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Influence of type and state of crystallisation on the water activity of honey

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Abstract

In total, 249 samples of different honey types were analysed concerning water content and water activity. The samples were identified by using physico-chemical parameters and melissopalynological methods.

The water content was determined at 20 °C via refractometric measurement by using the refractive index. The water activity of liquefied and crystallised honeys was measured at 25 °C, using the instrument Novasina a_w-Sprint.

It was found that the water activity of crystallised honeys is higher than that of liquid honeys. Furthermore, a difference between flower- and honeydew honeys could be detected. In liquid state, honeydew honeys show higher water activities than flower honeys having the same water content. However, no significant difference between the water activities of different types of honeys could be found when the honey was crystallised.

The results are dependent on the fact that the water activity in honey mainly depends on the glucose content.

Keywords: Honey; Water activity; Water content; State of crystallisation; Glucose/fructose ratio

1. Introduction

Fermentation of honey is a big problem due to osmophilic yeast occurring everywhere. These specialised yeast are able to spoil honey having higher water content. The higher the water content of the honey the more likely is fermentation and spoilage. The absolute water content is not responsible for the metabolism of the yeast but the amount of free water, described as water activity (Rockland, 1987). The water activity is defined as the relation of the water vapour pressure of the food (p) to the water vapour pressure of pure water (p_0) at the same temperature. Consequently, the water activity of pure water is 1, each addition of water-fixing substances causes that $p < p_0$ and that the water activity becomes <1. The water activity of honey is within a range of 0.5–0.65.

The water activity needed for development of micro-organisms is below 0.98 and depends on the class of micro-organisms (around 0.70 for mould; 0.80 for yeast and 0.90 for bacteria). Osmophilic yeast are specialists which have an obligate need for high sugar concentrations and are able to grow to a minimal water activity until 0.6. Such osmophilic yeast are causing honey fermentation.

Molecular-fixed water has no influence on the water activity, this parameter is dependent on the free water content. The water in honey is mainly fixed to sugars via hydrogen bonding. The monosaccharides glucose (27–45%) and fructose (33–42%) are the main components of honey (Hadorn & Zürcher, 1974). During crystallisation of honey mainly glucose crystallises by

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forming glucose monohydrate (Assil, Sterling, & Sporns, 1991; Doner, 1977), fructose is more soluble and stays in solution for longer time (Duisberg, 1967). The water fixed to glucose in solution is set free during the crystallisation process which means that the water activity increases. Honeys having higher water contents sometimes are separating into a crystallised phase at the bottom and a liquid phase on top. This layer containing high water contents increases the risk for spoilage of honey via fermentation (Assil et al., 1991; Hadorn & Zürcher, 1974; Horn & Lüllmann, 2002).

Determinations concerning the water activity of honey in addition to different honey types are sparse. Tabouret (1979) analysed the connection between water activity and honey crystallisation. He found a relation between the water activity, the glucose content and the moisture content. Multiple correlation and mathematical models were developed to convert water content into water activity (Rüegg & Blanc, 1981; Sanz, Gradillas, Jimeno, Perez, & Juan, 1995). This was quite difficult because it is known that crystallised honeys show water activities which are different from liquid honeys having the same water content (Martin, 1958). These mathematical models are based on the data of different sugar solutions (Audu, Loncin, & Weisser, 1978; Chirife, Favetto, & Ferro Fontán, 1982; Rüegg & Blanc, 1981; Starzak & Peacock, 1997) and can be applied for liquid honeys only. But there were no separate considerations for different types of honey. Schroeder (2002) found differences in the water activity between honeydew honeys and flower honeys but did not analyse single honey types.

The object of this paper was to find out how far different types of honey and their state (liquid/crystallised) influence the water activity.

2. Materials and methods

In total, 249 samples belonging to different honey types were analysed. The samples were identified by using physico-chemical parameters and melissopalynological methods.

Crystallised honeys were liquefied in an incubator (ca. 50 °C) without loss of water.

The determination of the water content was done with an Abbe-Refraktometer 131680 (Zeiss, Jena) by measurement of the refractive index at 20 °C. From the refractive index, the water content could be determined by using the tables of Chataway (1932).

The water activities of liquid and crystallised honeys were checked at 25 ± 0.2 °C by using the instrument Novasina a_w-Sprint. The Novasina a_w-meter is sensitive to the change in equilibrium relative humidity (ERH) around the sample, not directly to moisture content (water vapour sorption isotherms give the correlation between ERH and moisture content). The instrument is equipped with an algorithm, the so-called "humidity stability factor", a time span during which the results may only change by a minimal value (less than $0.001 a_w$ and 0.1 °C) to be accepted as stable. The time span for the measurement was fixed for 2 min only, because determination of water activity in honey makes no problems. The result is expressed with three decimals, the detection limit is $\pm 0.003 a_w$.

