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HONEYDEW HONEY ADULTERATION: E-TONGUE AND PHYSICO-CHEMICAL ANALYSES

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Abstract: *The aim of this study is to evaluate the usefulness of the e-tongue and physico-chemical analyses (pH, electrical conductivity (EC), colour parameters (L*, a*, b*, chroma and hue angle)) for honeydew honey adulteration detection. For this purpose the honeydew honeys have been adulterated with inverted sugar and malt wort in different percentages (5, 10%, 20%, 30%, 40% and 50% respectively). The e-tongue used consisted of three electrodes: the reference electrode (Ag/AgCl), counter electrode (Glassy Carbon Electrode Rod - GC) and working electrodes (Ag and Au). The measurement has been made using the cyclic voltammetry. The addition of malt wort and inverted sugar influenced all the physico-chemical and e-tongue parameters. The addition of malt wort decreased the magnitude of the colour parameters (L*, a* and b*) and pH, and increased free acidity and electrical conductivity. The addition of inverted sugar increased the colour parameters' values and free acidity and decreased the electrical conductivity and pH. According to the principal component analysis (PCA) the samples with 5% and 10% inverted sugar and 5% malt wort are placed near to the authentic samples, so we can conclude that the samples have physico-chemical and e-tongue parameters closed to the authentic honeydew honey.*

Keywords: *honey, physico-chemical parameters, e-tongue, adulteration, PCA.*

1. Introduction

Honeydew honey is defined by the European Commission Council directive 2001/110/CE [1] as a food obtained from secretions of living parts of plants or from excretions of plant-sucking insects. Honeybees collect honeydew honey from the green parts of plant and at the same time, with honeydew, they may collect other attached structures, e.g. hyphae or fungal spores of plant pathogens and microalgae [2], [3]. Honeydew honeys contains different concentrations of carbohydrates and smaller amounts of proteins, minerals, vitamins, amino acids, phenolic acids [4].

Adulterated honeys are not just a issue for consumers only, but they raise problematic aspects for the authorities and retailers as well [5], [6]. The honey samples have been adulterated with many substances, which replace the main compounds (e.g. glucose and fructose) with industrial compounds obtained from cereals, sugar beet etc. [6]–[10].

The aim of this study is to evaluate the influence of the adulteration with inverted sugar and malt wort on honey physico-chemical properties (pH, electrical conductivity (EC) and colour parameters (L*, a*, b*, chroma)) on honeydew honeys and to check the usefulness of the e-tongue

and physico-chemical analyses for the adulteration detection.

2. Materials and methods

Materials

The honeydew honey has been purchased from local beekeepers located into Suceava County, in the North-East part of Romania.

Physicochemical parameters

Physico-chemical properties

The physicochemical properties (pH, electrical conductivity, colour parameters (L*, a*, b*, chroma and hue angle) were determined accordingly to the Harmonised methods of the International Honey Commission [11].

E-tongue

Electrodes

The electrodes used for the electrochemical measurement were: reference electrode (Ag/AgCl), counter electrode (Glassy Carbon Electrode Rod) and working electrodes (Ag and Au) (Metrohm, Germany).

Measurement system and experimental procedure – cyclic voltammetry

The measurement system consists in a PGSTAT 204 with FRA32M module (Metrohm, Germany), coupled to the electrodes presented above. The experimental data were recorded by using a NOVA 2.0 software (Metrohm, Germany). The voltage has been set between – 1V to + 1 V, with a scan rate of 0.5 V/s for the electrodes, and the frequency was set at 100 Hz. The electrodes were immersed in a vessel with 50 ml of honey solution (40 g honey completed to 200 ml with deionized water). To reach the electrochemical balance, the experimental data acquisition was made 10 minutes after the electrode has been placed into the honey solution. The experimental procedure was set for 45 s (1664 readings). All the samples were warmed to 25 °C before the experiment. To control the baseline drifts of the metallic electrodes, the electrodes were placed into a buffer solution at pH 7 before starting the measurements. The final values of current intensity were obtained subtracting their potential values from that of the buffer solution. Each experiment was made in triplicates.

Statistical analysis

Statistical analysis (Principal Component Analysis and Linear Discriminant Analysis) was performed using Unscrambler X 10.1 software system (Camo, Norway).

