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THE PHISICO-CHEMICAL CARACTERISATION OF SUN FLOWER HONEY FROM BIHOR COUNTY

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Abstract

Honey has two sources, floral nectar and honeydew. In respect to the floral source, some monofloral honeys are available in every country. Sunflower honey is among them for Romania. In this experiment five samples of Sunflower honey from beekeepers in Bihor County, years 2013, 2014 and 2015were analysed in order to determinate their physicochemical characteristic: moisture, electrical conductivity, ash, acidity (T, free, lactonic, total), sugars (glucose, fructose, sucrose). HMF content and diastase number was also determinate as freshness parameters. All tested parameters comply with both Romanian and European quality requirement and, except for ash content, there are not significant differences to the references values.

Keywords: Sunflower honey, physicochemical characterisation, quality criteria

INTRODUCTION

Honey is an animal origin food produced by bees (*Apismellifera)* from two different sources, floral nectar and honeydew, which is the excretions of plant sucking insects (*Hemiptera*) on the living part of plants or secretions of living parts of plants*(Mărghitaş, 2005).* Due to its high sugars content honey is used as a healthy natural sweetener and as an important energetic source (1,272 kJ (304 kcal) /100 g). Fructose and glucose represent minimum 60% of honey sugars (Zielińska et al, 2014),but more than 25 oligosaccharides were identified too (Anklam, 1998) and until sugar ware produced on an industrial scale, after 1800, honey was the only sweetener used from millennia. Apart from water which must be under 20%, minor components of honey are antioxidantssuch as phenolic compounds Phenolic acids and flavonoides), aminoacids as proline, vitamins (vitamin C) and enzymes as catalase, peroxidase, glucose-oxidase, amylase. Among those components, fructosewhich can transform in hydroxymethilfurfurol (HMF) (White, 1994) and amylase are related to a specific freshness indicator or to an improper technological handling (Tosi, 2002, Turhan, 2008).

Beside its nutritional value, honey has multiple applications for improving human health (Bogdanov, 2010). A branch of alternative medicine called apitherapy offer a great deal of cures based on honey and others bee's products. The main effects are antimicrobial, antiviral and antiparasitical (Molan 1992 a, b, 1997). On the other hand, the phenolic compounds were found to be responsible for the antioxidant capacity of honey (Utthuty, 2011). Manystudies emphisise that antioxidand activity is correlated to the botanical origin of honey and their source (Weselowska et al, 2014,Vela et al, 2007, Baltrusaityte et al., 2007, Al-Mamary, 2002). Honey effect on cancer was studied recently (Orsolic, 2009) and the researches were review by Erejuwa et al, 2014.

In respect to the floral source, some monofloralhoneys are available in every country, depending of their climate(Purcărea et al, 2014, Şarba et al, 2014). For Romania, more specific the western part, the most predominant as quantity are acacia honey, rape honey, lime honey but there are in smaller amount other types as: Chestnut, heather, dandelion, fruit trees. Sunflower **(***Helianthus Annuus*L. – ASTERACEAE**) i**s cultivated in Bihor County on large areasfor its oilyseeds, it representsan important source of nectar and pollento bees so Sun Flower honey can be obtain as monofloral assortment. The variability of the floral source regarding the pollen production, leads to a big variability inpollen content, from 20% to90%, with a PG/10 g value mostly below 30 000 (PersanoOddo and Piro, 2004).

MATERIALS AND METHODS

Materials

The tested materials consist infive samples of Sunflower (*HeliantusAnnus*.) honey, two from 2013, two from 2014 and one from 2015. The samples were purchased directly from beekeepers in Bihor County. All samples were purchased in glass bottles and stored in dark at ambient temperature bellow 25^0C until analyzed. The samples were liquefied by gentle warming at 40^0C in a thermostatic bath.

All the used reagents were p.a. grade: sodium metabisulphitepotassium hexacyanoferrate(II), $K_4Fe(CN)_6.3H_2O$, double sublimate Iodine and starch from Merck Germany, $Zn(CH_3.COO)_2.2H_2O$,KCl, NaOH,HCl, CuSO4·7H2O, Seignette salt, NaCl, $NaHCO_3$, $Na_2S_2O_7$from Chimopar Romania.

The laboratory devices used in the present study were: VortexHettrich,Digital pH-meter/ConductometerSensiION HACH, Thermostatic OvenNitech Pol Eko-Aparatura, Calcination Oven

Nabertherm, LE 2/11/R6, ,spectrophotometerUVMini-1240 Shimatzu,Digital refractometerKruss Germany.

