Impact of Microwave Heating on Hydroxymethylfurfural Content in Czech Honeys

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Abstract

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As far as honey is concerned, microwave oven heating finds its use especially for crystallised honey reliquefying. We focused on monitoring the changes in hydroxymethylfurfural content which is an indicator of heat damage done to honey, among others. Microwave honey heating was carried out in four degrees of microwave power levels over seven variously long time periods. In total, 22 analysed honey samples came directly from bee-keepers from the Czech Republic from the 2004 and 2006 harvests. Hydroxymethylfurfural content was determined by HPLC method using a liquid chromatograph Alliance 2695 with a PDA detector 2996. We obtained relatively interesting results: despite the honey having reached relatively high temperature levels (80–90°C) at the highest power levels and the longest time periods, there was no gradual significant increase in hydroxymethylfurfural content which could be expected at conventional heating. On the other hand, hydroxymethylfurfural content varied in the course of heating of the individual samples, which is a very interesting result. A significant role was played also by the botanic origin of the honeys because the course of the changes in hydroxymethylfurfural content due to microwave heating was not the same in all honeys analysed.

Keywords: honey; hydroxymethylfurfural; HMF; microwave heating

Hydroxymethylfurfural (HMF) content is one of the most important quality parameters of the quality and health safety of honey. This cyclic aldehyde develops in honey either by hexose dehydration (glucose and fructose) in acidic environment or as a result of Maillard's reaction. HMF content in fresh honey is very low or nonexistent, its concentration increases in the course of storing (in relation to pH, the length of storing) and also in the course of the honey heating. Therefore, HMF content can serve to judge the honey freshness and also the potential unsuitable treatment when processing and storing honey, the time when this dietetically important food can be depreciated. HMF content is limited in the Czech and European legislation by the value of 40 mg/kg (Kubiš & Ingr 1998; Wunderlin *et al.* 1998; Council Directive 2001/110/EC; Decree No. 76/2003 Coll.).

In recent years, microwave heating has become a common method for heat treatment of food. Microwave ovens find a broad range of application not only in households but also in industry. Compared

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with conventional heating, microwave technology offers a number of advantages, including shorter intervals of heating, which helps save energy, and space-saving compactness of the microwave equipment. Combined with the ease and comfort of use, the above given benefits are at present significant reasons for microwave heating.

A number of studies are under way to elucidate comprehensively the processes taking place in food exposed to microwave radiation. Microwaves are known to belong to a broad group of electromagnetic waves in the frequency range from 300 MHz to 300 GHz. In the Czech Republic, the 2450 MHz frequency is the only one registered for use in food applications. In some EU states, an alternative frequency for food applications is 915 MHz (Houšová *et al.* 1999). When food is exposed to electromagnetic waves at a microwave frequency, food components capable of producing dipoles (water, salts, etc.) try to orientate themselves by the electric field. The polarity of the high frequency electromagnetic field changes more than 10^9 times per second. The attempts to conform to the constantly changing conditions produce vibrations accompanied by collisions and friction between neighbouring molecules, and this generates heat. The above described heating effect is the only one effect of microwaves on food demonstrated up to now. At present, the effects of microwave radiation on individual food ingredients, and also any changes in the nutritional value of food compared with conventional heating, are being investigated (Hebbar *et al.* 2003).

Since honey contains a substantial amount of water (about 20%) as well as large amounts of dissolved saccharides (70–80%), microwave radiation could be effectively used for heating honey (Hebbar *et al.* 2003). While this system of the heat treatment may seem simple and comfortable, we still need to answer the question whether microwave radiation might have a negative effect on the honey quality. It is generally acknowledged that high temperatures used in reliquefying honey will destroy the thermolabile nutritionally important substances contained in honey.

Bath and Singh (2001) report that in the past no significant changes in pH and total acidity, and ash, glucose, fructose, and sucrose contents of honey were seen during microwave heating. These authors then reported in their papers (1999 and 2001) that in two Indian honey types, HMF developed due to microwave heating, growing in volume with the increasing power of the microwave ovens and prolonged time of microwave heating. Similar results on the gradual development of HMF due to microwave heating of Indian forest honey were obtained also by Hebbar *et al.* (2003).

Our study was aimed at the monitoring of the dynamics of hydroxymethylfurfural content due to microwave heating of several types of Czech honey.

