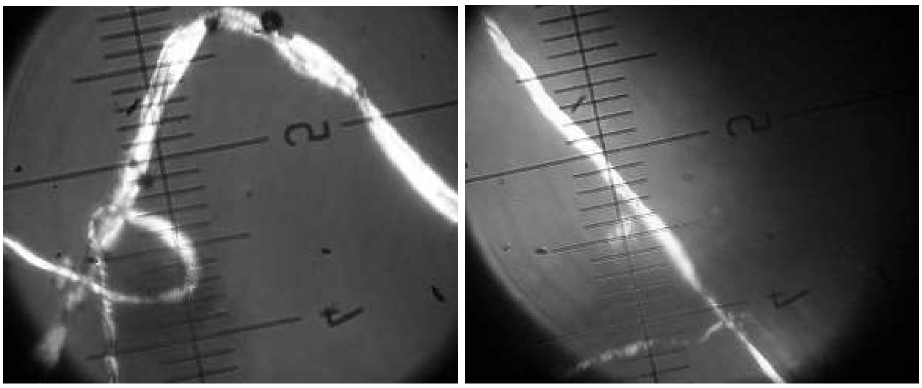

Photo. 4. Images of fibrous crystals identified in honey exposed to high temperatures

At higher temperatures, the presence of fibrous crystals was found in all honey varieties. Images of those crystals are shown in photo 4 and, earlier on, in photo 1. It should be emphasized that those objects are crystals. The proof of it is in the fact that they glow when viewed with the use of the polarizer and the analyzer, and that they show the characteristic features of birefringence. Additionally, a simple experiment consisting in introducing a few drops of water between the slides demonstrates that those crystals disappear fast by dissolving in water. It is those objects that have to be removed from honey by filtration because, as demonstrated by research, they fail to melt even at 83.3°C. By analyzing the geometrical dimensions of fibrous crystals one can determine the mesh of the sieve or the parameters of the filtration membrane to be used to separate them from liquid honey.

Further down in the text, in table 1, there are detailed descriptions of 20 instances of fibrous crystals identified in heated honey of different origin. It must be emphasized that up to 60°C fibrous crystals in honey are accompanied by few remaining flaky crystals. At very high temperatures above 60°C., though, only fibrous objects were observed. Generally, their length was several dozen times their width reaching a macroscopic size as large as a few millimeters. The longest identified object was 1.67 mm long. By moving the slides it can be seen that the crystals are slender and that they easily bend without breaking. Detailed observation of the fibrous crystals under the microscope furnished evidence that, most frequently, their shape is that of narrow twisted ribbons. sometimes being rod- or, less frequently, bar-shaped. They are extremely heat-resistant. They could not be melted even with the temperature of honey raised to 85°C. Due to that reason they ought to be removed from honey by filtration. Their separation requires the use of a filtration medium with mesh size lower than the transverse section of the smallest object, the relevant value found in the study being 10.36 μm. None-the-less, the elongated shape and various “barbs” on the surface more likely than not facilitate separation of those objects from liquid honey. It must be borne in mind that the large area of fibrous objects as related to their transverse dimension may result in rapid clogging of a sieve-type filtration medium. Because of that, it seems justified to use a spatial medium such as quartz sand [6] or diatomaceous earth [1]. It is also possible to employ spiral polymeric membranes as in the clarification of sugarcane juice [5]. It facilitates intercepting long structures in labyrinthine channels of the filtration deposit as well as increases the life of the medium.

Table 1. Geometric parameters of fibrous crystals arising in honey of different origin exposed to high temperature

No. of measurement	Crystal surface area	Crystal perimeter	Transverse dimension (thickness) of fibrous crystal measured at five different positions					Crystal equivalent diameter
	μm^2	µm	µm					µm
			1	2	3	4	5	
1	28600	2794	21.85	21.21	29.25	23.16	24.18	190.8
2	25520	1783	32.40	39.22	35.67	45.01	40.04	180.3
3	13163	1782	15.38	12.9	11.05	14.36	10.36	129.5
4	9724	1729	13.38	20.29	19.92	10.29	14.56	111.3
5	26790	3401	35.44	31.41	34.01	14.04	35.01	184.7
6	55560	1987	37.00	40.88	34.49	36.93	47.23	265.9
7	10052	1755	12.21	18.00	15.57	12.38	16.28	113.1
8	10233	2006	15.33	20.63	22.37	20.66	14.43	114.1
9	20260	1562	36.64	44.32	36.63	40.62	40.96	160.6
10	9542	1635	18.70	19.37	18.02	18.23	15.94	110.2
11	6441	1375	11.29	11.85	14.26	18.31	15.93	90.56
12	14265	1825	26.6	26.77	27.98	35.50	25.89	134.8
13	9618	1048	23.16	25.42	16.33	18.15	15.35	110.7
14	13297	1654	26.89	25.87	24.81	19.73	21.76	130.1
15	12491	1834	22.07	18.75	16.98	19.95	18.82	126.1
16	15205	1344	46.21	32.00	41.21	29.54	31.98	139.1
17	4556	1056	12.6	13.48	16.77	13.22	13.54	76.17
18	7812	1348	11.38	14.50	14.12	19.68	16.20	99.7
19	10998	1506	28.39	31.58	27.82	27.02	30.36	118.3
20	21910	1380	49.72	50.26	33.31	50.75	48.45	167.0

DISCUSSION AND CONCLUSIONS

To sum up the study, the following conclusions can be drawn:

1. It is difficult to determine a single melting temperature for honey, since exposure to as high a temperature as 83°C fails to destroy all the crystals. The melting process is most intensive at temperatures from 40 to 50°C with not all flake crystals melting at that temperature.

2. The duration of heating is also of importance in the process of phase transition. The results show that honey cannot be melted by simply heating it up to a certain temperature. It must be maintained at that temperature for some time. The results show that after honey has remained for 30 min at a given temperature, thermo-dynamic equilibrium sets in and the remaining crystals cease to melt.

3. Temperature-resistant fibrous crystals are formed as honey is exposed to heating. They have the structure of twisted fibers or they are shaped as narrow bars or ribbons. Those crystals do not break upon bending. They are few and occur in all honey varieties.

4. In order to free the honey of fibrous crystals it must be mechanically purified by filtration or sedimentation. Based on the dimensions and shapes of the fibrous crystals, especially on their transverse dimensions the mesh size of the filtration element required for complete separation can be precisely determined.

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OPIS ZJAWISK ZACHODZĄCYCH W TRAKCIE OGRZEWANIA MIODU SKRYSTALIZOWANEGO

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Streszczenie. W pracy przedstawiono wyniki badań procesów zachodzących w strukturze miodu skrystalizowanego w trakcie ogrzewania. Wykorzystując interferometrię birefrakcyjną w świetle odbitym oraz stolik grzewczy obserwowano bezpośrednio zmiany zachodzące w trakcie topienia się kryształów miodu. W wyniku badań stwierdzono. iż najintensywniej miód się topi w przedziale temperatury od 40 do 50°C. Niemniej w wysokiej temperaturze nawet powyżej 83°C występują zawsze struktury krystaliczne, które nazwano kryształami włóknistymi. Przeprowadzono opis jakościowy tych struktur oraz szczegółową charakterystykę ilościową z wykorzystaniem komputerowego programu do obróbki obrazu. Wyniki tej analizy pozwalają dobrać parametry przegrody filtracyjnej, która umożliwia usunięcie wszystkich struktur krystalicznych z płynnego miodu.

Słowa kluczowe: kryształy miodu pszczelego, dwójłomność optyczna, kryształy włókniste