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Characterisation of the aroma profiles of different honeys and corresponding flowers using solid-phase microextraction and gas chromatography–mass spectrometry/olfactometry

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ABSTRACT

The aroma profiles of thirteen different honey samples from four botanical origins: heather (*Calluna vulgaris*), raspberry (*Rubus idaeus*), rape (*Brassica napus*), alder buckthorn (*Frangula alnus*) and the blossoms of the four corresponding flowers were investigated to find odour-active compounds exclusively representing specific honeys based on odour-active compounds from the blossoms. Gas-chromatography–mass spectrometry (GC–MS) and gas-chromatography–olfactometry were used to determine and identify the odour-active compounds. Data was analysed using agglomerative hierarchical clustering and correspondence analysis. Honeys from the same botanical origin clustered together; however, none of the identified compounds were exclusive to a particular honey/blossom combination. Heather honey had the flavour profile most different to the others. Isophorone and 2-methylbutyric acid were found only in heather honeys. Heather honey was characterised by having more "sweet" and "candy-like" notes, raspberry honeys had more "green" notes, while alder buckthorn had more "honey" and "floral" notes.

1. Introduction

Honey is a highly regarded food product in all parts of the world. The main parameters of honey quality, which also influence its price, are derived from its botanical origin. Several articles have been published on marker compounds from the volatile fraction, which could be used to identify the floral origin (Castro-Vazquez, Diaz-Maroto, Gonzalez-Vinas, & Perez-Coello, 2009; Castro-Vazquez, Diaz-Maroto, & Perez-Coello, 2007; de la Fuente, Sanz, Martinez-Castro, Sanz, & Ruiz-Matute, 2007; Guyot, Bouseta, Scheirman, & Collin, 1998; Guyot, Scheirman, & Collin, 1999; Jerković, Tuberoso, Marijanović, Jelić, & Kasum, 2009; Piasenzotto, Gracco, & Conte, 2003). Instrumental analysis has also been combined with descriptive sensory analysis, where, for example, heather honey was described with attributes "ripe fruit", "spicy", "woody" and "resin" (Castro-Vazquez et al., 2009). Cuevas-Glory, Pino, Santiago, and Sauri-Duch (2007) reviewed volatile analytical methods for determining the botanical origin of honey, pointing out extraction methods, fibres and extraction conditions used.

Solid-phase microextraction (SPME) as an aroma extraction method eliminates the use of (toxic) organic solvents, allows the quantification of a large number of molecules, requires little or no manipulation/preparation of samples, substantially shortens the time of analysis and, moreover, it is simple (Pontes, Marques, & Cámara, 2007). SPME has been widely used in analysis of different food products including honey (Piasenzotto et al., 2003; Plutowska, Chmiel, Dymerski, & Wardencki, 2011; Wolski, Tambor, Rybak-Chmielewska, & Kędzia, 2006).

SPME sampling can be performed in three basic modes: direct extraction, headspace extraction (HS) and extraction with membrane protection. The main advantage of the HS analysis is that it is carried out on an untreated sample (Piasenzotto et al., 2003) and the profile of the isolated volatiles is closely associated with sensory perception (Kaškoniene, Venskutonis, & Čeksteryte, 2008).

Heather honey has been previously characterised by a relatively high content of phenolic compounds, such as guaiacol, p-anisaldehyde and propylanisole (Castro-Vazquez et al., 2009). Phenylacetic acid was found exclusively in *Calluna vulgaris*

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(heather) honey (Guyot et al., 1999). Radovic et al. (2001) analysed 43 authentic honey samples of different botanical and geographical origins by means of dynamic headspace GC–MS, in order to assess marker compounds (if/when existing) of both botanical and geographical origin. Honey samples were of nine different botanical origins (seven acacia, nine chestnut, three eucalyptus, eight heather, two lavender, four lime, four rape, two rosemary and four sunflower) and from eight different countries (one from Denmark, ten from Germany, thirteen from Italy, eight from France, four from The Netherlands, two from Spain, two from Portugal and three from England). Radovic et al. (2001) identified phenylacetaldehyde as a characteristic compound to heather honeys.