MATERIAL AND METHODS

Samples of honey. In this study, a total of 22 honey samples were investigated which came directly from Czech bee-keepers from the harvest of 2004 (12 samples) and of 2006 (10 samples). HMF content analysis and microwave heating were carried out

Table 1. The 2004 and 2006 harvest honey characteristics

	HMF (mg/kg)	Water (%)	Conductivity (mS/m)
2004			
Helianthus sp. + *Robinia* sp.	5.87	17.5	48.9
Helianthus sp. + *Brassica* sp.	6.70	18.3	35.2
Tilia sp. + *Helianthus* sp.	6.80	20.6	42.2
Brassica sp.	6.16	18.1	48.9
Brassica sp. + *Robinia* sp.	9.88	19.3	44.2
Brassica sp.	3.90	19.6	67.7
Brassica sp.	5.81	19.6	48.5
Forest	0.16	17.2	64.0
Honeydew	3.77	17.5	95.2
Honeydew	4.05	17.0	132.1
Trifolium sp. + *Robinia* sp.	6.73	19.8	54.6
Robinia sp. + *Tilia* sp.	7.11	19.1	73.6
2006			
Tilia sp.	2.09	19.9	64.8
Helianthus sp.	2.81	18.5	34.3
Brassica sp.	2.33	19.7	17.7
Multifloral	1.69	18.9	61.8
Multifloral	5.51	17.9	47.2
Forest	2.49	18.0	78.0
Robinia sp. + Forest	0.51	21.5	19.0
Helianthus sp. + *Trifolium* sp.	3.43	18.0	40.4
Robinia sp.	22.84	16.7	10.4
Carthamus tinctorius L.	17.04	18.6	46.8

always in the course of summer in the following year, i.e. in summers 2005 and 2007. The honeys were stored in a shaded area in well enclosed glass containers in volumes of 900–1000 g at the laboratory temperature.

The honey samples were characterised by their botanic origin, based on the information from the bee-keepers that are in most cases very well informed as to the botanic origin of their honey (we confirmed that in our earlier study by Bartáková *et al.* (2007)). In the samples from the 2004 harvest, the botanic origin was also confirmed by a simplified pollen analysis: after dissolving honey in distilled water and subsequent centrifugation, the dominant pollens were determined by the plant species or species groups in the sediments formed using a microscope .

The characteristics of the analysed honeys given by the basic physical and chemical parameters (water content, conductivity and HMF content before microwave heating) are presented in Table 1.

Treating honey with microwave heating. Each honey sample was divided up into doses of 65.0 g which were put into 12 or 14 beakers of the volume of 100 ml. One of these samples was used to determine the initial HMF content. The remaining samples were treated with microwave heating in

Table 2. Microwave heating treatment and HMF content in the 2004 and 2006 harvest honeys

Power settings (W)	Heating interval (s)	Attained temperature (°C)*	HMF content (mg/kg)			
			average	SD	maximum	minimum
2004						
	unheated	–	5.58	2.29	9.88	0.16
90	15	28	5.80	2.33	9.82	0.14
	30	38	5.87	2.40	10.40	0.18
	45	42	5.89	2.36	9.88	0.11
350	15	52	5.81	2.46	10.81	0.20
	30	65	4.25	1.99	8.95	0.20
	45	77	3.17	1.90	6.32	0.11
500	15	54	5.44	2.37	10.27	0.10
	30	74	2.50	1.44	6.23	0.16
	45	93	3.04	1.48	6.69	0.85
800	15	55	4.65	1.78	6.57	0.17
	30	90	2.95	1.67	6.74	0.00
2006						
	unheated	–	6.07	7.16	22.84	0.51
90	60	47	5.68	6.97	23.34	0.41
	120	63	4.70	6.46	22.96	0.36
	180	81	4.87	6.91	24.14	0.29
	240	95	8.79	9.26	26.15	0.35
350	15	51	5.59	7.08	23.19	0.40
	30	65	4.75	6.74	23.51	0.35
	45	75	4.74	6.71	23.48	0.30
	60	93	8.46	9.40	27.52	0.50
500	15	55	5.33	6.88	23.17	0.36
	30	74	4.67	6.65	23.38	0.34
	45	92	7.30	8.01	24.97	0.42
800	15	55	5.36	6.92	22.95	0.37
	30	88	6.65	7.66	24.88	0.41

*SD (Standard deviation) 1–3°C

a microwave oven (Whirlpool MW 201, made in USA) at a certain level of power and time period according the Table 2.

