PHYSICOCHEMICAL CHARACTERISTICS OF PRODUCTS BASED ON HONEY AND HAWTHORN (*CRATAEGUS SPP.*)

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:

Medicinal plants have become an increasing subject of interest worldwide due to the large amount of biologically active substances that have potential beneficial health properties. One of the more interesting popular medicinal plants is hawthorn (*Crataegus spp.*), a deciduous branched shrub that is increasingly used for health purposes. Various parts of this plant, including berries, flowers and leaves, are rich in nutrients and beneficial bioactive compounds that are effective in the treatment of numerous diseases. Honey is a natural sweetener produced by bees from plant secretions. Known for its nutritional and medicinal values, it gives strength to the body, which is why it is indispensable in the human diet. The combination of these two ingredients represents a significant source of vitamins and minerals in daily use, but also for use in various pharmaceutical and medical purpose. Taking into account all of the above, the aim of the work is to test samples of the mixture of honey and hawthorn in different proportions and determine the physical and chemical characteristics: pH value, electrical conductivity, refractive index, viscosity, water activity, HMF, DPPH. Based on the analysis, appropriate conclusions will be drawn and more information will be obtained about their quality and possible use as a food supplement. On the basis of the conducted analyses, it can be concluded that the parameter values are within the permitted limits defined by the Rulebook (Official Gazette Bosnia and Herzegovina No. 37/09). The analysis of the mentioned parameters showed that the chemical composition of the sample plays a major role in the value of the measurement results, and that Sample III has the best antioxidant properties.

KEYWORDS: physicochemical characteristics; honey; hawthorn (*Crataegus spp.);* mixture; food suplement

INTRODUCTION

Hawthorn (*Crataegus spp.*) is a shrub or tree with ramified branches. It belongs to the family Rosaceae, subfamily Maloideae, genus Crataegus.[1] It is widely distributed in Asia, Africa, North America and Northern Europe, and there are 165-200 species in the world. [2] The chemical composition of hawthorn depends on the part of the plant, so we distinguish the chemical composition of the flower, leaf or fruit. The ripe fruit has the highest concentrations of glucose and fructose, while the hawthorn leaf and flower contain sugars and sugar alcohols, organic acids, terpenes, plant essential oils, phenylpropanoids, hydroxycinnamic acids, lignans and flavonoid oils.[3] Various parts of this plant, especially the berries, flowers and leaves are rich in nutrients and traditionally associated with many health, medicinal or pharmaceutical positive effects on health, e.g. antimicrobial, anti-inflammatory, antioxidant, anticancer and anticoagulant action, which is why this plant has been used as a traditional medicine, herbal remedy and food supplement for a long time. For example Hawthorn fruit has long been used as a functional food in China due to its effects of increasing appetite, promoting digestion and protecting the gastrointestinal tract. [4] Unlike other common fruits, hawthorn has more dietary fiber, pectin, ascorbic acid, minerals and antioxidant capacity, which is why it has been approved as a medicinal fruit by the Chinese National Health Commission.[5],[6] Studies have confirmed that hawthorn is rich in amino acids (8 essential amino acids and 3–8 times more amino acids than fruit), protein (17 times more protein than apple fruit), sugars, minerals (1st in calcium content among fruits), vitamins (vitamins A, C, B1, B2, about 10 times more vitamins), and has a high nutritional value. [7]

Honey is a naturally sweet product produced by honey bees (Apis mellifera) from nectar of honeydew

plants, secretions of living parts of plants or secretions of insects that suck living parts of plants, which bees collect, add their specific substances, store, excrete water and deposit in the cells of the comb until maturation. [8] Chemically, honey is a very complex mixture of more than 70 different ingredients. [9] Different types of honey, as well as honey within one type, differ in their composition depending on the sort of plant and geographical origin, climatic conditions, type of bees and the ability of the beekeeper himself. The most common ingredients are carbohydrates, mostly fructose and glucose, and water, which together make up more than 99% of honey. [10] The rest consists of proteins (including enzymes), mineral substances, vitamins, organic acids, phenolic compounds, aroma substances (volatile compounds) and various chlorophyll derivatives, which is why it gives strength, gives strength to the body and ensures physical endurance and psychological stability.

Because of all the above, the combination of these two ingredients represents a significant source of vitamins and minerals in daily use, but also for use in various pharmaceutical and medical purposes. In order to obtain specific data of products based on honey and hawthorn, the purpose of the work is the analysis of physical and chemical parameters such as: pH value, electrical conductivity, viscosity, refractive index, water activity, HMF, DPPH. As the literary data is scarce when it comes to the combination of these two natural ingredients, the aim of the analysis is to determine the physical and chemical characteristics of products based on honey and hawthorn in different proportions, in order to obtain more information about their quality and possible use as a food supplement.

