



IMPACT OF ADULTERATION WITH GLUCOSE, FRUCTOSE AND HYDROLYSED INULIN SYRUP ON HONEY PHYSICO-CHEMICAL PROPERTIES

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Abstract: *The aim of this study is to evaluate the influence of the adulteration with glucose, fructose, hydrolysed inulin syrup on honey physico-chemical properties (pH, a_w , electrical conductivity (EC), water activity and colour parameters (L^* , a^* , b^* , chroma)) of three honey samples of different botanical origins (acacia, tilia and polyfloral). The honeys were adulterated in different percentages (10%, 20%, 30%, 40% and 50% respectively) with glucose, fructose and hydrolysed inulin syrup. The moisture content of all the three samples did not exceed the maximum allowable level of 20% established by the European Commission. The physico-chemical parameters (pH, a_w , electrical conductivity (EC), water activity and colour parameters (L^* , a^* , b^* , chroma)) of the analysed honeys are in agreement with other studies reported in the international scientific literature. The physico-chemical parameters prediction, in function of the botanical origin, adulteration agent and adulteration agent percentage have been made using the analysis of variance (ANOVA). According to the ANOVA it was observed that in the case of L^* , pH and electrical conductivity (EC) there is a good correlation ($R^2 > 0.90$) between the parameters and the botanical origin, adulteration agent and adulteration agent percentages.*

Keywords: honey, physico-chemical parameters, adulteration, ANOVA

1. Introduction

Honey is a natural product produced by honey bees (*Apis mellifera* L.) from various secretions of plants [1]. The act of deliberately adulteration degrades the quality of food meant to sale, either by the addition or exchange of low-grade materials or by the elimination of various important chemical compounds is termed as “food adulteration” [2]. Adulterated honey samples are labelled as natural pure honey and have the same price like original ones. Normally, honey adulterations do not have an impact on the human health. The identification of the adulterated honey is an important process

and it is difficult to identify this fact by producers, consumers, retailers and for the authorities too [3], [4]. The honeys have been adulterated over the last years with different agents such as: starch syrup [4], fructose and glucose [5], high fructose corn syrup (HFCS) [6], sugar syrups [7], glucose [8] and maltose syrup [9].

The aim of this study is to evaluate the influence of the adulteration with glucose, fructose, hydrolysed inulin syrup on honey physico-chemical properties (pH, a_w , electrical conductivity (EC) and colour parameters (L^* , a^* , b^* , chroma)) of three samples of honey of different botanical origins (acacia, tilia and polyfloral).

2. Materials and methods

Materials

3 honey samples of three different botanical origins (acacia, tilia and polyfloral) were purchased from local beekeepers from the Suceava County. The honey samples have been adulterated with glucose, fructose and hydrolysed inulin syrups in different percentages 10%, 20%, 30%, 40% and 50%, respectively.

Physico-chemical properties

The physico-chemical properties (pH, a_w , electrical conductivity, colour parameters (L^* , a^* , b^* , chroma and hue angle) were determined accordingly to the Harmonised methods of the International Honey Commission [10].

Statistical analysis

Statistical analysis was performed using a Unscrambler X 10.1 (Camo Norway) software system. The data corresponding to each variable were analyzed by one-factor analysis of variance (ANOVA).

3. Results and discussion

In this study the influence of the adulteration agents (glucose, fructose and hydrolysed inulin syrup) on the physico-chemical parameters (colour (L^* , a^* , b^* , C^* , hue angle), pH, a_w and electrical conductivity) of three difference honeys (acacia, tilia and polyfloral) was evaluated. The experimental data were subjected to ANOVA in order to establish if the honey type, adulteration agent or adulteration agent percentage are influencing significantly the physico-chemical parameters and if these parameters can be used in the identification of honey adulteration. Table 1 presents the physico-chemical parameters of the authentic honey analysed.

Table 1.