Microwave heating of the honey from the 2004 harvest was our pilot study for this topic. We set the power based on the power range of the above mentioned microwave oven, the interval of heating used being the same for all power settings. This was not possible only with the highest power setting of 800 W, 30 s had to remain as the heating duration limit because if a longer interval had been used with the power set at 800 W, honey would have formed froth and started spilling over from the beaker.

In microwave heating of the 2006 harvest honeys, we modified the length of honey heating at the power levels of 90 W and 350 W so as there would be a gradual increase of the honey temperature and the longest heating interval at every power would be limit, i.e. the result was total liquefaction of the honey and froth formation in many cases. In the power settings at 500 W and 800 W, the given heating intervals already met these requirements.

After heating, honey samples were immediately stirred with a piercing probe also measuring the honey temperature at the same time. Later on, they were left to cool at the laboratory temperature, and then their HMF content was determined.

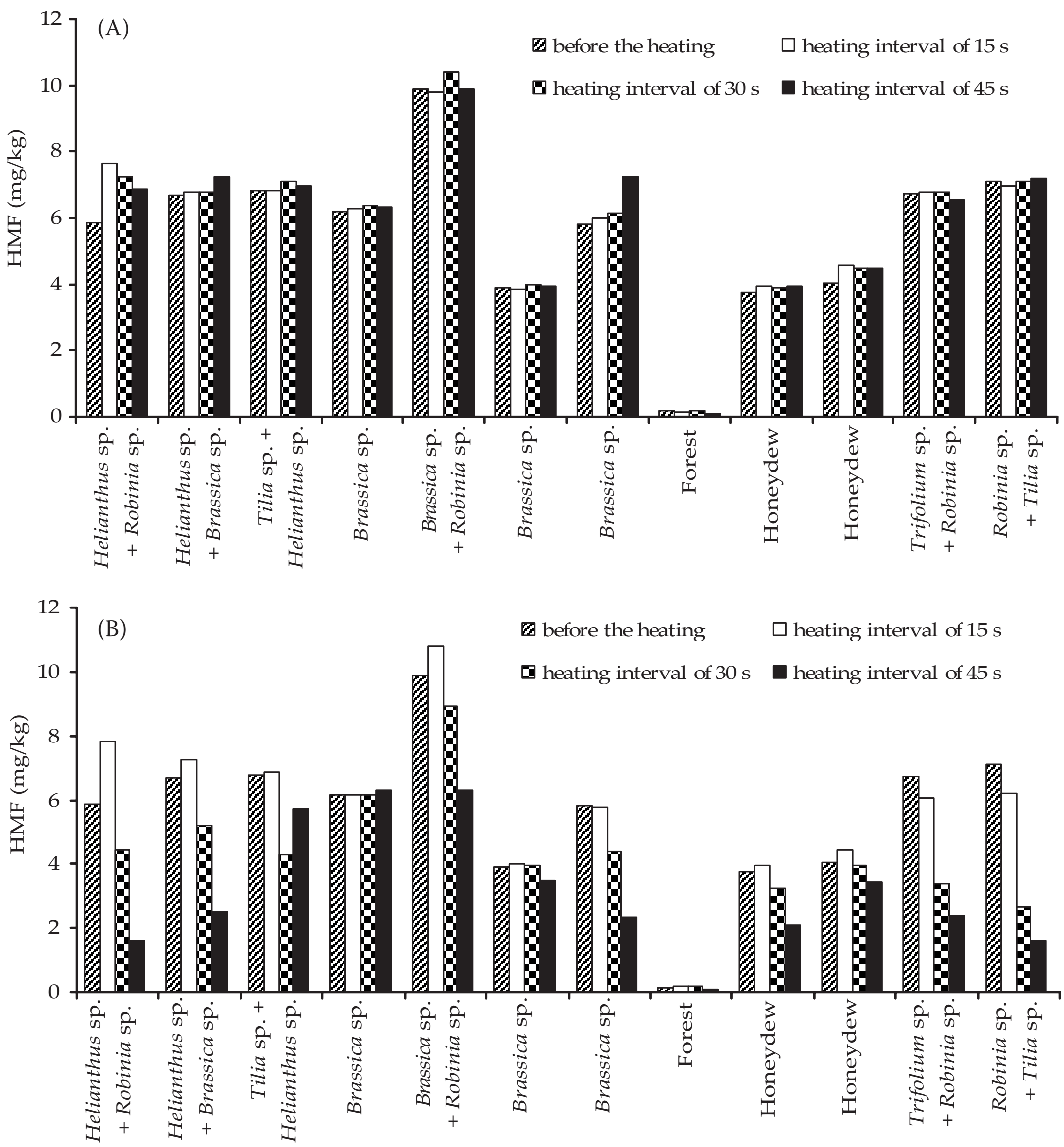

Figure 1. HMF content in honeys from the 2004 harvest before and after microwave heating at the power setting of 90 W (A) and 350 W (B)

HMF content determination. Hydroxymethylfurfural content in honey was determined using the HPLC method which is listed in the Harmonised methods of the European Honey Commission (Bogdanov *et al.* 1997). We used a liquid chromatographer Alliance 2695 with PDA detector 2996 (Waters, Milford, USA) and a ZORBAX Eclipse XDB-C18, 4.6 × 150 mm, 5 µm column (Agilent Technologie, Santa Clara, USA). The method was modified slightly in such way that instead of using an isocratic ordering, gradient one was used where the ratio of the mobile phases (water and methanol) was 90:10 from the start of the sixth minute of the analysis, switching to 50:50 from the seventh to the eleventh minute, which provided for the elution of all components of the honey sample analysed. Up to the end of the twentieth minute, the ratio of the mobile phases (water and methanol) then changed back to 90:10 and it remained like that until the end of the analysis of the given honey sample (until the sixteenth minute). When assessing the results, HMF was used as external standard. For every sample, two parallel measurements were performed.

RESULTS AND DISCUSSION

The overall results of HMF formation in the analysed honeys due to microwave heating are pre-