MATERIAL AND METHODS

MATERIAL

For the research, three samples of honey and hawthorn (*Crataegi folium cum flore*) of different proportions with a total weight of 50 g were prepared. Meadow honey bought in a supermarket was used. Hawthorn was ground into powder and mixed with honey in the following proportions:

Table 1. Content of used sample

Name of sample	Content
Sample I	5g Hawthorns + 45 g honey
Sample II	10 g Hawthorns+40 g honey
Sample III	20 g Hawthorns + 30 g honey

The prepared samples were left to stand for 10 days after which they were used for analysis.

METHODS

, Determination of the pH value was performed using a Mettler Toledo 220 pH meter. The measurement is based on immersing the electrode of the pH meter in the sample, with prior calibration of the instrument with exactly known standard solutions. Electrical conductivity was determined with the help of a conductometer, also with previous calibration of the instrument with accurately prepared standard solutions. The refractive index for the mentioned samples was determined with the help of an Abbe refractometer, while the water activity was determined with the help of determination water activity device.
Viscosity was determined using an Ostwald viscometer at temperatures of 25°C (room temperature) and 40°C. From each sample, a mixture was prepared in such a way that 5 g of the sample was weighed and dissolved in 95 ml of water, and then measurements were made at the given temperatures. The density was determined using a pycnometer, and the viscosity value was calculated according to the following relation:

$$\eta_1 = \eta_2 \frac{\rho_1 \cdot t_1}{\rho_2 \cdot t_2} \quad \text{.....(1)}$$

where is:
η_1-viscosity of sample;
η_2-viscosity of destilled water;
ρ_1-density of sample;
ρ_2-density of destilled water;
t_1- time of sample;
t_2-time of destilled water.

The hydroxymethylfurfural content was determined by the White method at two wavelengths, 284 and 336 nm. The measurement for the samples and the standard was performed at 284 and 336 nm, after which the *HMF* value was calculated according to the following relation:

$$HMF\ (\text{mg/kg}) = (A_{284} - A_{336}) \times 149 \times 5 \times D/W \quad \text{.....(2)}$$

$$\left(149{,}7 = \frac{126 \cdot 1000 \cdot 1000}{16830 \cdot 10 \cdot 5}\right)$$

where is:
126 - is the molecular weight of HMF;
16,830 molar absorbance at 284 nm;
1000 is the conversion of grams to kg;
0.5 is the theoretical weight of the sample;
D is the dilution factor if dilution is necessary:
W is the weight of the honey sample in g.

The determination of DPPH was performed in ethanol solution because it facilitated the extraction of antioxidant compounds from the sample. 1g was taken from each sample and ethanol, acetate buffer (pH 5.5) and DPPH reagent were added, after which the measurement was performed on a spectrophotometer at a wavelength of 517 nm. Along with the samples, a blank test measurement was also performed.

RESULTS AND DISCUSSION

The physical properties of honey and hawthorn are closely related to the chemical composition of honey. Due to differences in the composition of honey, the values of these parameters can be specific and different.[11] It has been proven that viscosity, refractive index and specific mass depend on the proportion of water. Optical activity is related to the composition and content of certain carbohydrates, while electrical conductivity primarily depends on the content of mineral substances.[12]

Table 2. Values of physicochemical caracteristic products of the analyzed samples

Name of sample	pH	κ, μS/cm	Index of refraction	Water activity	Viscosity N·s/m^2		HMF mg/kg
					25°C	40°C	
Sample I	3.88	4.80	1.4978	0.557	933.440	761.622	2.6
Sample II	4.03	3.53	1.5284	0.545	970.583	780.88	6.4
Sample III	4.10	2.16	1.6325	0.508	980.281	814.70	7.1

The analysis of the samples showed that the highest measured pH value was sample III (4.10), while the lowest pH value was sample I (3.88), which shows that the chemical composition plays a big role. The pH value of hawthorn is acidic, which has been confirmed by other authors.[13] Generally, the pH value of honey ranges from 3.2 to 4.5 [14] and is not directly related to free acidity, due to the buffering properties of phosphates, carbonates and other mineral salts, which are naturally present in honey, which further implies that the obtained values of samples with honey content are in accordance with the literature. The lowest value of electrical conductivity was sample III (2.16 μS/cm), while sample I had the highest value (4.80 μS/cm). The electrical conductivity of honey depends on the content of minerals, organic acids, proteins, as well as complex compounds in honey. The electrical conductivity of honey, due to the high concentration of sugar, reduces the mobility of ions, and the electrical conductivity is also lower.[15]

Water activity is a physical property that shows the amount of free water available for the metabolism of the microorganisms present. Many types of bacteria grow at a water activity value (aw) of 0.94 - 0.99, that is, for most yeasts around 0.88, and for mold 0.75 - 0.80. The value of water activity is influenced by factors such as temperature, pH of the environment, content of added salt and others. [16] Sample analysis showed that sample I (one) had the highest water activity value of 0.557 and sample III had the lowest value of 0.508. The average activity of water in honey ranges from 0.56 to 0.62 [17], which shows that the analyzed samples based on honey and hawthorn have values that correspond to the average values of water activity for honey.

