PhD Thesis

Comparative study of honeys with different origin, the effect of production-forming on the quality

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1. Introduction

Honey has an important role in human nutrition since ancient times, due to its positive dietary and health effect. There is evidence in a petroglyph on the walls of Arana cave in Spain, where a girl can be seen, taking out honey–comb from a cavern. Ancient Assyrians used the honey in medicines, in Egypt it was widely used, for example in embalmment process. In the Arabic culture or in the ancient China honey was a very important medicine, and was willingly consumed as a food, also. Honey and other products of apiary were used not only as delicacy but they were applied as medicines, too. Nowadays, due to its physical and chemical characteristics, honey is considered having health-promotion, or health improving effect. For example, the organic acids in honey improve appetite and support digestion Similarly to the amino acids, which are present in a free form, and there is no need for their decomposition in the intestine, they can get through the wall of intestines without any transformation. Due to its relatively high Potassium content, honey can be used for compensation of potassium deficiency in case of strong perspiration, diarrhoea or high temperature.

Though bees collect nectar from more than 800 flower species in Hungary, there are only a few honey types. The most important honey-type is the acacia honey in our country. Great amount and good quality acacia honey is produced here due to the large, continuous and entirely acacia forests that give the 20 percent of the woodland of Hungary. Climate and apiary technology have an important role in forming the high quality. Besides the special honey types the mixed (flower) honeys are also very important. Though the nutritional parameters of these honeys are excellent, they are not always appreciated by the consumers.

Natural and technological circumstances are favourable for apiary work in our country that is why about 22 thousand tonnes honey is produced per year, 80 % of this product is is exported. As a member of the European Union, Hungary applies the Codex Hungaricus 1-3-2001/110 regulation for honey from 1st August 2003, that was formed based on the 2001/110 EC directive.
2. Aims of the research

Recently, there is abundant coverage in newspapers about quality problems of Hungarian honeys. The main problem is the adulteration with different sugar products.

Therefore, my aim was to establish the notable differences in main characteristics regarding the different honey types. My other question was, if it is possible to determine the plant origin of the honey on the base of notable differences. Revealing the differences, I compared my results to the data of other researchers to prove that the differences between honey types can be originated to the plant. This way we can establish ranges regarding the main parameters of the honey types. Furthermore, I have studied the differences of some honey-types originated from different countries.

It was important for me to study the effect of the heating of the honeys, as heating is applied all over the world to dissolve the crystallization of honeys. I have studied the changing of quality parameters on the effect of heating in laboratory samples and in samples that were heated by beekeepers. As data can be found in the literature only for HMF content and diastase-activity, I wanted to examine some other quality parameters, too.

Because of the growing number of cases of honey adulteration performed with different sugar products, my aim was to find out, how can the mixing of some commercial sugar products (Isosweet 252, Mylose 461 and sucrose) effect the quality of honey. I studied, whether adding these sugar products to the honeys can cause significant difference in the quality parameters.


3. Materials and Methods

3.1. Honey samples

Flower- and speciality honeys were used for the experiments, some of them were purchased, and the others came directly from beekeepers. Samples originated from the years of 2007-2009. Among the honeys from beekeepers, there were acacia honeys (19), linden (13), rape (7), fruit (5), sunflower (5), asclepiad (5), chestnut (5), coriander (3), lavender (3), wild garlic (3), honeydew(4) and mixed flower (23) honeys.

The 18 honey samples – acacia (2) and mixed flower (16) – used for heating experiment, came also from beekeepers in original and heated state.

Hungarian origin was indicated on one part of the commercial honey samples. There were samples from Croatia, Greece, Turkey, France, Germany and Austria, and some speciality honeys, like Tasmanian leather-wood honey, New-Zealand tawary honey and Malaysian tropical jungle honey.

Altogether, 113 honeys from Hungarian beekeepers, 11 commercial honeys, 17 honeys from abroad, and 20 special honeys were involved in the experiments.

Three different sugar products were used for mixing: invert sugar (Isosweet 252), glucose syrup (Myleose 461), and sucrose syrup prepared in the laboratory.