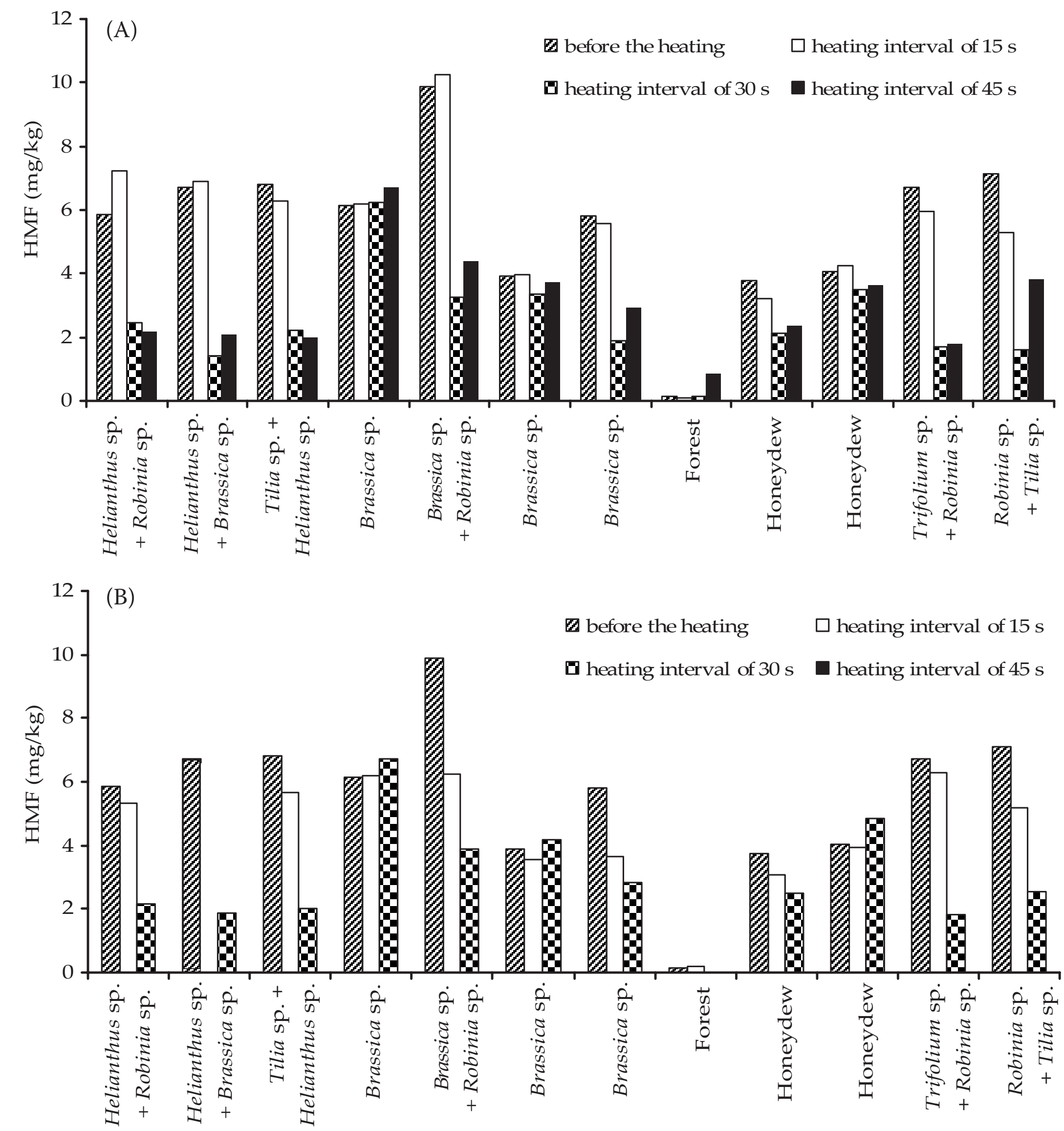

Figure 2. HMF content in honeys from the 2004 harvest before and after microwave heating at the power setting of 500 W (A) and 800 W (B)