Methods

The quality parameters were determined according to the instructions of the International Honey Commission (Bogdanov, 2002) and SR 784-3/ 2009 excepted for glucose content (Popescu et al, 1986) and free, lactonic and total acidity(Silva et al, 2009).

3.1. Moisture content - refractometric method. All measurements were corrected for temperature and the corresponding % moisture (g/100 g honey) was obtained from the table for the purpose.

3.2. Electrical conductivity - was determined for a solution corresponding to 20g dry matter of honey in 100 ml distilled water by conductometric assay. The cell constant was determined by measuring the conductivity of a 0,1M potassium chloride solution and the results were corrected for the temperature of the sample.

3.3. Ash content - After the removal of water from the samples on an electric plate, the honey is burnt to ashes at 600°C and the residue is weighed.

3.4 pH - was measured in solution of 10 g honey in 75 ml of CO_2 free distilled water.

3.5 Free, lactonic and total acidity - were determined as follows, by titrimetric method: the addition of 0.05 M NaOH was stopped at pH 8.50 (free acidity), immediately a volume of 10 ml 0.05 M NaOH was added and, without delay, back-titrated with 0.05 M HCl to pH 8.30 (lactonic acidity). Total acidity results were obtained by adding free and lactone acidities.

3.6 Acidity, ^{0}T – 10% honey solution was titrated with NaOH solution 1N until pale pink (phenolphthalein)

3.7 HMF content - spectrophotometric White method. This method involves measurement of UV absorbance of clarified aqueous honey solutions with and without sodium metabisulphite. The absorbance of the solutions at 284 and 336 nm was determined.

3.8 Diastase activity- Shade method using a buffered solution of soluble starch and honey incubated in a thermostatic bath at 40 ^{0}C. The diastase value was calculated using the time taken for the absorbance to reach 0.235, and the results were expressed in Gothe degrees as the amount (mL) of 1% starch hydrolyzed by an enzyme in 1 g of honey in 1 h.

3.9 Sugars - Reducing sugars were determined by Elseriodometric method. Glucose was determined by Auerbach and Bodlander method when only sugar whit aldehydicfunction is reduced by iodine in basic environment. The difference between inverted sugars and glucose gave fructose. The difference in concentrations of inverted sugar before and after

the hydrolysis procedure (inversion) was multiplied by 0.95 to reach the apparent sucrose content.

Procedures were applied on fresh samples and the experiment was performed between July 2013 and July 2015

Statistical analysis -All tests were performed as triplicateand are presented as mean ± SD. The results of different experimental variants were compared by T-test for independent samples. Differences between means at 95% ($p<0.05$) confidence level were considered statistically significant.

RESULTS AND DISCUSSIONS

The obtained values are shown in Table 1 for the physicochemical characteristics and in Table 2 for the freshness parameters.The results are compared to those accepted by European Union (Council Directive 2001/110/EC, 2001) and Romanian Legislation (SR 784/1,2-2009). In the same time the tables presents the reference values for this type of honey which proceed from the descriptive sheets of the main European monofloral honeys (PersanoOddo and Piro, 2004), a reliable source of a large work from The International Honey Commission and Apimondia (IHC). As for Sunflower honey the number of data taken into consideration was between 157 for sucrose value and 243 for electrical conductivity.

Table 1

Physicochemical characterisation of Sunflower honey (n=5)

Nr.	Parameter	UM	Experimental values Mean ±SD	Legislation limit		Reference value mean±SD
				CE nr. 2001/110	SR 784-1,2/ 2009	
1	Moisture	g/100 g honey	18,7±1.18	Max 20	Max 20	17,8±1,1
2	Electrical conductivity	mS/cm	0.301±0.059	Min 0,8	Min 0,8	0.34±0,08
3	Ash content	Mg/kg	0,112±0.018	-	0.5	-
4	pH	pH units	3.656±0.185	-	-	3.8±0.2
5	Acidity	^{0}T	2.408± 0.472	-	4	-
6	Free acidity	MEQ/1000 g	22.36±1.045	Max 50	-	23.1±6.3
7	Lactones	MEQ/1000 g	9.892±0247	-	-	10.1±5.8
8	Total acidity	MEQ/1000 g	32.252±1.24	-	-	32.1±5.8
9	Fructose + Glucose	g/100 g	76.54±2.731	Min 60	Min 70	76.7±2.7
10	Glucose	g/100 g	37.88±1.37	-	-	37.4±1.5
11	Fructose	g/100 g	38.66±1.472	-	-	39.2±1.6
12	Fructose/Glucose		1,021±0.021	-	-	1,05±0.04
13	Sucrose	g/100 g	0.528±0.301	Max 5	Max 5	0.3±0.2
14	Glucose/Water		2.05±0.145	-	-	2.1±0,13

From both Romanian and European regulations (parameters 1, 2, 3, 5, 9, 13 from Table 1) the tested samples show a good frame to the admitted values. Regarding to the reference values, the statistic analysis (Student test) shows no significant differences ($p>0.05$) between all obtained experimental values and the reference ones excepted the sucrose content. In this case, significant differences occur between the observed mean values.The experimental ratios involving sugars content (F/G and G/W) comply with the references values and are typical for this kind of honey (PersanoOddo and Piro, 2004).