3.2. Methods of Analysis

3.2.1. Moisture content and total sugar content

These parameters were determined using DIGFIT-5890 handy refractometer, developed specially for honey analysis.

3.2.2. Proline content

Proline content was measured by the method of OUGH (Meda et al., 2005), and also by the official method AOAC 979.20, using Spectronic® Genesys™ spectrophotometer.

3.2.3. Electrical conductivity

Electrical conductivity was determined by the method reported by Bogdanov (1997). Honey solution (20 %) was prepared with distilled water and the conductivity of the solution
was measured using Radelkis OK-102/1 type conductometer és Radelkis OK-9023 type bell-electrode.

3.2.4. Diastase activity

For determining diastase activity the decisive SCHADE-WHITE-HADORN method was applied, which is the base of the MSZ 6943-6:1981 Hungarian patent. The result was expressed in Goethe diastase number (the amount of 1 m/m % starch solution that is degraded by the diastase enzyme in 1 gram of honey, during one hour at 45-50 °C.

3.2.5. HMF- (hidroxy-mehyl-furfurol)

HMF content of the honey samples was determined by MSZ 6943-5:1989 (AOAC 980.23) method, using Spectronic® Genesys™ spectrophotometer.

3.2.6. Total phenolic compounds

The Folin-Ciocalteu method was applied (Meda et al., 2005). Result was expressed in mg GAE (gallic acid equivalent) / 100 g honey.

3.2.7. Flavonoid content

Flavonoid content was determined using the method published by Kim et al. (2003). Result was expressed in mg CE (catechin equivalent) / 100 g honey.

3.2.8. pH measurement

The pH of the honey was determined on the base of MSZ 6943/3-80 with Radelkis OP-211/1 type pH-meter ands Schott Geräte L 7 37 BNC type electrode.

3.2.9. Determination of free- lactones- and total acid content

AOAC 962.19 method was used. The main principle is, that the honey solution with distilled water is titrated to end point (pH 8,5) with alkali solution. After the hydrolysis of lactones with more alkali, the sample is titrated to end point (pH 8,3) with acid.

3.2.10. Element content

After the digestion of the honey samples with nitric acid and hydrogen peroxide the element content was determined using Optima 3300 DV ICP-OES (Kovács et al., 1996).
4. Evaluation of results

4.1. Quality parameters of the Hungarian honeys originated directly from beekeepers

In order to determine the quality of honeys, 22 parameters were measured (Table 1, Table 2 and Table 3). In case of half of these quality indicator the lowest value was obtained in acacia honeys for the next characteristics: proline content, electrical conductivity, total phenolyc compounds, flavonoide content, free acid content and macro-elements, like Calcium, Potassium, Sulphur, Phosphor, Sodium and Magnesium. Similarly low values were obtained in rape, wild garlic and Acslepias honeys. The best nutritional values were measured in honeydew honeys, coriander and chestnut honeys also proved to be very valuable.