All determinations were done twice, the results are expressed as the mean value.

3. Results and discussion

Fig. 1 shows the water activity of flower honeys at different water content. In these results, the honey types "Flower, Dandelion, Locust and Rape" are summarised as flower honeys. When comparing the water activity of liquid and crystallised samples, it can be seen that crystallised samples show higher water activities than liquid honeys having the same water content.

In Fig. 2 the samples of honeydew honeys are compared. They include the honey types "Spruce" and "Pine". Similar to the results of flower honeys, crystallised honeydew samples have higher water activities than liquid ones. However, in general the difference in the water activity between liquid and crystallised samples is higher among flower honeys than among honeydew honeys.

The water activity of honey depends mainly on the glucose content. During crystallisation, glucose starts to crystallise first. Fructose has a higher solubility and stays in solution for a longer time. All the five hydroxyl groups of glucose interact with water molecules. After crystallisation glucose is found as glucose monohydrate, each glucose molecule fixes only one molecule of water. Therefore, less water is fixed in the crystallised state. The content of free water is higher and in accordance with the water activity. The fact that the difference between crystallised and liquefied flower honeys is higher than the difference among the honeydew honeys can also be explained by the behaviour of glucose. Honey types have different fructose/glucose ratios. Flower honeys show a fructose/glucose-ratio of about 1.0 (Bauer, 2001), honeydew honeys of about 1.5–2.0. In general, flower- honeys contain more glucose than honeydew honeys. Therefore, the crystallisation of glucose has a stronger effect on those types of honey which contain relatively more glucose.

Fig. 3 presents the comparison of the water activities of flower- and honeydew honeys in liquid state. When comparing honeys with the same water content the water activity of honeydew honeys is always above those of flower honeys. The water activity depends mainly on the fructose and glucose content. The difference between the water activities of the different honey types is the result of its diverse sugar compositions. Honeydew honeys

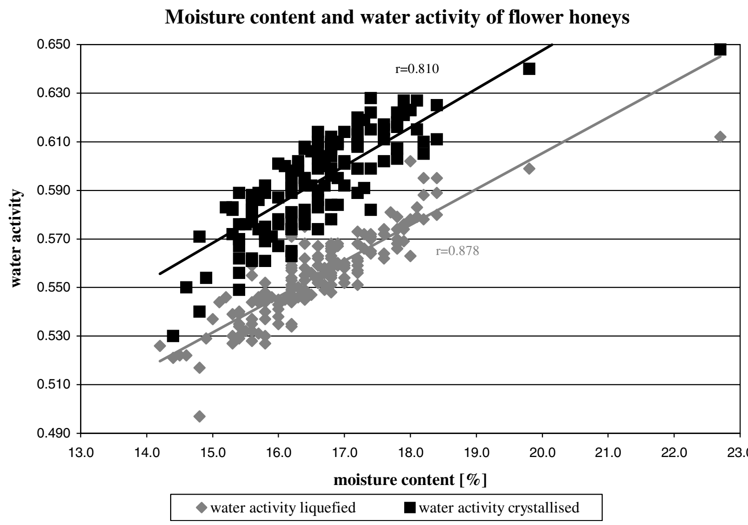

Fig. 1. Water activity of crystallised flower honeys ($n = 145$) compared with the water activity of liquid flower honeys ($n = 166$).

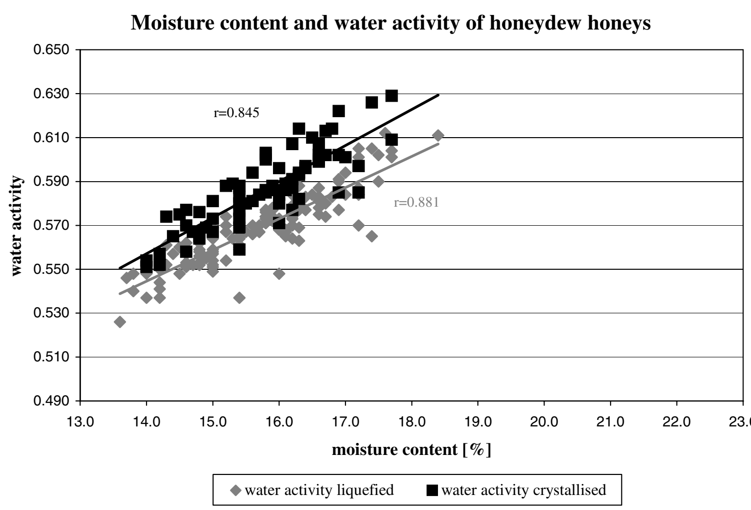

Fig. 2. Water activity of crystallised honeydew honeys ($n = 76$) compared with the water activity of liquid honeydew honeys ($n = 128$).