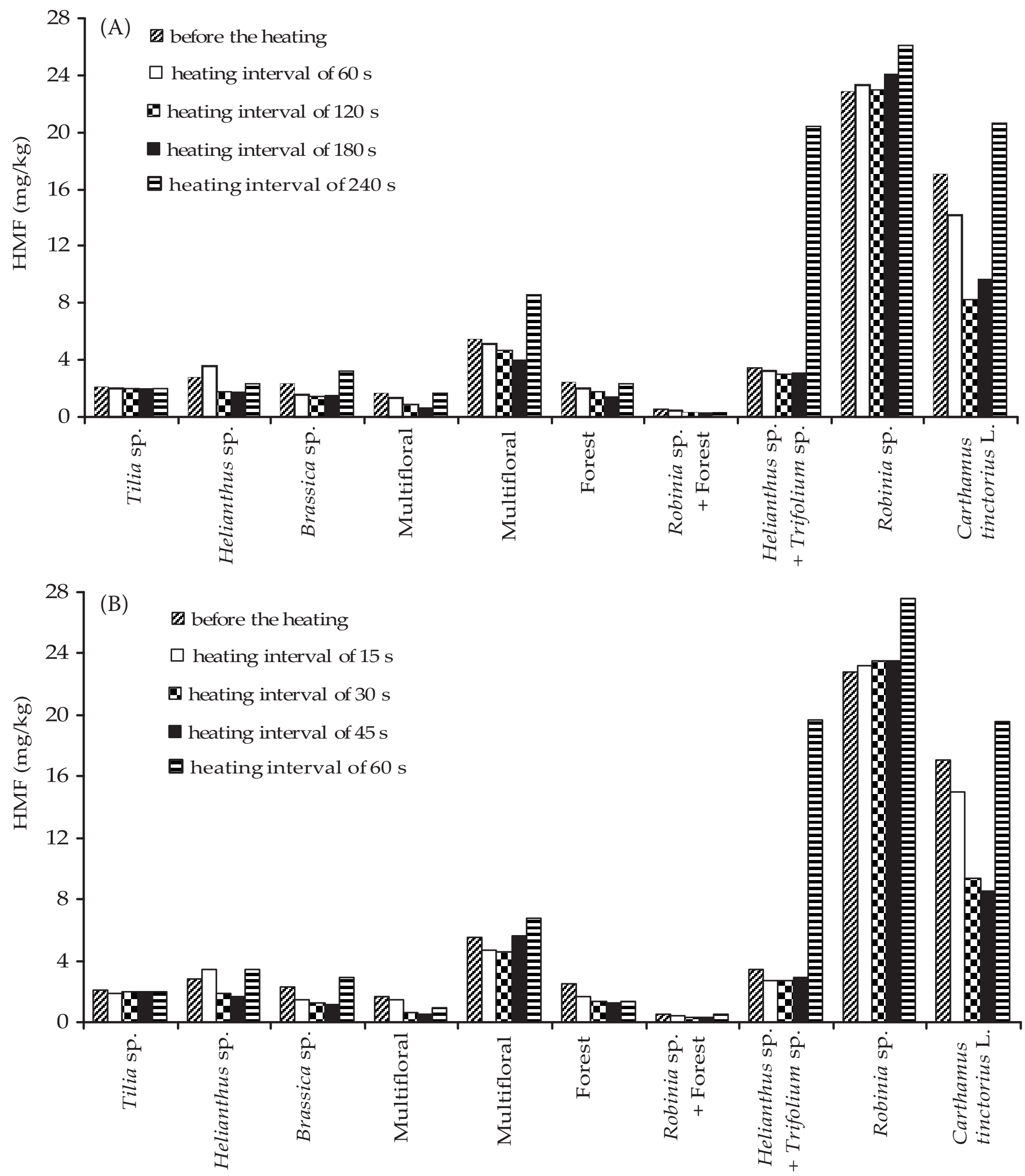

Figure 3. HMF content in honeys from the 2006 harvest before and after microwave heating at the power setting of 90 W (A) and 350 W (B) (for better clarity, an enlarged insert is placed in the figure, containing honey samples with low HMF contents – from *Tilia* to *Robinia*-Forest honeys)

sented in Table 2. HMF formation in the individual honey samples is also depicted in Figures 1–4. It is obvious that during microwave heating, together with simultaneous increase in the power used and lengthening interval of heating, no gradual increase occurred in HMF content, as could be expected with conventional heating. On the contrary, HMF content decreased and increased to various levels in the course of heating of the individual samples, which is a very interesting result. However, none of these changes was statistically significant in the end because variations in HMF content due to microwave heating took place in the separate honeys analysed in various ways. The figures make it clear that a significant role in the HMF content changes due to microwave heating is played not only by the power setting and heating interval used but also by the botanic origin of the honey, which corresponds with the conclusions of Bath and Singh (2001) whose two Indian honeys analysed (*Helianthus annuus* and *Eucalyptus lanceolatus*) displayed various HMF formation levels under similar microwave heating conditions. As