By measuring the refractive index, it was determined that sample III had the highest refractive index of 1.6325, while sample I had the lowest refractive index of 1.4978.

Viscosity is the degree of liquidity, i.e. the liquid state, and it particularly affects the processing and storage flow. Viscosity is affected by several factors such as the composition of honey (mainly water content), type of honey, temperature and the number and size of crystals in honey. As the water content increases, the viscosity decreases. As the temperature increases with a constant proportion of water, the viscosity of honey decreases. A higher proportion of di- and trisaccharides contributes to higher viscosity.[18] Along with the water content, temperature has the greatest influence on viscosity.[19] As the temperature increases, the viscosity of honey decreases, and this effect is most pronounced at temperatures below 15 ºC. When determining the viscosity, sample I showed the lowest viscosity, and as the temperature increased, its viscosity further decreased. With the increase in the percentage of honey in the samples, the viscosity also increased, but with the increase in temperature, it decreased in each sample.

Hydroxymethylfurfural (HMF) is a cyclic aldehyde and is naturally present in honey. Its content in fresh honey is very low and amounts to less than 1

mg/kg. The increase in its value is influenced by various parameters such as the use of metal containers for storage, exposure to UV radiation, mineral composition, content of organic acids and moisture, etc. [20] The temperature also has a great influence on the value of HMF, the content of HMF increases rapidly if the temperature of the environment is above 20°C. According to research, the time required for the formation of 30 mg/kg of HMF in honey at a temperature of 30 °C is up to 300 days, and at a temperature of 80ºC it takes less than 2 hours to achieve the same amount of HMF. [21],[22],[23] According to the Ordinance on honey and bee products (Official Gazette Bosnia and Herzegovina No. 37/09), the value of HMF must not exceed 40 mg/kg, which further shows that in the analyzed samples, which are based on a mixture of honey and hawthorn within borders. Notably, the sample with the highest amount of honey had the lowest proportion of HMF.

When determining the antioxidant capacity with the DPPH method, different observations were recorded. With the increase in sample concentration, the ability to capture free radicals also increased. When we compare all three samples, we notice that with the increase in the percentage their antioxidant capacity also increased. Thus, we can say that the third mixture with the highest percentage of hawthorn showed the best ability to trap free radicals. Therefore, we can conclude that the third mixture has the best antioxidant properties.

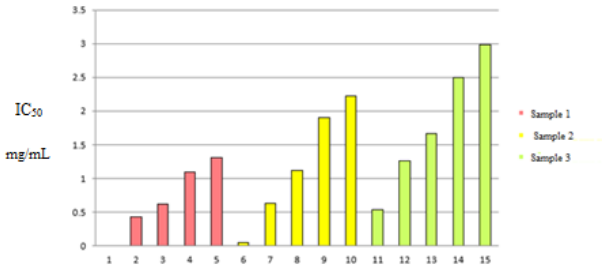

Figure 1. Radical scavenging ability of analyzed samples

CONCLUSION

The analysis showed that the highest pH value was sample III (4.10), the lowest sample I (3.88), which shows that the chemical composition plays a big role. Sample I had the highest electrical conductivity value (4.80 μS/cm), and sample III had the lowest value (2.16 μS/cm). Analysis of the samples showed that sample I had the highest water activity value of 0.557, and sample III had the lowest value of 0.507. The average water activity in honey ranges from 0.56 to 0.62, which shows that the analyzed samples based on honey and hawthorn have values that correspond to the average values of water activity for honey.

By measuring the refractive index, it was determined that sample III had the highest refractive index of 1.6325, while the sample had the lowest refractive index of 1.4978. Sample I showed the lowest viscosity, where as the temperature increased, its viscosity further decreased. With the increase in the percentage of honey in the samples, the viscosity also increased, but with the increase in temperature, it decreased in each sample.

The low value of HMF showed that it is this year's honey, and the obtained values are in accordance with the Ordinance on honey and bee products (Official Gazette of FBiH No. 37/09). The analyzed DPPH value showed that with the increase in sample concentration, the ability to capture free radicals also increased, and that the third mixture with the highest percentage of hawthorn showed the best ability to capture free radicals and the best antioxidant properties.

From the aspect of use and the analyzed physical chemical parameters, sample III showed the best antioxidant properties, but due to its taste consistency, it would be required for use. Sample II also showed good antioxidant properties, easier mixing, and therefore consumption, which would make this sample an excellent choice as a food supplement.

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