3. Results and discussion

In this study the influence of inverted sugar and malt wort on the physico-chemical parameters (pH, a_w, electrical conductivity, colour parameters (L*, a*, b*, chroma and hue angle)) of honeydew honey was investigated. Two adulteration agents has been used for two different reasons: the inverted sugar has been added into the honeydew honey because it is the cheap adulteration agent on the market (it can be made at home by just boiling a sugar solution with some citric acid) and the malt wort has been added into the honeydew honey because it has the same colour and appearance as the honeydew honey, respectively.

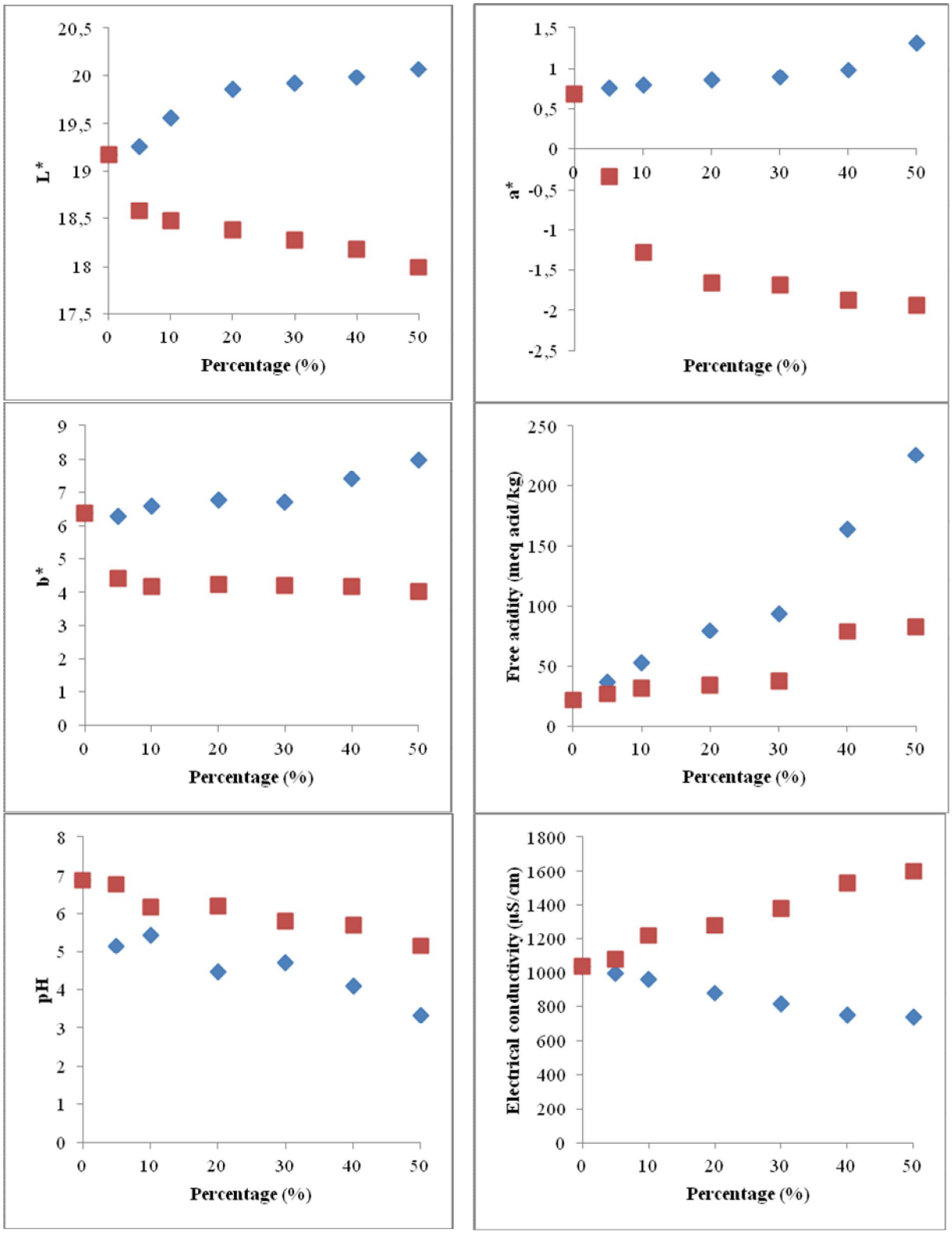

Fig. 1. The evolution of physico-chemical parameters in function of adulteration agent (rhombus –inverted sugar, square - malt wort) and adulteration agent percentage

The evolution of the physico-chemical parameters with the adulteration agent type and percentage is shown in figure 1. In the case of the L* it can be observed that the addition of inverted sugar is increasing the parameter values for the adulteration agent as the addition percentage is increasing, while in the case of malt wort addition the parameter is decreasing, respectively. Inverted sugar has a higher L* value than the honeydew honey, while the L* value for the malt wort is lower. However, the addition of inverted sugar or malt wort changes the L* value up to 6.1%, which is not normally observed by the human eye. The other two colour components (a* and b*) are negatively influenced by the addition of malt wort and positively by the addition of inverted sugar.

The two adulteration agents (inverted sugar and malt wort) have a positively impact on free acidity. In the case of malt wort the influence on free acidity is due to the presence of different acids which are being produced during the malting process, while in the case of the inverted sugar the acidity is given by the citric acid used for the hydrolysis process. The pH decreases with the increase of both adulteration agents in honey, the decrease of pH is due to the presence of acids in the malt wort and inverted sugar. The electrical conductivity of the honeydew honey is in agreement with the literature, being higher than 800 µS/cm [11]. The malt wort addition in the honey increased significantly the electrical conductivity (the malt wort has high content of minerals), while the inverted sugar decreased the electrical conductivity.

E-tongue

The maximum positive and negative voltage observed using the cyclic voltammetry with two different working electrodes (Au and Ag) are presented in the table 2. As it can be observed, the addition of inverted sugar is decreasing the Au+ and Ag+ and decreasing the Ag- and Au- because of the samples' acidity. In the case of malt wort adulterated honey samples, the addition of the agent is increasing the Ag+ and Au+, and decreasing the Ag- and Au- due to the high content of minerals and acids.

Table1.
The evolution of current with the adulteration agent on the two working electrodes

	Current (V)			
Sample	Ag+	Ag-	Au+	Au-
Honey	0.000985	-0.00054	9.39E-06	-4.4E-05
H 5%IS	0.000893	-0.00054	9.1E-06	-6.6E-05
H10%IS	0.000873	-0.00054	8.8E-06	-9.4E-05
H20%IS	0.000808	-0.00052	8.61E-06	-0.00014
H30%IS	0.000753	-0.00049	8.49E-06	-0.00017
H40%IS	0.000736	-0.0005	8.33E-06	-0.00019
H50%IS	0.000726	-0.00051	8.18E-06	-0.00021
H5%M	0.000981	-0.00059	8.7E-06	-5.1E-05
H10%M	0.001018	-0.00058	8.93E-06	-5.2E-05
H20%M	0.001103	-0.00051	9.55E-06	-5.1E-05
H30%M	0.001205	-0.00054	1.01E-05	-5.3E-05
H40%M	0.001271	-0.00055	1.05E-05	-5.7E-05
H50%M	0.001361	-0.00058	1.11E-05	-5.6E-05

Principal component analysis

The principal component analysis has been conducted to evaluate the influence of adulteration agent using the physico-chemical and e-tongue on honey based on a descriptive point of view. As it can be observed in the fig. 1, the honey samples

adulterated with 5%IS, 10% IS and 5% M, are very closed to the authentic honey, this aspect being explained by the fact that adulteration in small percentages does not change significantly the physico-chemical and e-tongue parameters. The samples with high concentration of malt wort are placed in a single dial; so according to the PCA the samples with high concentration of malt wort have the same characteristics. In the case of inverted sugar, the honey with 50% inverted sugar is placed in a different dial due to its chemical composition. According to the principal component loadings, the colour parameters are correlated with Au+, the pH with Ag+ and electrical conductivity with Au-. The electrical conductivity and free acidity are negatively correlated.

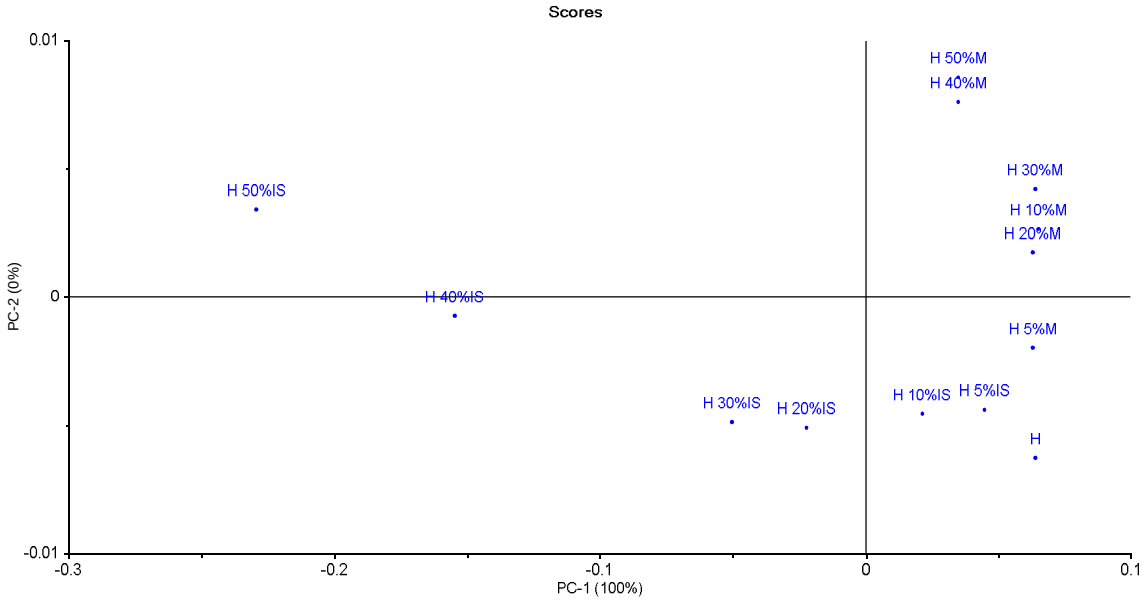

Fig. 2. Principal component analysis scores – H – honeydew, IS- inverted sugar, M – malt worth

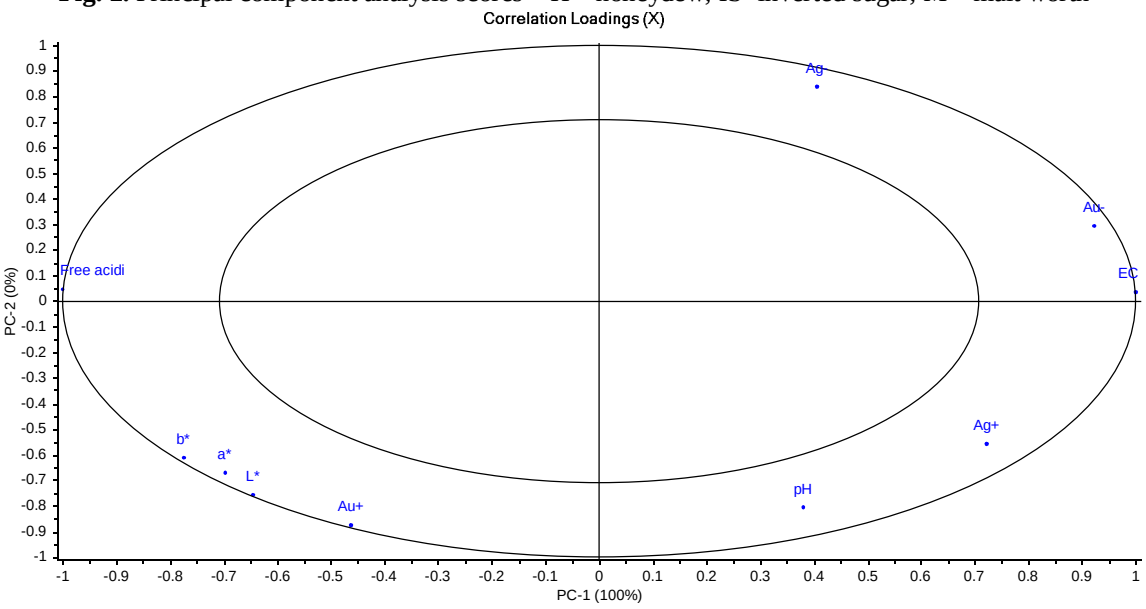

Fig. 3. Principal component analysis -loadings

4. Conclusions

The adulteration of honeydew with inverted sugar and malt wort influenced significantly the physico-chemical and e-tongue parameters. According to the principal component analysis (PCA) the samples with 5% and 10% inverted sugar and 5% malt wort are placed near to the authentic samples, so we can conclude that samples display physico-chemical and e-tongue parameters closed to the authentic honeydew honey.

Acknowledgement

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