<table>
<thead>
<tr>
<th>Honey type</th>
<th>Moisture content (%)</th>
<th>Total sugar (%)</th>
<th>Proline (mg/kg)</th>
<th>Electrical conductivity (mS/cm)</th>
<th>HMF (mg/kg)</th>
<th>Diasztase activity (DN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia</td>
<td>18,7±0,8</td>
<td>79,5±0,6</td>
<td>252±38</td>
<td>0,135±0,020</td>
<td>9,8±9,3</td>
<td>16,1±3,1</td>
</tr>
<tr>
<td>Linden</td>
<td>19,2±0,7</td>
<td>79,1±0,7</td>
<td>697±248</td>
<td>0,623±0,071</td>
<td>21,8±3,2</td>
<td></td>
</tr>
<tr>
<td>Rape</td>
<td>18,9±0,9</td>
<td>79,0±0,5</td>
<td>376±60</td>
<td>0,196±0,040</td>
<td>10,1±6,7</td>
<td>23,9±5,4</td>
</tr>
<tr>
<td>Mixed flower</td>
<td>18,7±1,1</td>
<td>78,1±1,7</td>
<td>542±139</td>
<td>0,320±0,089</td>
<td>15,5±9,7</td>
<td>19,8±5,8</td>
</tr>
<tr>
<td>Fruit</td>
<td>19,7±0,3</td>
<td>78,5±0,5</td>
<td>693±128</td>
<td>0,579±0,082</td>
<td>20,4±13,6</td>
<td>24,0±6,4</td>
</tr>
<tr>
<td>Sunflower</td>
<td>18,7±1,0</td>
<td>79,6±1,0</td>
<td>809±60</td>
<td>0,386±0,077</td>
<td>6,5±10,5</td>
<td>18,4±2,8</td>
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<tr>
<td>Asclepias</td>
<td>19,1±1,3</td>
<td>78,8±0,5</td>
<td>483±114</td>
<td>0,214±0,019</td>
<td>22,8±2,4</td>
<td>10,3±0,9</td>
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<tr>
<td>Chestnut</td>
<td>17,2±0,2</td>
<td>81,1±0,2</td>
<td>644±155</td>
<td>0,584±0,112</td>
<td>19,8±11,5</td>
<td>16,7±3,2</td>
</tr>
<tr>
<td>Coriander</td>
<td>19,2±0,1</td>
<td>79,1±0,1</td>
<td>2283±128</td>
<td>0,632±0,050</td>
<td>12,2±3,5</td>
<td>49,4±1,6</td>
</tr>
<tr>
<td>Lavender</td>
<td>19,1±0,1</td>
<td>79,2±0,1</td>
<td>589±23</td>
<td>0,355±0,127</td>
<td>7,5±6,1</td>
<td>22,3±0,5</td>
</tr>
<tr>
<td>Wilde garlic</td>
<td>19,1±0,7</td>
<td>79,2±0,7</td>
<td>476±27</td>
<td>0,238±0,017</td>
<td>18,2±2,7</td>
<td>22,4±4,5</td>
</tr>
<tr>
<td>Honeydew</td>
<td>19,9±0,1</td>
<td>78,3±0,1</td>
<td>1089±137</td>
<td>0,995±0,120</td>
<td>29,2±6,7</td>
<td>16,9±1,9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Honey type</th>
<th>Total phenolic compound (mgGAE/100g)</th>
<th>Total flavonoid (mgCE/100g)</th>
<th>pH</th>
<th>Free acid (meq/kg)</th>