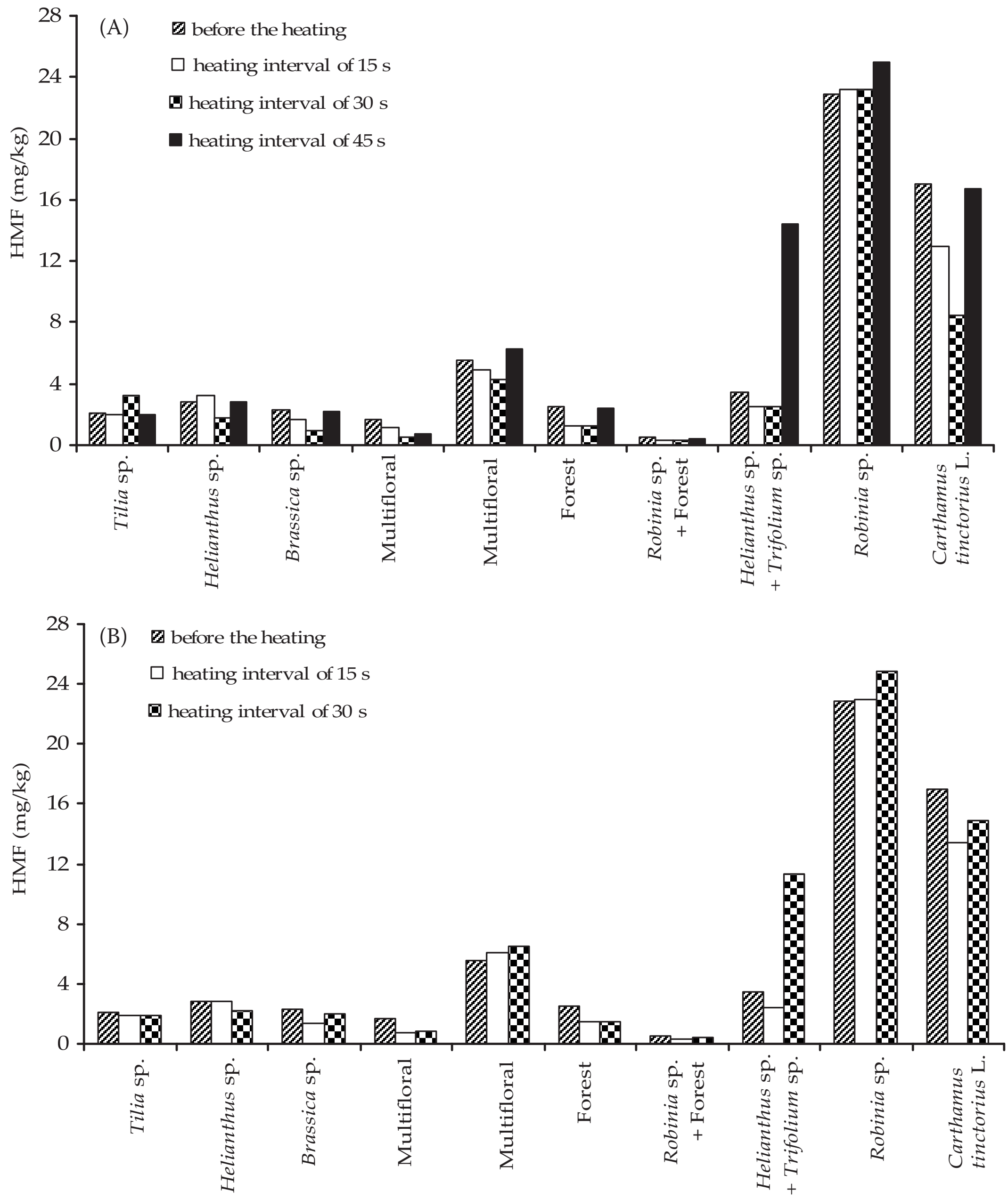

Figure 4. HMF content in honeys from the 2006 harvest before and after microwave heating at the power setting of 500 W (A) and 800 W (B) (for better clarity, an enlarged insert is placed in the figure, containing honey samples with low HMF contents – from *Tilia* to *Robinia*-Forest honeys)

opposed to our results, however, these authors found out that the formation of HMF gradually increased with the increase in microwave power levels and heating duration. However, these authors used only lower power levels of the microwave oven – 70 W, 140 W, 210 W, and 280 W applied for 1, 2, 3, and 4 minutes. Similarly, Hebbar *et al.* (2003) reported that the higher the power level and the longer the interval of microwave heating were used, the more HMF formed in honey. These authors did not detect any decrease in HMF content although they used a similar range of the microwave oven power (175–800 W) and length of microwave heating (15–90 s) as were used in our experiments. The variance in the results may have been caused by the fact that both latter publications came from India analysing honeys from bee species of the *Apis dorsata* genus while in our experiments Czech honeys were analysed coming from bees of the *Apis mellifera* genus. It is obvious that also the botanic origins of the honeys used were different.

As becomes clear from the text above, HMF formation due to microwave heating did not take place in the individual honeys in the same way. Figures 1–4 show that the changes in HMF content due to microwave heating depend to a larger extent on the initial HMF content before heating and on the honey type. The concentration of HMF was impacted by microwave heating more significantly in the honeys from *Carthamus tinctorius* L., *Brassica* sp., *Helianthus* sp. or *Trifolium* sp. What happened was that with some heating methods, there was a change in HMF content as much as by 100% while HMF concentration in honeydew or *Tilia* honeys appeared to be more resistant to microwave treatment. By saying that there was a change in HMF content by as much as 100%, the meaning is that there is a decrease in HMF concentration at medium length heating times (120 s and 180 s at the power level of 90 W, 30 s, and 45 s at the power level of 350 W and 15 s and 30 s at the power levels of 500 W) while the longest heating times at all power setting levels did not cause major changes in HMF content although the honeys were warmed to temperatures ranged from 80°C to 90°C. The only exception was *Helianthus-Trifolium* honey whose HMF content grew very significantly due to the longest heating times at the power levels used, in some cases as much as three times more.