According to Radovic et al. (2001) the authenticity of rape honeys could be confirmed by the absence of 2-methyl-1-propanol; however, this compound was absent also in one of the seven acacia honeys analysed, therefore it was emphasised that the simultaneous presence of dimethyl disulphide is necessary in order to confirm the authenticity of rape honeys. Plutowska et al. (2011) determined volatiles from popular Polish honeys (rape, acacia, linden, buckwheat, heather, polyfloral and honey-dew) by HS–SPME and found that the presence of dimethyl disulphide is not a peculiar feature of rape honey and can also be found in other honeys. Authors also emphasised that a much more significant feature to rape honeys is the lack or much lower concentrations of characteristic volatile compounds occurring in other honeys, e.g., linalool oxides, furfural and phenylacetaldehyde, which were present in most honey samples of different botanical origins. Kaškoniene et al. (2008) also found in their study that dimethyl disulphide was present only in six rape honeys out of eleven, while 2-methyl-1-propanol was absent in all of them.

Raspberry honey is characterised by the presence of 2-ethenyl-2-butenal, 3-methylhexane, 3-methylnonane, 3-pyridinemethanol, β-myrcene, cyclopentanemethanol, norbornane, and undecanal (Špánik et al., 2013), while tere is no literature available on volatile fraction of alder buckthorn honey.

Not all volatile compounds have significant impact on honey aroma due to different odour thresholds and interactions between compounds. GC–olfactometry (GC–O) can be used to select key odour-active compounds affecting the aroma of the honey. There is very limited information available about GC–O analysis of honey. Pino (2012) carried out a study on black mangrove honey using aroma extraction dilution analysis (AEDA) complemented by quantitative analysis and calculation of odour activity values. It was concluded that (*E*)-β-damascenone, nonanal and decanal are primarily responsible for the distinctive and characteristic aroma of black mangrove honey.

Alissandrakis, Tarantilis, Pappas, and Pashalis (2011) and Amtmann (2010) have conducted studies on volatile compounds present in honey and flower using GC–MS. It was found that relatively high percent of volatile compounds were overlapping in flowers and honeys, which allowed on floral markers to be proposed. However, since many of the compounds were common in the plant kingdom, they were present in various plants and honeys.

The aim of the present study was to determine floral markers influencing the aroma profile of honeys from different botanical origins by using HS–SPME–GC–O. Additionally, blossoms from representing plants were studied to find odour-active compounds that are carried over from the blossom to the honey. To the authors' best knowledge, GC–O has not been used on this purpose before.

2. Materials and methods

2.1. Materials

Honey samples were collected from local beekeepers in Estonia. Thirteen different honey samples were analysed. Samples 1 and 2 were unifloral raspberry honeys, 3–5 unifloral rape honeys, 6–8 honeys with high rape pollen content, 9–10 unifloral heather honeys, 11 honey with high heather pollen content and 12–13 honeys with high alder buckthorn pollen content. Samples 12–13 could also be unifloral honeys, but there is no literature available determining the content of pollen of alder buckthorn in unifloral honey. Visually samples 12 and 13 were rather different from other samples because of their dark colour and liquid consistency. Honey samples were stored at 4 °C until analysis. Plant blossoms were chosen according to the honey pollen analysis and harvested at the time of blossoming.

2.2. Melissopalynological analysis

Melissopalynological analysis was carried out according to the non-acetolytic method described by Louveaux, Maurizio, and Vorwohl (1978). The pollen counts were expressed as percentages after counting 500–600 pollen grains (Table 1). The identification of the pollen types were based mainly on the reference collection of the department of Food Processing in Tallinn University of Technology and data provided by Ricciardelli ĎAlbore (1997). An Olympus CX21 (Japan) binocular light microscope with 40 x 15 magnification was used. Required pollen contents to consider honeys unifloral can be found from previous research carried out by Kivima et al. (2014).

Table 1
The main pollen types of honey samples (%). Percentages in boldface refer to unifloral honeys; the plus sign (+) stands for minor pollen (<1%).

Pollen type	Honey samples												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Cruciferae													
Brassica napus s.l.	17	11	**60**	**77**	**76**	51	50	43	40	27	9	+	23
Ericaceae	1										3		
Calluna vulgaris									**16**	**27**	4		
Leguminosae													
Melilotus officinalis s.l., *Trifolium repens* s.l.	1	4	5	10	2	5	10	4	18	28	3	21	1
Trifolium pratense s.l.	+		1	5	+	+	5	+	3	4	19	1	+
Rhamnaceae													
Frangula alnus			1		2				2	3	1	**42**	**22**
Rosaceae													
Rubus idaeus s.l.	**67**	**79**	17	2	8	7	17	14	6	5	31	33	32
Salicaceae													
Salix spp.	6	5	9	+	6	27	7	34	1	1	14	+	5