<th>Laktone acid (meq/kg)</th>
<th>Total acid (meq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia</td>
<td>42,3±8,4</td>
<td>1,7±1,2</td>
<td>3,5±0,1</td>
<td>15,2±4,0</td>
<td>4,2±1,8</td>
<td>19,1±3,8</td>
</tr>
<tr>
<td>Linden</td>
<td>85,1±16,3</td>
<td>2,8±1,7</td>
<td>4,2±0,3</td>
<td>21,1±6,5</td>
<td>8,5±1,6</td>
<td>29,5±6,3</td>
</tr>
<tr>
<td>Rape</td>
<td>69,8±11,3</td>
<td>4,1±2,1</td>
<td>3,5±0,1</td>
<td>18,8±3,6</td>
<td>6,0±1,6</td>
<td>24,8±2,5</td>
</tr>
<tr>
<td>Mixed flower</td>
<td>76,7±29,3</td>
<td>6,2±3,0</td>
<td>3,5±0,2</td>
<td>24,9±9,5</td>
<td>7,1±2,8</td>
<td>30,0±7,9</td>
</tr>
<tr>
<td>Fruit</td>
<td>111,8±8,7</td>
<td>5,6±1,6</td>
<td>4,3±0,2</td>
<td>18,9±3,7</td>
<td>6,4±1,8</td>
<td>25,3±2,5</td>
</tr>
<tr>
<td>Sunflower</td>
<td>108,3±8,7</td>
<td>4,2±0,5</td>
<td>3,7±0,3</td>
<td>32,4±4,8</td>
<td>6,1±1,1</td>
<td>38,5±4,8</td>
</tr>
<tr>
<td>Asclepias</td>
<td>102,4±10,8</td>
<td>4,2±1,0</td>
<td>3,3±0,0</td>
<td>24,7±2,6</td>
<td>6,5±1,5</td>
<td>31,2±1,8</td>
</tr>
<tr>
<td>Chestnut</td>
<td>140,5±32,5</td>
<td>11,5±1,3</td>
<td>4,1±0,4</td>
<td>23,5±5,1</td>
<td>5,4±2,4</td>
<td>29,3±3,9</td>
</tr>
<tr>
<td>Coriander</td>
<td>181,0±7,7</td>
<td>13,9±1,3</td>
<td>4,1±0,0</td>
<td>30,5±1,8</td>
<td>10,8±0,8</td>
<td>43,3±2,2</td>
</tr>
<tr>
<td>Lavender</td>
<td>107,1±20,4</td>
<td>5,2±1,5</td>
<td>3,6±0,3</td>
<td>25,2±4,3</td>
<td>7,7±1,3</td>
<td>32,0±3,1</td>
</tr>
<tr>
<td>Wilde garlic</td>
<td>87,7±3,8</td>
<td>5,8±0,4</td>
<td>3,6±0,0</td>
<td>15,0±3,3</td>
<td>6,3±1,0</td>
<td>22,0±2,6</td>
</tr>
<tr>
<td>Honeydew</td>
<td>141,2±9,6</td>
<td>8,9±0,8</td>
<td>4,2±0,1</td>
<td>39,1±2,1</td>
<td>6,4±0,8</td>
<td>45,5±2,8</td>
</tr>
</tbody>
</table>
Most of the samples meet the requirement of the Codex Alimentarius Hungaricus, but in some cases we could find differences in one or more parameters. In 12 mixed honey samples higher moisture content was measured, than the expected value. Proline content was lower than the minimal 180 mg/kg in three acacia and two asclepias honeys. The electrical conductivity of all chestnut honeys was lower than the 0.8 mS/cm limit, pH and total phenolic content were also very low.

