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Chemistry and biological properties of berry volatiles by two-dimensional chromatography, fluorescence and Fourier transform infrared spectroscopy techniques

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ABSTRACT

In this study, three-dimensional fluorescence spectroscopy in combination with ultraviolet visible (UV–Vis) absorption spectroscopy, Fourier transform infrared spectroscopy (FTIR) and two-dimensional chromatography techniques were employed to investigate the main compounds in gooseberries, blueberries and cranberries. The determination of the terpenes (the main group of secondary metabolites) in the three berries was done by headspace solid-phase microextraction coupled with comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (HS-SPME/GC × GC–TOFMS). Main volatiles were assigned in each of the three berries' chromatograms. The compounds were organized in different groups: monoterpene hydrocarbons and monoterpene oxygen-containing compounds (oxides, alcohols, aldehydes, and ketones). The highest amount of alcohol and ester compounds (85%) was estimated in blueberry; carboxylic acids, ketones and aldehydes were found in cranberry (62%) and terpenes in cape gooseberry (8%). Human serum albumin (HSA) has been used as a model protein to study drug–protein interaction. Specific binding of polyphenols from berries to HSA under the physiological conditions was a result of the formation of a polyphenol–HSA complex. The berries' extracts interact with HSA before and after incubation with different binding affinities which are related to their antioxidant properties. The effect of the complexation on the secondary protein structure was verified in the changes of amide bands. Principal component analysis (PCA) was applied to discriminate the differences among the samples' compositions.

1. Introduction

The health benefits of berries are well documented due to their rich content in bioactive phytochemicals (pigments, phenolics and vitamins) as well as volatiles responsible for specific flavors (Arancibia-Avila et al., 2011; Caprioli et al., 2016; Dembitsky et al., 2011; Gorinstein et al., 2013; Namiesnik et al., 2014a, 2014b). There are a few reports on the properties of cranberry. The antioxidant, radical scavenging, antibacterial, antimutagen and anticarcinogen properties of cranberry's major bioactive compounds (anthocyanins, flavonols, flavan-3-ols, proanthocyanidins, and phenolic acid derivatives) were investigated by Cote, Caillet, Doyon, Sylvain, and Lacroix (2010). European cranberry is rich in biologically active substances, making it valued by both the phyto-pharmaceutical and food industries (Cesoniene, Jasutiene, & Sarkinas, 2009). Overall results by Kim, Jung, Kim, and Kwak (2008) suggested that freeze-dried cranberry powder might have the serum lipid improving and antioxidative effects demonstrated by their protection against protein and lipid oxidation. At present cape gooseberry (*Physalis peruviana*) fruit is one of the less consumed raw materials of plant origin for human nutrition. This fruit, as well as alimentary products made of it, was used by healers in folk medicine in the distant past (Rop, Mlcek, Jurikova, & Valsikova, 2012). The volatile compounds are good biomarkers of berry freshness, quality and authenticity (Caprioli et al., 2016; Dragović-Uzelac et al., 2008; Gutiérrez, Sinuco, & Osorio, 2010; Hanene et al., 2012; Rodriguez-Saona, Parra, Quiroz, & Isaacs, 2011). There are some reports

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about determination of volatile substances in different berries (Carvalho, 2014; Croteau & Fagerson, 2006; Mayorga, Knapp, Winterhalter, & Duque, 2001; Wang, Wang, & Chen, 2008; Yilmaztekin, 2014a; Yilmaztekin & Sislioglu, 2015). Application of a headspace solid-phase microextraction (HS-SPME) method for analysis of volatiles by comprehensive two-dimensional gas chromatography (GC × GC) time-of-flight mass spectrometry (TOFMS) is presented in a number of reports (Dymerski et al., 2015; Nicolotti et al., 2013; Yilmaztekin, 2014b). Some recent reports proposed as well different procedures for volatile substances determination in different berries. A fast and efficient GC–MS method including a minimal sample preparation technique for the discrimination of sea buckthorn varieties based on their chromatographic volatile fingerprint was proposed by Socaci, Socaciu, Tofana, Rati, and Pintea (2013). Fast gas chromatography–surface acoustic wave detection (FGC–SAW) was employed to characterize blueberry volatile profiles according to genotypes and fruit maturity (Du, Olmstead, & Rouseff, 2012; Du, Plotto, Song, Olmstead, & Rouseff, 2011; Du & Rouseff, 2014), which was effective for major blueberry volatiles, but could not determine many mid- and low-level volatiles as they were often coeluted with higher concentration volatiles. The information of a combination of spectroscopic and fluorometric methods for the comparison of different berries is limited. Evaluation of the antioxidant properties of gooseberries, cranberries and blueberries was done in our recent reports (Namiesnik et al., 2014a, 2014b). Based on the cited data the main purpose of this study was to determine the volatile and bioactive substances in cape gooseberry (*Physalis peruviana*) and to compare them with those from blueberry (*Vaccinium corymbosum*) and cranberry (*Vaccinium macrocarpon*). For this purpose the volatile substances were determined by headspace solid-phase microextraction coupled with comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (HS-SPME/GC × GC–TOFMS) as was shown in other reports as well (Kupska, Chmiel, Jedrkiewicz, Wardencki, & Namiesnik, 2014; Ozel, Gogus, & Lewis, 2008). Pharmaceutical interactions with human serum albumin (HSA) are of great interest, because HSA is a pharmacokinetic determinant and a good model for exploring the protein–ligand interactions. Naturally occurring flavones due to their hydrophobic nature possess various pharmacological activities and bind to HSA in human plasma (Liu, Bao, Ding, Jang, & Zou, 2010; Singh, Ghosh, & Dasgupta, 2013; Xiao et al., 2011). It is well known (Caruso, Vilegas, Fossey, & Cornelio, 2012; Poor et al., 2012) that natural flavonoids can also bind to HSA at the same binding site as achratoxin A does (site I, subdomain IIA). The bioactivity of the berry extracts and monoterpenes was determined by two antioxidant methods ABTS and CUPRAC (Apak, Guclu, Ozyurek, & Karademir, 2004; Apak, Özyürek, KGüçlü, & Çapanoğlu, 2016). The polyphenol extracts of berries were submitted to the interaction with HSA. Such interaction was studied at natural conditions and during incubation of the protein–polyphenol complex by fluorimetry and FTIR spectroscopy and radical scavenging assays (Magalhaes, Segundo, Reis, & Lima, 2008; Shi, Dai, Liu, Xie, & Xu, 2003; Simões, Esteves da Silva, & Leitão, 2014; Tang, Zuo, & Shu, 2014). To our knowledge, there has been no study reporting a combination of the volatile and antioxidant contents of these kinds of berries. Therefore, the characterization of biological properties of berries will be done by radical scavenging assays, two-dimensional chromatography, three-dimensional fluorescence and FTIR techniques.