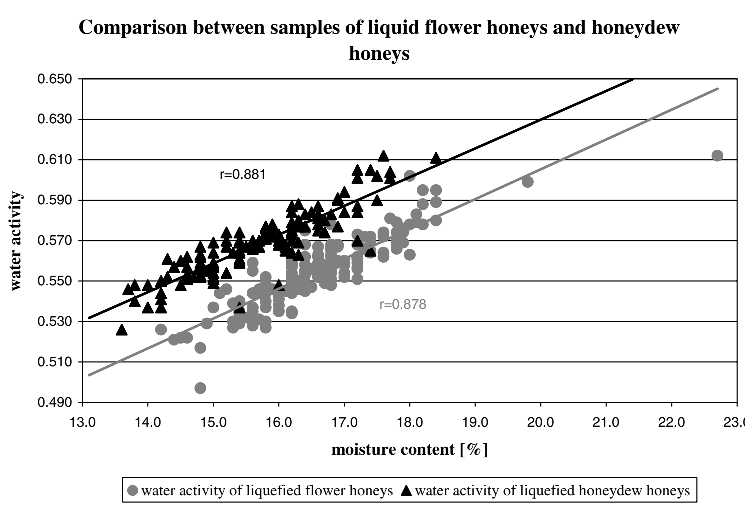

Fig. 3. Comparison of the water activity of flower- ($n = 166$) and honeydew honeys ($n = 128$) in liquid state.

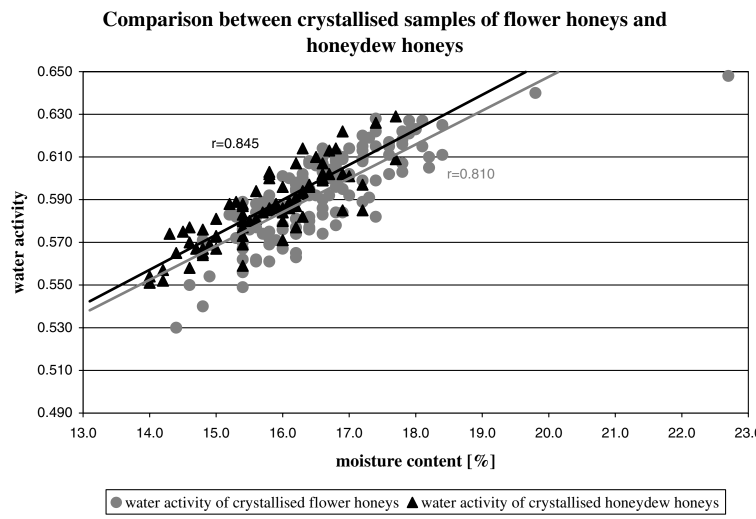

Fig. 4. Comparison of the water activity of flower- ($n = 145$) and honeydew honeys ($n = 76$) in crystallised state.

contain less glucose than flower honeys, on an average 30–35 g/100 g dry matter, for flower honeys the glucose content is within a range of 40 to almost 50 g/100 g dry matter (Bauer, 2001). Concerning the fructose content, there are also big differences between different honey types. Honeydew honeys have about 35–40 g fructose per 100 g dry matter, local flower honeys show about 40–50 g fructose per 100 g dry matter. The smaller amount of monosaccharides of honeydew honeys is compensated by a higher content of oligosaccharides (Doner, 1977). With regard to the water activity the oligosaccharides are less important than the monosaccharides. Due to the higher amount of monosaccharides, flower honeys are able to fix more water than honeydew honeys. If comparing different liquid types of honey having the same water content, flower honeys in general are characterised by lower water activities than honeydew honeys. Comparing the same samples in the crystallised state (see Fig. 4), no differences can be found between crystallised flower and honeydew honeys. In the solid state of honey glucose is crystallised, fructose stays in solution for a longer time. The behaviour between the liquid honey types is due to the different amount of monosaccharides and the different fructose/glucose ratios. After crystallisation of glucose and fructose, the different fructose/glucose ratio of the honey types is of no further relevance. The glucose is now crystallised as glucose monohydrate and fixes only a small amount of water. That means that the water activities of the different honey types in crystallised state reach the same level.

4. Comments and conclusion

It was found that the water activities of crystallised honeys are higher than those of liquid honeys having the same water content. Furthermore, a difference between honeydew honeys and flower honeys could be detected. Liquid honeydew honeys show higher water activities than liquid flower honeys having the same water content. However no differences between the water activities of different types of honeys could be found in crystallised state.

The observed a_w-values between 0.53 and 0.63 are absolutely safe for other foods as concerns the risk of microbiological spoilage. The problem in honey is fructose. The hydrogen bonding between water molecules and fructose gives weak-energy H-bonds, which means that water retained around fructose molecules to hydrate them is mobile enough to be available for micro-organism growth. The crystallisation of glucose releases water, but the most important phenomenon is the change in glucose/fructose ratio in favour of fructose.

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