The experimental values for water content, pH, electrical conductivity, ash, sugars (glucose, fructose and sucrose) the investigated parameters comply to reported ones in Romania (Isopecu et al, 2014, Stihi et al, 2013, Diacu et Tânţăveanu, 2007, Mărghitaş et al, 2008) and in other countries like Turkey - Sari and Ayyeldiz, 2012 and Tukac et al, 2007 and France - Devilliers and al, 2004.

Table 2

Freshness parameters of Sunflower honey (n=5)

Nr.	Parameter	UM	Experimental values Mean ±SD	Legislation limit		Reference value mean±SD
				CE nr. 2001/110/	CE nr. 2001/110/	
1	HMF	mg/kg	0.71± 0.593	Max 40	Max 10/15*	-
2	Diastase activity	Shade scale	15.01±0.903	Min 8	Min 10.9	20.8±5.6

*The values refer to the artisanal, respectively to the marketable honey

As for the freshness parameters,(Table 2), experimental values are much under (for HMF) of above the limitation even if Romanian requirements are less permissive than the European Directive.The value for HMF content really demonstrates the freshness of the tested samples and because HMF practically doesn't exists in fresh honey (White, 1994). In the same time it demonstrate the lack of thermal mistreatment often applied on Sunflower honey due to itsquickly crystallisation rate. Isopescu et al, 2014 find the same situation for Sunflower honey collected in 2011-2012. Higher values reported by Devilliers and al, 2004(3.15±1.85) and Tukac et al, 2007 (2,3±1.43) are acceptable but demonstrate the necessity of thermal treatment for packaging.

CONCLUSIONS

The experiment leads to some conclusions, as follows:

The Sunflower honey samples tested meet both Romanian and European minimal quality criteria for this type of honey. The HMF content and Diastase number certify the freshness of the product and seem to indicate that no thermal treatment was performed and the samples are really from the harvesting year declared by beekeepers.

Except the ash content, the tested samples have similar physicochemical properties as the reference ones for this type of honey in Europe. The values for ash were not an accident because the samples came from the same area but in different years. Further determination on mineral content could give more clarifications in this subject as well as the extension of the experiment on a greater number of samples.

Further testing on greater number of samples, with different initial HMF values are needed in order to extrapolate the mathematical correlation between HMF content ant periods.

REFERENCES

1. Al-Mamary M, Al-Meeri A, Al-Habori M, 2002, Antioxidant activities and total phenolics of different types of honey. Nutr Res 22:1041-1047, 2002.
2. Anklam, E. 1998. A review of the analytical methods to determine the geographical and botanical origin of honey. *Food Chemistry*, 63 (4), 549-562.
3. Baltrusaityte V, Venskutonis PR, Ceksteryte V: Radical scavenging activity of different floral origin honey and beebread phenolic extracts. Food Chem 32 101:502-514, 2007.
4. Bogdanov S., 2002, Harmonised methods of the International Honey Commission, pages. 1–54
5. Bogdanov, S, Book of Honey, Chapter 8, Honey in Medicine**,** Bee Product Science, 24 March 2010, Bee Product Science, www.bee-hexagon.net
6. Devillers, J., Morlot M.,. Pham-Delegue M.H,. Dore J.C, 2004, Classification of monofloral honeys based on their quality control data, *Food Chemistry* , 86, (2), 305–312
7. Diacu, E., Tantaveanu, E.F., 2007, Determination of Moisture Content and its Correlation with other Parameters in Honey Quality Control, REV. CHIM. (Bucureşti), 58(12), pages 1310-1312
8. Erejuwa, O., Siti A., Sulaiman and Mohd S. Ab Wahab, 2014, Effects of Honey and Its Mechanisms of Action on the Development and Progression of Cancer, *Molecules*, *19*, pages 2497-2522
9. European Union Directive (EU). (2002). European Union Directive 2001/110/EC relating to honey
10. Isopescu RD., Josceanu AM., Minca I.,, Colta T, Postelnicescu P., Mateescu C, 2012, Characterization of Romanian Honey Based on Physico-Chemical Properties and Multivariate Analysis, *REV. CHIM*. (Bucharest), 65 (4), 381-385
11. Mărghitaş, L. Al, Dezmirean, D., Moise, A., Bobiş, O., Laslo, L., Bogdanov, S., 2008,Physico-chemical and bioactive properties of different floral origin honeys from Romania, *Food Chemistry,* 112 (4), 863-867