HMF content of two mixed flower honeys, two asclepias and two chestnut honeys was much higher than the maximum 40 mg/kg. Diastase activity was too low in one asclepias honey, while the free acid content was found in excess of requirement (50 meq/kg) in two linden honeys.

Table 2 shows the micro-element content of the honeys. Linden, rape, asclepias honeys contained the less amount of Aluminium. Boron content was very low in linden honeys; the lowest Iron content was measured in sunflower honeys. Zink and Copper content was very low in wild garlic honeys, and Asclepias honeys also contained very few Copper. The highest Aluminium content was detected in the honey-dews honeys; the highest Boron in the rape honeys, the most iron was measured in coriander honeys.

**Table 2**

<table>
<thead>
<tr>
<th>Honey type</th>
<th>Aluminium (mg/kg)</th>
<th>Boron (mg/kg)</th>
<th>Iron (mg/kg)</th>
<th>Zink (mg/kg)</th>
<th>Strontium (mg/kg)</th>
<th>Copper (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia</td>
<td>1.46±0.56</td>
<td>4.75±0.69</td>
<td>2.87±1.33</td>
<td>1.48±0.97</td>
<td>0.29±0.05</td>
<td>0.32±0.22</td>
</tr>
<tr>
<td>Linden</td>
<td>1.01±0.50</td>
<td>2.95±1.98</td>
<td>3.31±0.81</td>
<td>2.48±1.67</td>
<td>0.43±0.05</td>
<td>0.44±0.19</td>
</tr>
<tr>
<td>Rape</td>
<td>1.17±0.26</td>
<td>10.08±2.86</td>
<td>4.52±0.47</td>
<td>1.83±1.36</td>
<td>0.33±0.07</td>
<td>0.25±0.22</td>
</tr>
<tr>
<td>Mixed flower</td>
<td>1.89±1.06</td>
<td>6.01±2.55</td>
<td>3.01±1.59</td>
<td>3.15±2.87</td>
<td>0.36±0.05</td>
<td>0.38±0.18</td>
</tr>
<tr>
<td>Fruit</td>
<td>1.40±0.17</td>
<td>17.29±3.88</td>
<td>2.96±0.64</td>
<td>2.31±0.74</td>
<td>0.38±0.06</td>
<td>0.39±0.19</td>
</tr>
<tr>
<td>Sunflower</td>
<td>2.12±1.37</td>
<td>9.08±3.95</td>
<td>1.63±0.25</td>
<td>1.93±0.87</td>
<td>0.29±0.03</td>
<td>0.35±0.14</td>
</tr>
<tr>
<td>Asclepias</td>
<td>1.20±0.17</td>
<td>4.73±0.37</td>
<td>3.54±1.15</td>
<td>1.45±0.07</td>
<td>0.32±0.02</td>
<td>0.12±0.03</td>
</tr>
<tr>
<td>Chestnut</td>
<td>1.64±0.22</td>
<td>3.96±1.05</td>
<td>2.89±0.63</td>
<td>1.39±0.94</td>
<td>0.42±0.02</td>
<td>0.35±0.20</td>
</tr>
<tr>
<td>Coriander</td>
<td>2.28±0.14</td>
<td>9.37±0.32</td>
<td>5.75±0.18</td>
<td>2.69±0.35</td>
<td>0.31±0.01</td>
<td>0.20±0.01</td>
</tr>
<tr>
<td>Lavander</td>
<td>1.69±0.0</td>
<td>6.92±0.72</td>
<td>2.96±1.82</td>
<td>1.73±0.46</td>
<td>0.29±0.06</td>
<td>0.29±0.06</td>
</tr>
<tr>
<td>Wilde garlic</td>
<td>1.54±0.19</td>
<td>9.11±0.29</td>
<td>3.32±0.11</td>
<td>0.73±0.67</td>
<td>0.41±0.06</td>
<td>0.11±0.01</td>
</tr>
<tr>
<td>Honeydew</td>
<td>2.91±0.95</td>
<td>3.91±2.71</td>
<td>4.17±0.92</td>
<td>3.82±1.17</td>
<td>0.43±0.09</td>
<td>0.54±0.19</td>
</tr>
</tbody>
</table>
All the six measured macro-element was present in a very low concentration in the acacia honeys. Similarly low Sulphur content was detected in the asclepias honeys. Phosphor was detected in a low concentration in linden, wild garlic and rape honeys, while asclepias and honeydew honeys were poor in Sodium. The highest Calcium content was measured in linden honeys, the highest Potassium content in linden and honeydew honeys. Fruit and sunflower honeys contained the most Sulphur. Phosphor and Sodium content was the highest in coriander honeys, fruit, chestnut and honeydew honeys were rich in Magnesium.

Evaluating the examined element content of the honeys we can state, that Strontium can be found in the least amount in the Hungarian honeys, and the ascendant row of element is Copper, Aluminium, Zink, Iron, Boron, Sodium, Magnesium, Phosphor, Sulphur, Calcium an Potassium.

### 4.2. Quality parameters of the commercial honeys

Most of the samples purchased from mainly supermarkets, meet the requirements. Moisture content of the Hungarian linden honey bought in Spar, and acacia honey bought in Croatia was higher than the allowable value. The pH value and Potassium content was also very low in this linden honey. Regarding proline content, all the purchased samples contained more, than those honeys that originated from beekeepers. Linden honey from Spar, Argentine forest honey were exceptions with their much lower proline content. Electrical conductivity of these later samples was also very low, in case of forest honey it was lower than the requirement. HMF content of mixed honeys from Croatia, Turkey, and other countries were in excess of 40 mg/kg limit.
4.3. Changing of quality parameters of the honey on the effect of heating

4.3.1. Heating of honeys from beekeepers

There was no changing in the moisture and sugar content of the samples, but proline content decreased significantly. In the three samples heated by the beekeeper in Vámospércs, the rate was 47% in the acacia honey from 2006, 43% (2006) and 36% (2007) in the mixed flower honeys. The examined acacia honey did not meet the requirement after the heating process, as its proline content became 157 mg/kg instead of 180 mg/kg. There was less decrease in proline content in the mixed flower honey from Biharnagybajom (14%), and even less (10%) in all the other samples.

There was also a decrease in the electric conductivity on the effect of heating. The biggest differences (31%, 32% and 37%) were detected in the samples from Vámospércs. The decrease was lower than 10 % in all the other samples.