Table 1
Volatiles identified using chromatograms obtained after analysis of blueberry, cranberry and cape gooseberry by SPME–GC × GC–TOFMS in TIC mode.

No.	Compounds
Blueberry	
1	Linalyl butyrate
2	Nonanal
3	Phenylethyl alcohol
4	α-Ethylcaproic acid
5	Isomethyl ionone
6	Acetic acid phenethyl ester
7	n-Hexyl acetate
8	1-Hexanol
9	*cis*-3-Hexen-1-ol
10	3-Nonyne
11	Isopentyl alcohol
12	Isopentyl alcohol, acetate
13	Isovaleric acid
14	Methyl isovalerate
15	Ethyl butanoate
Cranberry	
1	Oxalic acid, 2-methylphenyl pentadecyl ester
2	Propanoic acid
3	Benzeneethanol
4	(E)-2-Octen-1-ol
5	1-Hepten-3-ol
6	(E)-2-Octen-1-al
7	n-Caproaldehyde
8	Benzyl formate
9	*trans*-2-*trans*-4-Heptadienal
10	Propenal
11	*trans*-2-Pentenal
12	2-Methyl-1-butanol
13	Pentyl alcohol
14	*cis*-3-Hexen-1-ol
15	Benzaldehyde
Cape gooseberry	
1	Ethyl dodecanoate
2	Caryophylene oxide
3	Octanoic acid, 3-methylbutyl ester
4	Dodecanoic acid, methyl ester
5	Ethyl caprate
6	Capric acid methyl ester
7	n-Dodecane
8	γ-Butyl-γ-butyrolactone
9	Methyl-2-methoxyoct-2-enoate
10	Caprylic acid methyl ester
11	Butyl 3-hydroxybutyrate
12	Ethyl caproate
13	Methyl benzoate
14	γ-Caprolactone
15	Benzyl alcohol
16	3-Methyl-3-vinyl-1-cyclopropene
17	Benzaldehyde
18	6-Methyl-5-heptene-2-one
19	3-Methyl-1-penten-3-ol
20	Methyl β-methylcrotonate
21	n-Butyl acetate
22	Hexanal
23	Pentyl alcohol
24	γ,γ-Dimethylallyl alcohol
25	3,4-Pentadienal

2. Materials and methods

2.1. Reagents and materials

Analytical terpene standards were used to confirm the identity of selected compounds (Sigma-Aldrich, St. Louis, MO, USA). The standards of 19 in quantity included: β-pinene, camphene, β-myrcene, α-pinene, α-phellandrene, terpinolene, *p*-cymene, eucalyptol, limonene, α-ocimene, γ-terpinene, fenchone, (E)-linalool oxide, linalool, camphor, terpinen-4-ol, α-terpineol, β-cyclocitral, and α-ionone. As an internal standard the borneol substance was used (Sigma-Aldrich, St. Louis, MO, USA). A high purity deionized water from MilliQ A10 Gradient/Elix System (Millipore, Bedford, MA, USA) and GC grade sodium chloride (Sigma-Aldrich, St. Louis, MO, USA) were used throughout the experiment.

2.2. Sample preparation

All berries were from West Pomerania Province, harvested in late June, Poland. During the studies, three types of the fruit samples