Another interesting thing is that the course of the HMF concentration change at the given power levels used was very similar in all honey types (with the exception of the 90 W power setting in the harvest 2004 honeys – their heating times did not exert such effects on honey as at the other power levels), e.g. the already mentioned increase in HMF concentration in *Helianthus-Trifolium* honey (from the 2006 harvest) at the longest heating time took place at 90 W, 350 W as well as 500 W and, to a lesser degree, also at 800 W. Also, a significant drop in HMF content in the honey from *Carthamus tinctorius* L. (from the 2006 harvest) at medium heating times took place also at three levels of the power settings, namely 90 W, 350 W, and 500 W, while with the longest heating times at these three levels, the HMF content changed only very little as compared to the initial level.

As far as the consistency of the analysed honeys is concerned, one can generalise that the honeys reliquefied and turned browner due to microwave heating: the longer the heating interval at the given heating level, the greater the reliquefaction and browning. Crystallisation of honey was suppressed by the microwaves because the honeys stayed liquid at least a year and a half after reliquefaction.

CONCLUSIONS

The results of this study indicate that HMF could be dissolved with microwave radiation which would change the HMF role into somewhat as an indicator of overheating and thus also of the damage done to honey when using microwave heating for the thermal honey treatment. As it is clear from our previous research (Bartáková *et al.* 2008), market honey processing businesses produce honey for the market only to profit from the retail sales. They do not care whether the overheating of honey at high temperatures destroys its protective action, which is what the consumers expect from honey. These honey producers only care whether their honey sells well, which applies to those liquefied and browned in the Czech Republic. That is why commercial honey is overheated at high temperatures in order to make the honey browner and liquefy it for a long period of time. For these reasons, the Czech market offers honeys that look very appealing thanks to their brown colouring and liquefaction. However, they contain HMF volumes that exceed the legislation limit sometimes several times while enzyme activity is almost null. This study indicates that the liquefaction and browning of honey could be done without any significant increase in HMF content, which could be positive for commercial honey producers but negative from the authorities' and consumers' perspective because HMF content could not be used as an unambiguous proof of honey overheating anymore.

References

Bartáková K., Vorlová L., Titěra D., Lutzová M. (2007): Physicochemical parameters and botanical origin of Czech honeys. Journal of Food and Nutrition Research, **46**: 167–173.

Bartáková K., Borkovcová I., Dračková M., Vorlová L. (2008): Honey produced by the Czech beekeepers – high quality foodstuffs. Veterinářství, **58**: 739–742.

Bath P.K., Singh N. (1999): A comparison between *Helianthus annuus* and *Eucalyptus lanceolatus* honey. Food Chemistry, **67**: 389–397.

Bath P.K., Singh N. (2001): Effect of microwave heating on hydroxymethylfurfural formation and browning in *Helianthus annuus* and *Eucalyptus lanceolatus* honey. Journal of Food Science and Technology-Mysore, **38**: 366–368.

Bogdanov S., Martin P., Lüllmann C. (1997): Harmonised methods of the European Honey Commission. Apidologie (Extra issue): 1–59.

Council Directive 2001/110/EC of 12th December 2001 relating to honey. Official Journal of the European Communities, **10**: 47–52.

Decree No. 76/2003 Coll. laying down the requirements for natural sweeteners, honey, sweeties, cocoa powder and mixtures of cocoa with sugar, chocolate and chocolate confections. Collection of laws of the Czech Republic, 32: 2470-–2487.

Hebbar H.U., Nandini K.E., Lakshmi M.Ch., Subramanian R. (2003): Microwave and infrared heat processing of honey and its quality. Food Science and Technology Research, **9**: 49–53.

Houšová J., Hoke K., Korečková I. (1999): Potravinářské výrobky pro mikrovlnný ohřev: metodická příručka k vývoji a výrobě. VÚPP, Praha.

Kubiš I., Ingr I. (1998): Effects inducing changes in hydroxymethylfurfural content in honey. Czech Journal of Animal Science, **43**: 379–383.

Wunderlin D.A., Pesce S.F., Amé M.V., Faye P.F. (1998): Decomposition of hydroxymethylfurfural in solution and protective effect of fructose. Journal of Agricultural and Food Chemistry, **46**: 1855–1863.

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