As an effect of heating there was explicit increase in the HMF content of honey samples. The rate of increase was 10% in only one sample, notably bigger increase was found in the others. The HMF content of honey from Vámospércs (2006) became ten times higher, from 1,5 mg/kg to 15,3 mg/kg. Similarly high, eightfold increase was detected in the mixed flower honey also from Vámospércs (2007). The increase of HMF content was fivefold in the mixed flower honey from Kertészsziget and triple in the sample from Hortobágy, therefore the HMF content exceeded the maximum 40 mg/kg value defined by the Codex Alimentarius Hungaricus.

There was a decrease in diastase activity of the honey samples as a result of heating. The decrease in the three samples from Vámospércs was over 65%, and similar change was detected in the samples from Biharnagybajom. As a result, the enzyme activity of the acacia honey, the mixed flower honeys from Vámospércs and Biharnagybajom (2006) decreased beneath the required value. The enzyme activity of the mixed flower honey from Vámospércs

Decrease was also experienced in the amount of total phenolic compounds on the effect of heating. The rates were 41%, 34% and 40% in the samples from Vámospércs, 30% in the sample from Biharnagybajom, and the difference was less than 10% in all the other samples. Similarly, flavonoid content decreased in the highest degree in the three samples from Vámospércs. The rate was 90% in the sample collected in 2006. The flavonoid content of the sample from Biharnagybajom decreased by 17%.
There was no change observed in the pH value in the majority of samples. A slight decrease (4-10 %) was detected in the three samples from Vámospércs and in one from Biharnagybajom. Total acidic content of the honeys lowered on the effect of heating, the biggest change was found in the samples from Vámospércs (2006) and in the mixed flower honeys from Kertészsziget.

The decrease of proline content, electric conductivity the total phenolic and flavonoid content on the effect of heating was most professed in the samples from Vámospércs and Biharnagybajom. Coincidently, the rate of the change in diastase activity was also the highest in these samples. These data are indicative of the error of heating process. Such a big decrease in enzyme activity shows clearly that the temperature was too high or the duration of heating was excessive. At the same time, the HMF content indicate different conclusion.

4.3.2. Change of quality parameters of honeys as a result of heating under laboratory conditions

There was no change in moisture and total sugar content and electric conductivity and pH-value in the honey samples on the effect of heating under laboratory conditions. A definite decrease was detected in proline content (Figure 1.) The highest rate of decrease (50%) was found in the samples heated for 20 minutes at 100°C.

In accordance with the expectations, there was an increase in HMF content (Figure 2.) HMF concentration increased with time and temperature linearly. The amount of HMF exceeded the 40 mg/kg maximum value defined by the Codex Alimentarius Hungaricus after 10 minutes at 40°C and 50°C, after 5 minutes at 60°C, in the fifth minute at 80°C and 100°C.
It is important to note that the initial HMF content influences the value in the heated samples: at a low initial HMF content the increase is moderate.

*Figure 2: Changing of HMF content of mixed flower honey on the effect of heating*

Diastase activity decreased on the effect of heating under laboratory conditions (Figure 3). The rate of decrease was linear with the increasing time and temperature. The enzyme activity was over the prescribed minimum value in the samples heated at 40, 50 and 60°C even after 20 minutes. But at 80°C the diastase activity decreased beneath 8 DN after 15 minutes heating, at 100°C for ten minutes this value decreased dramatically.

*Figure 3: Changing of diastase activity of mixed flower honey on the effect of heating*

There was also a linear decrease in the amount of total phenolic content of the honeys. The rate was not higher than 16% even at 100°C for 20 minutes (Figure 4).
Contrarily, there was a definite decrease in flavonoid content. The rate under the same conditions (100°C for 20 minutes) was 74%, and reached the 33% at 40°C for 20 minutes. (Figure 5).

To sum up, the heating experiment was performed at 40, 50, 60, 80 and 100°C, for 5, 10, 15 and 20 minutes. Results show, the higher the temperature, the faster the change of the parameters. The pH is the only exception, heating had no effect on the pH, or considerable change could only be detected at relatively long heating time.