12. Molan P. C, 1999, Why honey is effective as a medicine. Its use in modern medicine, *Bee World*, 80(2), pages 80-92
13. Molan PC: The antibacterial activity of honey. 1. The nature of the antibacterial 40 activity. Bee World 73:5-28, 1992.
14. Molan PC: The antibacterial activity of honey. 2. Variation in the potency of the2 antibacterial activity. Bee World 73:59-76, 1992.
15. Oršolić, N, 2009, Bee honey and cancer Journal of ApiProduct and ApiMedical Science 1 (4): pages 93 - 103
16. PersanoOddoLivia and Roberto Piro, 2004, Main European unifloral honeys: descriptive sheets, *Apidologie* 35, S38–S81
17. Popescu, N., Popa, G., Stănescu, V., 1986, Determinărifizico-chimice de laboratorpentruproduselealimentare de origineanimală, Editura CERES, Bucureşti
18. Purcărea C, Chiş A., M. Dżugan, D. Popovici, 2014 - Physical-chemical and biochemical characterization of selected romanian and polish honeydew honey. StudiaUniversitatis "VasileGoldiş", SeriaŞtiinţeleVieţii (LIFE SCIENCES SERIES) Vol. 24, issue 2, ISSN 1584-2363 pp.251-256
19. Sari, E, Ayyildiz, N., 2012, Biological activities and some physicochemical properties of sunflower honeys collected from the Thrace region of Turkey, Pak J Biol Sci. Dec 1;15(23), pages 1102-1110.
20. Standard Român SR 784-1, Miere de albine, *Cerinţe de calitate la preluarea de la producător*, Bucureşti 2009
21. Standard Român SR 784-2, Miere de albine,*Cerinţe de calitate la comercializare*, Bucureşti 2009
22. Standard Român SR 784-3, , Miere de albine, M*etode de analiză*, Bucureşti 2009
23. Stihi, C., Radulescu, C., Chelarescu, E.D., Chilian, A., Toma, L.G., 2013, Characterization of Nectar Honeys According to Their Physicochemical Parameters and Mineral Content, REV. CHIM. (Bucharest), 64(9), pages 1000-1003
24. Şarba AC, Liviu Al. Mărghitaş, Timar A, 2014,Honey Sterilization and Mead Production, Bulletin UASVM Animal Science and Biotechnologies 71(2) / pag
25. Tosi E., M. Ciappini, Ré E. and H. Lucero, 2002, Honey thermal treatment effects on hydroxymethylfurfural content, *Food Chemistry*77, pages. 71–74.
26. Tucak Z., Periškić M., Škrivanko M., Konjarević A., 2007, The influence of the botanic origin of honey plants on the Quality of honey, ISSN 1330-7142, UDK = 638.132, p 234, http://hrcak.srce.hr/file/24438
27. Turhan I., N. Tetik, M. Karhan, F. Gurel and H. ReyhanTavukcuoglu , 2008, Quality of honeys influenced by thermal treatment,LWT - Food Science and Technology, Volume 41, Issue 8, November 2008, pages 1396-1399
28. Uthurry, C.A., Hevia, D., Gomez-Cordoves, C., 2011, Role of honey polyphenols in health, *Journal of ApiProduct and ApiMedical Science,* 3(4), 141 - 159
29. Vela L, de Lorenzo C, Pérez RA: Antioxidant capacity of Spanish honeys and its correlation with polyphenol content and other physicochemical properties. J Sci Food Agric 87:1069-1075, 2007.
30. Wesołowska, M., Kačániová, M., Dżugan, M., 2014, The antioxidant properties and microbiological quality of Polish honeys, *Journal of Microbiology, Biotechnology and Food Sciences,* 3(5), 422-425
31. White J. 1994, The role of HMF and diastase assays in honey quality evaluation, *Bee World*,75(3), pages 104-117
32. White, J., 1979, Spectrophotometric method for hydroxymethyl furfural in honey, *Journal of the Association of Official Analytical Chemists,* 62, pages 509–514.

33. Zielińska S., Wesołowska M., Bilek M., Kaniuczak J, Dżugan M., 2014, The Saccharide Profile of Polish Honeys Depending on TheirBotanical Origin,*Journal of Microbiology, Biotechnology and Food Sciences*,3(5), pages 387- 390