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A new model to identify botanical origin of Polish honeys based on the physicochemical parameters and chemometric analysis

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ABSTRACT

Confirmation of the authenticity or adulteration detection is a difficult, laborious and costly process. The aim of this study was to construct a honey botanical origin classification model on the basis of its characteristic physicochemical features. The experimental material comprised of 72 samples of varietal honeys. The botanical origin and the purity of honey samples were verified using a savoriness profiling method, and a pollen analysis. The following parameters of chosen honeys were determined: water, total ash, reducing sugar, total sugar and sucrose content, pH, total acidity solutions, specific electrical conductivity, dynamic viscosity, diastatic number, 5-HMF and proline content. The classification model was constructed with the use of all variables and with an employment of C&RT data mining method. A v-fold cross-validation proved that the model does reproduce the structure of dataset very well and in this particular case, incorrectly classifying only in one case heather honey as a multifloral one.

1. Introduction

Authenticity verification of honeys is linked with their varietal identification (Bogdanov & Gallmann, 2008; Hastie, Tibshirani, & Friedman, 2009). For many years, the varietal identification of honey has been a research subject in many scientific centers (Bogdanov & Gallmann, 2008). Pollen analysis has been the most often applied method when identifying varietal honey. It is a traditional method used to confirm the biological origin of honey elaborated and proposed by the International Commission for Bee Botany (ICBB) in 1970, and later revised and updated in 1978 (Louveaux, Maurizio, & Vorwohl, 1978). Nevertheless, this method is highly time-consuming and its accuracy depends strongly on the skills of professional experts (Karabagias, Badeka, Kontakos, Karabournioti, & Kontominas, 2014). Over recent years, this method has also been applied together with advanced statistical methods. Honey bees collect floral pollen from various plants, thus, pure mono-pollen honeys are very rarely encountered. Since the content of various pollens in honey is very large, currently this method is used collaterally with the sensory and physicochemical analyses to increase accuracy of the test (Bogdanov & Gallmann, 2008). Nevertheless, Stephens et al. (2010) reported that melissopalynological analysis was of no practical use in differentiating between manuka and kanuka honeys from New Zealand. However, identification of DNA markers present in pollen to specifically confirm the botanical origin of honey is a novel and promising method (Soares, Amaral, Oliveira, & Mafra, 2015).

Sensory analysis on its own is also used in the varietal identification of honey (Kerlvliet, 1992). This method, however, is considered as subjective. Therefore, many researchers endeavored to use the analysis of physicochemical parameters of honey in the varietal and geographical identification of honey, instead or additionally (Persano Oddo et al., 2004; Ruoff et al., 2007).

Amidst all the physicochemical parameters of honey quality, specific electrical conductivity appears to be the most effective when identifying varietal honey. This parameter is mainly used to distinguish some varietal nectar honeys from nectar blossom and honeydew honeys (Popek, 1998). Researches concerning honey identification on the basis of dyes contents in honey, mainly flavonoids (Meda, Lamiec, Romito, Millogo, & Nacoulma, 2005), or of color parameters' measurements in L* a* b* and X Y Z systems (Castro, Escamilla, & Reig, 1992) did not bring anticipated results. Multi-element analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) and by inductively coupled plasma mass spectrometry (ICP-MS) showed negative results as well (Di Bella et al., 2015).

Another approach concerns chemometric analysis of

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physicochemical parameters such as: contents of: saccharides, nitrogen, sucrose, 5-hydroxymethylfurfural, ash, water, aromatic acids and amino acids or glucose to fructose concentration ratio, pH level, total acidity, specific rotation (Ojeda de Rodríguez, Sulbarán de Ferrer, Ferre, & Rodríguez, 2004; Serrano, Villareho, Espejo, & Jodral, 2004). The combination of the above mentioned parameters makes it possible to recognize some of the monofloral honeys (Terrab, González, Díez, & Heredia, 2003). Yet, the results of those analyses are not satisfactory. It is, though, not possible on their basis to classify all honeys according to their individual types and varieties.

Some of the volatile fractions determination methods facilitate the discrimination of honey of different botanical origin. Escriche, Kadar, Juan-Borras, and Domenech (2011) proved the usefulness of flavonoids, phenolic compounds and headspace volatile profile together with statistical data evaluation techniques (PCA and PLS2) for verification of the botanical origin of lemon and orange honeys. Aliferis, Tarantilis, Harizanis, and Alissandakis (2010) proved that HS-SPME–GC/MS fingerprinting of honey volatiles combined with state-of-the-art chemometrics (OPLS™-DA) provides a potential honey origin discrimination tool. Additionally, in their research some biomarkers were detected. The existence of certain marker compounds useful for selected honeys' origin verification was also confirmed with GC–MS aroma compounds analysis performed by Castro-Vázquez, Leon-Ruiz, Alañon, Pérez-Coello, and González-Porto (2014). According to Špánik, Pažitná, Šiška, and Szolcsányi (2014), the GC-MS evaluation of differences in distribution of enantiomers of chiral volatile organic compounds holds a potential for distinguishing botanical origin of honey. The results of the Gašić et al. (2015) study showed that the analysis of the phenolic characteristics of honey achieved using UHPLC DAD–MS/MS as well as sugar and sugar alcohols determined by HPAEC/PAD and mineral content specified with the use of ICP-OES has a significant potential for the characterization of honey typical for a certain area. Zhao et al. (2016) proved that by establishing chromatographic fingerprints with the use of HPLC–ECD it is possible to identify three types of monofloral honey (Chinese jujube, longan and chaste). Moreover, a chemometric analysis of selected volatile compounds and physicochemical parameters (Karabagias, Badeka, et al., 2014) or selected phenolic compounds and conventional physicochemical parameters (Karabagias et al., 2014) proved useful in identifying the botanical origin of Greek honey.