4.4. Change of the quality parameters of honeys on the effect of added sugar products

The measured quality parameters of invert sugar, glucose syrup and sucrose syrup are summarized in Table 4.
Table 4

Quality parameters of different sugar products

<table>
<thead>
<tr>
<th>Quality parameter</th>
<th>Invert sugar</th>
<th>Glucose syrup</th>
<th>Sucrose syrup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>23,00</td>
<td>19,80</td>
<td>34,90</td>
</tr>
<tr>
<td>Total sugar content (%)</td>
<td>76,00</td>
<td>78,50</td>
<td>63,20</td>
</tr>
<tr>
<td>Proline content (mg/kg)</td>
<td>47,0</td>
<td>213,0</td>
<td>28,2</td>
</tr>
<tr>
<td>Electric conductivity (mS/cm)</td>
<td>0,036</td>
<td>0,152</td>
<td>0,020</td>
</tr>
<tr>
<td>HMF content (mg/kg)</td>
<td>17,70</td>
<td>0,82</td>
<td>0,45</td>
</tr>
<tr>
<td>Diastase activity (DN)</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>Total phenolic content (mg GAE/100g)</td>
<td>26,07</td>
<td>12,70</td>
<td>20,32</td>
</tr>
<tr>
<td>Flavonoid content (mg CE/100g)</td>
<td>2,70</td>
<td>0,52</td>
<td>1,82</td>
</tr>
<tr>
<td>pH</td>
<td>3,90</td>
<td>4,26</td>
<td>3,30</td>
</tr>
<tr>
<td>Free acid (meq/kg)</td>
<td>8,0</td>
<td>4,0</td>
<td>2,5</td>
</tr>
<tr>
<td>Lactic acid (meq/kg)</td>
<td>3,0</td>
<td>5,0</td>
<td>3,5</td>
</tr>
<tr>
<td>Total acid content (meq/kg)</td>
<td>11,0</td>
<td>9,0</td>
<td>6,0</td>
</tr>
</tbody>
</table>

Added glucose syrup had no notable effect on the moisture content of the honey mixture, there was no change adding glucose syrup, but mixing sucrose syrup increased the moisture content significantly (Figure 6).

Figure 6: Effect of added sugar products on the moisture content of acacia honey

The same result was found examining the total sugar content (Figure 7). There was very little or no change mixing invert sugar and glucose syrup into the honey, but sucrose syrup decreased the total sugar content significantly.
10 % invert sugar decreased the proline content of the honey by 7,3%, the rate was 21,4% mixing in 30% ratio. Glucose syrup did not change the proline concentration due to its original prolin content. The decrease on the effect of added sucrose syrup was similar than using invert sugar (Figure 8).

The electric conductivity of invert sugar was 0,036 mS/cm, this way mixing it in 30% ratio decreased the electric conductivity with 26,1% in the honey mixture. There was similar effect mixing in sucrose syrup, but there was no change in case of glucose syrup (Figure 9).
Figure 9: Effect of added sugar products on the electric conductivity of acacia honey

Beside the external effects, invert sugar can increase the HMF content of honeys. It’s original HMF content was 17.70 mg/kg. Mixing it in 10 % ratio caused twofold increase in HMF content, mixing it in 30 % yielded 4.5 times increase in the value. Glucose and sucrose syrups decreased the original HMF content of the honey because of their original HMF content (Figure 10).

Figure 10: Effect of added sugar products on the HMF content of acacia honey

Diastatic activity of invert sugar, glucose syrup and sucrose syrup could be regarded as zero. Therefore, mixing them to honey in 10 % and 30% ratio caused 12% and 36% decrease (Figure 11).
There was no notable change in the total phenolic and flavonoid content on the effect of added sugar products (Figure 12. and 13).

Results show that detection of honey adulteration with invert sugar is complicated using the examined parameters. Mixing it to honey will not increases the HMF content, higher HMF
concentration can refer to addition invert sugar only in case of fresh honey sample. The value of diastase activity can be a good indicator. In those cases when the original diastase activity is low (acacia honey), on the effect of mixing in invert sugar, this value decreases below the minimal value defined in the standard. In case of honeys with higher enzyme activity, the addition of invert sugar results a lower diastase activity than the typical value for the given honey type.