Physico-chemical parameters of authentic honeys

Parameter	Acacia	Polyfloral	Tilia
L^*	48.96	37.90	36.13
a^*	0.20	0.30	0.10
b^*	7.90	3.40	0.18
C^*	1.33	3.40	1.86
Hue angle	-85.33	85.10	-87.70
pH	4.11	3.72	3.89
A_w	0.801	0.806	0.764
EC ($\mu S/cm$)	59.40	207.10	413.50

Honey colour depends on the content of phenolic compounds, pollen and minerals. In the present study acacia honey has exhibited the highest colour purity (Table 1), aspect highlighted by Kadar *et al.* [11] for acacia honey samples from Romania and Spain. Honey polyfloral presented the most pronounced yellow components, indicated by high values of b^* (Table 1) and chromaticity angle H.

Water is the second important parameter of honey. The water activity represents a proportional unit with the free water in the food products. A lower level of water activity than 0.60 is specific to microbiological stable products. The values of the water activity measured in this study are in agreement with those reported by other scientists [12], [13].

The pH of the honeys is an important parameter for the extraction and keeping of the products, because it influences texture, stability and shelf life [14].

The honeys' pH ranged between 3.72 and 4.57 in the same range with those reported in other papers in the case of Romanian honeys [15].

The electrical conductivity is influenced by the botanical origin, ash content, organic acids concentration and some complex sugars and polyols. The electrical conductivity was in the same range with those reported by other scientists in the case of Romanian honeys [16].

Influence of honey type

The influence of honey type on honey physico-chemical parameters after the adulteration is shown in Table 2. The a^* , pH and EC are not influenced by the addition of agents (P values are higher than 0.05). In the case of the other parameters, the honey types influence the evolution of

the parameters (L^* , b^* , c^* , hue angle and a_w). In the case of the electrical conductivity there can be observed higher values because the adulteration agents (glucose and hydrolysed inulin syrup) were prepared into acidified water (pH lower than 2).

Table 2.

Influence of honey type on physico-chemical parameters of adulterated honey

Parameter	Honey type			F-value
	Acacia	Tilia	Polyfloral	
L^*	52.23(51.16-53.30)a	39.55(38.48-40.62)b	39.7(38.7-40.8)b	202.8***
a^*	0.96(0.60-1.32)ab	0.88(0.52-1.24)b	1.37(1.02-1.73)a	2.39ns
b^*	-3.90(-5.68 - -2.13)c	1.46(-0.31-3.23)b	5.51(3.74-7.28)a	31.39***
C^*	5.56(4.40-6.68)a	2.69(1.57-3.82)b	5.26(4.12-6.38)a	8.73***
Hue angle	-60.64(-87.7—33.5)c	-4.43(-31.5-22.6)b	72.9(45.8-100.1)a	27.19***
pH	3.46(3.31-3.61)a	3.33(3.18-3.48)ab	3.21(3.06-3.65)b	3.13ns
A_w	0.80(0.80-0.81)a	0.79(0.79-0.80)b	0.81(0.80-0.81)a	9.24***
EC (μ S/cm)	425.84(186.3-665.3)a	501.95(262.4-741.47)a	480.5(241.0-720.1)a	0.12ns

Influence of adulteration agent

The evolution of the physico-chemical parameters of adulterated honeys according to the adulteration agent used (glucose, fructose and hydrolysed inulin syrup) is shown in Table 3. There can be observed that the addition of glucose, fructose or hydrolysed inulin syrup do not influence significantly the b^* and hue angle, while in the case of C^* , pH and electrical conductivity there can be observed a significant influence ($P < 0.001$). The addition of glucose and hydrolysed inulin syrup in the honey decreases the values of pH and increases the values of the EC because the solutions are prepared at lower pH values (pH lower than 2).

Influence of adulteration agent percentage

The evolution of the physico-chemical parameters of the adulterated honeys in

function of the adulteration agent percentage is shown in Table 4. In the case of L^* there can be observed that the parameter values increase because the addition of the adulterated agent (which has L^* values higher than honey) increases the luminosity. The addition of the adulteration agent influences significantly the evolution of the parameter. In the case of the a^* and C^* values there can be observed the same evolution like in the case of L^* because of the same conditions, but there it cannot be observed a significant difference in function of the percentage of the adulteration agent ($P > 0.05$). The water activity of the honey is influenced significantly by the addition of glucose, fructose or hydrolysed inulin syrup because these compounds influence the magnitude of the a_w [13]. The electrical conductivity increases with the increase of the percentage of sugars added because they are prepared at pH lower than 2.

Table 3.

Influence of adulteration agent on honey physicochemical parameters

Parameter	Adulteration agent			P-value
	Glucose	Fructose	Hydrolysed inulin syrup	
L*	44.1(42.9-45.2)b	44.05(42.9-45.2)ab	44.83(43.6-45.9)a	4,33*
a*	0.66(0.33-0.99)b	1.27(0.89-1.66)a	1.28(0.90-1.67)a	4,07*
b*	0.67(-0.94-2.28)a	2.23(0.32-4.13)a	0.16(-1.74-2.06)a	1,53ns
C*	2.85(1.83-3.87)b	5.33(4.12-6.53)a	5.33(4.13-6.54)a	6,76***
Hue angle	-13.1(-37.7-11.4)a	19.7(-9.4-48.7)a	1.33(-27.7-30.4)a	1,53ns
pH	3.98(3.84-4.11)a	4.01(3.85-4.17)a	3.98(3.89-4.11)b	236,9***
Aw	0.81(0.80-0.81)a	0.80(0.79-0.81)b	0.80(0.80-0.81)ab	3,48*
EC (μS/cm)	274.0(143.1-291.1)b	263.74(193.1-320.6)b	1270.5(1013-1527)a	34,87***

Table 4.

Influence of adulterated agent percentage on honey physico-chemical parameters

Parameter	Adulteration agent percentage						P-value
	0	10	20	30	40	50	
L*	42.17(39.6-44.7)c	42.4(41.0-43.8)c	43.2(41.8-44.6)bc	43.8(42.4-45.2)bc	44.3(42.9-45.7)b	47.0(45.6-48.5)a	5,91***
a*	0.61(-0.23-1.46)a	1.12(0.66-1.58)a	1.22(0.76-1.68)a	1.33(0.87-1.79)a	1.42(0.96-1.87)a	1.53(1.06-2.01)a	0,54ns
b*	4.71(0.52-8.91)b	-0.08(-2.63-2.18)ab	0.12(-2.15-2.40)ab	0.61(-1.66-2.88)ab	-0.02(-2.29-2.25)ab	0.78(-1.49-3.06)a	0,96ns
C*	3.85(1.19-6.50)a	4.68(3.24-6.12)a	4.01(2.57-5.45)a	5.27(3.83-6.71)a	5.28(3.84-6.72)a	5.94(4.50-7.38)a	0,74ns
Hue angle	-13.6(-77.6-50.4)a	-1.68(-36.41-33.04)a	-0.80(-35.5-33.9)a	7.86(-26.8-42.6)a	12.8(-25.8-47.5)a	21.2(-33.5-55.9)a	0,31ns
pH	3.26(2.91-3.62)a	3.52(3.32-3.71)a	3.31(3.11-3.50)a	3.31(3.11-3.50)a	3.31(3.11-3.50)a	3.32(3.13-3.51)a	0,80ns
a _w	0.78(0.77-0.79)d	0.80(0.79-0.80)c	0.80(0.80-0.81)bc	0.80(0.80-0.81)b	0.80(0.80-0.81)ab	0.80(0.80-0.81)a	10,55***
EC (μS/cm)	93.33(59.4-113.5)f	124.0(57.9-286)e	252.6(36-501)d	429.8(54-1352)c	613.6(34-1921)b	907.7(31-2920)a	3,31*

Parameter prediction

Based on the parameter values (experimental values), the evolution of the parameter based on honey type, adulteration agent and adulteration agent percentage using the ANOVA method has been predicted. The regression coefficients of the models obtained are shown in the Table 5. Based on the information data presented in the Table 5, the parameters

which are well predicted by the honey type, adulteration agent and adulteration agent percentage are: L*, pH and electrical conductivity. The experimental vs. predicted values of L* and pH and electrical conductivity (EC) are shown in the Figs. 1-3.

Table 5.

Statistical parameters of the linear models for the physico-chemical parameters

	L*	a*	b*	C*	Hue angle	pH	A_w	Electrical conductivity
R ²	0.990	0.583	0.663	0.480	0.823	0.920	0.649	0.975
F	147.788	2.001	2.805	1.320	6.636	16.401	2.637	54.645
Pr> F	< 0.0001	0.154	0.068	0.333	0.004	< 0.0001	0.080	< 0.0001

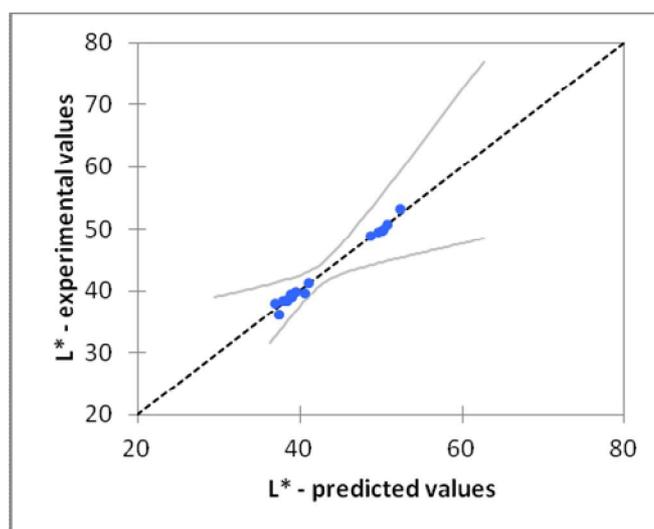


Fig. 1. Predicted vs. experimental data for L* according to the ANOVA

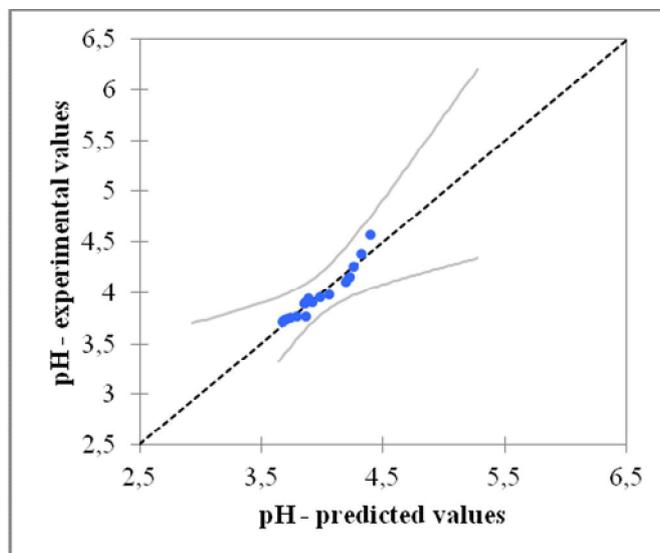


Fig. 2. Predicted vs. experimental data for pH according to the ANOVA

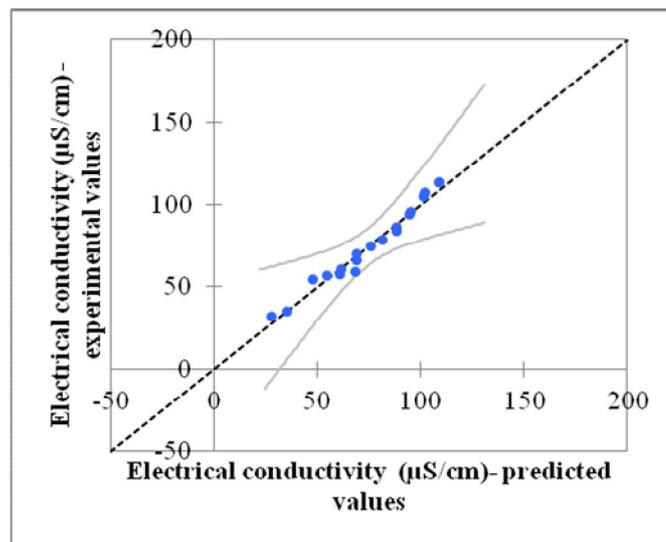


Fig. 3. Predicted vs. experimental data for pH according to the ANOVA

4. Conclusions

The honey analysed were of three different botanical origins (acacia, tilia and polyfloral) and their physico-chemical parameters were in agreement with the international literature. The adulteration agents influence strongly the evolution of the physico-chemical parameters. The ANOVA analysis was a good method for the prediction of L^* , pH and electrical conductivity (EC).

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5. References

- [1]. Official Journal of the European Communities, Directive 2001/77/Ec, *Communities*, 6: 33–40, (2001).
- [2]. SIDDIQUI A. J., MUSHARRAF S.G., CHOUDHARY M. I., RAHMAN A., Application of analytical methods in authentication and adulteration of honey, *Food Chemistry*, 217: 687–

698, (2017).

- [3]. LI S., SHAN Y., ZHU X., ZHANG X., LING G., Detection of honey adulteration by high fructose corn syrup and maltose syrup using Raman spectroscopy, *J. Food Compos. Anal.*, 28(1): 69–74, (2012).
- [4]. WANG S., GUO Q., WANG L., LIN L., SHI H., CAO H., CAO B., Detection of honey adulteration with starch syrup by high performance liquid chromatography, *Food Chem.*, 172: 669–674, (2015).
- [5]. YILMAZ M. T., TATLISU N., TOKER O.S., KARAMAN S., DERTLI E., SAGDI O., ARICI M., Steady, dynamic and creep rheological analysis as a novel approach to detect honey adulteration by fructose and saccharose syrups: Correlations with HPLC-RID results, *Food Res. Int.*, 64: 634–646, (2014).
- [6]. ÇINAR S. B., EKŞİ A., COŞKUN I., Carbon isotope ratio ($^{13}C/^{12}C$) of pine honey and detection of HFCS adulteration, *Food Chem.*, 157: 10–13, (2014).
- [7]. MOSUN T., Detection of adulteration in honey samples added various sugar syrups with $^{13}C/^{12}C$ isotope ratio analysis method, *Food Chem.*, 138: 1629–1632, (2013).
- [8]. DOWNEY G., FOURATIER V., KELLY J. D., Detection of honey adulteration by addition of fructose and glucose using near infrared transmittance spectroscopy, *J. Near Infrared Spectrosc.*, 11(6): 447–456, (2003).
- [9]. LI S., SHAN Y., ZHU X., ZHANG X., LING G., Detection of honey adulteration by high fructose corn syrup and maltose syrup using Raman spectroscopy, *J. Food Compos. Anal.*, 28(1): 69–

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- 74, (2012).
- [10] BOGDANOV S. *et al.*, Honey quality and international regulatory standards: review by the International Honey commission, *Bee World*, 80(2): 61–69, 1999.
- [11]. KADAR M., JUAN-BORRAS M., CAROT J. M., DOMENECH E., ESCRICHE I., Volatile fraction composition and physicochemical parameters as tools for the differentiation of lemon blossom honey and orange blossom honey, *J. Sci. Food Agric.*, 91(15): 2768–2776, (2011).
- [12]. MARGHITAS L. A., DEZMIREAN D. S., POCOL C. B., ILEA M., BOBIS O., GERGEN I., The development of a biochemical profile of acacia honey by identifying biochemical determinants of its quality, *Not. Bot. Horti Agrobot. Cluj-Napoca*, 38(2): 84–90, (2010).
- [13]. CHIRIFE J., ZAMORA M. C., MOTTO A., The correlation between water activity and % moisture in honey: Fundamental aspects and application to Argentine honeys, *Journal of Food Engineering*, 72(3): 287–292, (2006).
- [14]. GOMES T., FEÁS X., IGLESIAS A., Estevinho L. M., Study of organic honey from the northeast of Portugal, *Molecules*, 16(7): 5374–5386, (2011).
- [15]. OROIAN M., Physicochemical and Rheological Properties of Romanian Honeys, *Food Biophys.*, 7(4), (2012).
- [16]. OROIAN M., AMARIEI S., LEAHU A., GUTT G., Multi-element composition of honey as a suiTable tool for its authenticity analysis, *Polish J. Food Nutr. Sci.*, 65(2), (2015).