Research by Wei and Wang (2014) showed that potentiometric and voltammetric electronic tongues together with discriminant function analysis (DFA) are useful for discrimination of monofloral honeys. Scandurra, Tripodi, and Verzera (2013) used electrical impedance spectroscopy to determine the botanical origin of monofloral honeys. They showed that few parameters, such as parallel resistance and impedance of the circuit, can be used as indicators of the floral origin. The application of near-infrared and mid-infrared spectroscopy (Chen et al., 2012; Escuredo, González-Martín, Rodríguez-Flores, & Seijo, 2015), that involves analysis of spectra, enables distinguish honeydew honey from nectar honey. The research carried out by Tewari and Irudayaraj (2004) proved that also FT-MIR spectroscopy could be successfully applied when assessing the authenticity of food products including honey.

A further developed method is an isotope ratio mass spectroscopy (IRMS), which is based on the knowledge of the ratio of isotopes that are characteristic for individual plant species. (Kelly, 2003). Whereas, according to Spiteri et al. (2015) also ^{1}H NMR measurements together with Independent Component Analysis (ICA) can be used to identify specific markers that are typical of botanical origin of selected honeys.

Nevertheless, repeatedly the results of above mentioned, often complex analyses, that in many cases require expensive equipment, do not permit the authenticity of honey to be unfailingly confirmed or contested. Thus, other methods are suggested. They involve measurements of a couple or a dozen physicochemical characteristics of honey and chemometric analyses of the parameters measured (e.g.: variation analysis, canonical analysis, analysis of key components, multidimensional analysis, taxonomic analysis, and discriminant analysis) in order to reduce the complexity and to provide a better interpretation of data sets and consequently to choose a few characteristics of honey that could be then considered for an optimal varietal or geographic distinguishing feature (Terrab et al., 2003; Yücel & Sultanoglu, 2013).

The literature confirms the fact that although so many diverse honey identifying methods are applied, it is still necessary to improve them or to develop a more effective method to better and more successfully identify the type and the variety of honey. Therefore the aim of this study was to construct a honey classification model on the basis of its characteristic physicochemical features to enable confirmation of the botanical origin of honey.

2. Material and methods

The experimental material comprised of 72 samples of varietal honeys (nectar [from rape, acacia, heather, linden, buckwheat, and multifloral nectar from various plants] honeydew, and nectar-honeydew). The honey samples analyzed were produced in apiaries located throughout various regions of Poland: Lesser Poland (Małopolska) (19 samples), Warmia and Masuria (13 samples), Silesia (13 samples), Pomerania (14 samples) and Podlasie (13 samples). Each sample was acquired from a different apiary.

The botanical origin and the purity of honey samples were verified using a savouriness profiling method developed by Cairnocros and Sjöstrőm and modified by Tilgner (1962), and a pollen analysis with the use of method established by the International Commission of Bee Botany (Louveaux Maurizio & Vorwohl, 1978). The following parameters of chosen honeys were determined:

1) water content by measurement of refractive index with a use of Atago RX-5000i refractometer (AOAC, 1995; Anonymous, 2001);
2) total ash content by incinerating honey samples in a muffle furnace at a temperature of 550 °C;
3) reducing sugars, total sugars and sucrose content using Agilent 1200 series HPLC along with RI detector 20 μL of each sample was injected onto an Agilent Hi-Plex Ca, 7.7 × 300 mm, 8 μm column at 85 °C with a flow rate of 0.6 mL/min. Pure water was used as eluent;
4) active acidity (pH) of aqueous 20 g/100 g solutions using a CX-721 multi-function computer measuring instrument;
5) total acidity of aqueous 20 g/100 g solutions; acidic honey components were neutralized by a standard solution of sodium hydroxide;
6) specific electrical conductivity of aqueous 20 g/100 g solutions using a CX-721 multi-function computer measuring instrument;
7) dynamic viscosity of aqueous 20 g/100 g solutions using a Ubbelohde viscometer TC SI Analytics; a honey solution flow in a capillary of Ubbelohde viscometer was measured (PN-87/C-8929/20, 1987);
8) diastatic number using photometric method with insoluble starch conjugated with blue dye as a substrate. Amylase hydrolyzes starch into water-soluble fragments forming joints with blue dye, which absorbance is measured by spectrophotometry using a Spectrophotometer V5600 Vis at a wavelength of 620 nm;