According to international literature, sucrose content, proline content and electric conductivity are the most suitable parameters to demonstrate honey adulteration. Our results confirm that the two latter parameters can be indicators of mixing in extraneous components to the honeys, as their values decreases significantly with the addition of invert sugar. At the same time, we have to consider the type of the honey.

Proline content and electric conductivity of MYLOSE 461 glucose syrup produced by enzymatic fermentation of maize are rather high, they are similar than those in acacia honeys. For this reason these two parameters are not suitable to detect acacia honey adulteration with glucose syrup. But in case of other honey type, when the original concentration of these two parameters is higher, mixing in MYLOSE 461 causes decrease in proline content and electric conductivity. HMF content of glucose syrup is very low. Mixing it will decrease the concentration of HMF in every sample. Consequently, determining this parameter will not help us to detect addition of glucose syrup to honey. Diastase activity can be a suitable parameter to detect adulteration, as similarly to invert sugar, glucose syrup decreases the enzyme activity. We can state that it is very difficult to verify adulteration with glucose syrup in honeys with inferior quality parameters, as the main characteristics are similar in the two products. The examined parameters can be appropriate to confirm adulteration in case of honeys with higher quality.

Sucrose syrup modified the moisture and total sugar content. Due to its low proline content and electric conductivity, adding it to honey decreased the value of these two quality parameters. This fact can be important only in case of honeys with higher quality. As HMF concentration of sucrose syrup is very small, mixing it to honey will not raise the HMF content of mixture. That is why this parameter is inappropriate to detect adulteration. Diastase activity can be a suitable parameter, as the enzyme activity of this product comes near to zero. There was no change in pH value adding sucrose syrup to honeys.
The new results of research

- I have determined the quality parameters of honey types produced in Hungary. It was recognized that there is at least one parameter for every honey type that is appropriate to make difference from the others.

- Considering the quality parameters of acacia honey I can state that the nutritional value of this honey type is inferior among all the other honey types.

- I have established the ascendant row of element in Hungarian honeys:
  \[ \text{Sr} \leq \text{Cu} < \text{Al} < \text{Zn} < \text{Fe} < \text{B} < \text{Na} \leq \text{Mg} < \text{P} \leq \text{S} < \text{Ca} < \text{K} \]

- Heating has significant effect not only on HMF content and diastase activity, but on the proline and total flavonoid concentration, too.

- Plant origin can be verify by jointly evaluating proline content, electric conductivity or antioxidant activity, considering sensory parameters like colour, at the same time.

- Geographical origin has a moderate affect on the quality of honey, as the nutritional value of the different honey types depends mainly on plant origin, not on geographical origin.

- Results of the examined speciality honeys are in agreement with the result published in international literature. I have established that these honeys contained proline in a very big concentration, but compared to the Hungarian honey types, there were no outstanding values in the other quality parameters.
**Practical use of the results**

1. Evaluating together proline content, electric conductivity, total phenolic and flavonoid content and organoleptic characteristics, it is possible to determine the differences among the honey types or demonstrable the plant origin.

2. Proline content, electric conductivity, total phenolic and flavonoid content, total sugar and moisture content can be suitable to resolve adulteration with sugar products, other parameters, like pH is not.

3. Heating of honeys has effect not only the HMF content, there is significant changing in diastase activity, proline content and antioxidant activity, too.

4. In case of uncertainty regarding the type, the basic quality parameters mentioned in No. 1, are suitable to determine the plant origin of the honey.

5. These parameters are important from the point of view of adulteration, or heating of the honey. Contrary to the very expensive measurements, some simple and cheap measurement, like proline content, electric conductivity, total phenolic and flavonoid content, total sugar and moisture content can be suitable can be also suitable to determine the manipulation with honey.
References:

In periodicals:


Full size article in conference proceeding:


Abstract in conference proceeding:


Other:

Full size article in conference proceeding:


Abstract in conference proceeding:

