LWT - Food Science and Technology 55 (2014) 657–665

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

The effect of high pressure treatment and cryotexturization on odorant mixture binding by corn, sorghum and amaranth starch

Wioletta Błaszczak [a,*], Tamara A. Misharina [b], Jadwiga Sadowska [a], Adrian R. Górecki [a], Józef Fornal [a]

[a] Institute of Animal Reproduction and Food Research, Polish Academy of Sciences, Tuwima 10, 10-748 Olsztyn, Poland
[b] The Emmanuel Institute of Biochemical Physics, Russian Academy of Sciences, Kosygina 4, Moscow 119991, Russia

ARTICLE INFO

Article history:
Received 29 November 2010
Received in revised form
23 August 2011
Accepted 11 October 2013

Keywords:
Starch
Odorants
Sorption
High hydrostatic pressure
Cryotexturization

ABSTRACT

The binding extent of odorant mixtures from aqueous suspensions by native, high pressure-treated starches and starch cryotexturizates was studied using capillary gas chromatography. The materials were corn, sorghum and amaranth starches. The native and high pressure-treated (650 MPa/9 min) starches were mixed with odorants and incubated (24 h) at room temperature. To obtain the cryotexturizate-odorant product, starch gels were frozen with odorants (−24 °C), stored (48 h) and thawed. Terpene hydrocarbons were strongly bound from the mixture by all the starches analyzed. The nonpolar molecules of terpene hydrocarbons modified the nature of hydrophobic binding sites in starch which in turn affected binding affinity of alcohols, ketones and phenols to the preparations. The competition effect between odorants for the binding sites was found. The varied ability of starch preparations to bind odorants was also related to the granule morphology and alteration in their structure upon treatment used.

1. Introduction

Starch production systems offer a vast range of native and modified starches with highly different functionalities. Their ability to interact with low molecular weight compounds is a particularly important feature, especially in the production of starch-based flavorings, tablets and microspheres (Bravo-Osuna, Ferrero, & Jimenez-Castellanos, 2008; Dukic-Ott, Remon, Foreman, & Vervaet, 2007). The efficiency of binding of odorants by the matrices has been reported to depend among others on their molecular structure, chemical properties, concentration and composition of flavorings forming the essential oil mixture (Misharina, Samusenko, & Kalinchenko, 2003; Misharina, Samusenko, & Kalinchenko, 2004; Misharina, Samusenko, & Kalinchenko, 2006; Tapanapunnitikul, Chaiseri, Peterson, & Thomson, 2008).

The sorption of alcohols (n-hexanol, n-heptanol, n-octanol and linalool) in aqueous suspensions by gelatinized maize starches was associated with the formation of supramolecular complexes (Misharina et al., 2003). The referenced studies have also revealed that in comparison with normal and high amylose maize starches, gelatinized amylopectin maize starch demonstrates a high sorption capacity for the studied odorants. According to the cited authors, lateral amylopectin chains are able to form incorporation complexes with the added odorants. Amylose readily forms complexes with, for example, flavor compounds since helication is not hindered by side chains. Amylopectin's limited ability to form complexes was found to be related to its branching structure. The long external branches of amylopectin support the formation of complexes with guest molecules characterized by high binding capacity values and low stability (Conde-Petit, Escher, & Nuessli, 2006).

Literature data also pointed out the treatment of starch granules may influence the binding properties of the starch matrices (Błaszczak, Misharina, Yuryev, & Fornal, 2007; Polaczek, Starzyk, & Tomasik, 1999; Zhao, Madson, & Whistler, 1996).

It is generally known that starch granules gelatinize already at room temperature upon high hydrostatic pressure treatment (Błaszczak, Fornal, Valverde, & Garrido, 2005; Rubens & Heremans, 2000). The changes in the structure and physicochemical properties of starch granules treated with high hydrostatic pressure have been widely studied in literature (Bauer, Hartman, Sommer, & Knorr, 2004; Błaszczak et al., 2005; Błaszczak, Fornal, et al., 2007; Buckow, Heinz, & Knorr, 2007; Katopo, Song, & Jane, 2002; Vallons & Arendt, 2009). However, the data on the exact nature of odorants binding to high pressure-treated starches are rather

* Corresponding author. Tel.: +48 (89) 523 46 15; fax: +48 (89) 524 01 24.
E-mail address: w.blaszczak@pan.olsztyn.pl (W. Błaszczak).

0023-6438/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.lwt.2013.10.016

limited. The binding affinity of odorants to high pressure-treated maize starches with different amylose content has been analyzed by the referenced authors (Błaszczak, Misharina, et al., 2007). The results indicate that high pressure treatment (650 MPa for 9 min) significantly affects the ability of starch granules to bind odorants. When subjected to high pressure treatment, high amylose maize starch (Hylon VII) showed the highest odorant binding capacity in comparison with the other analyzed samples. The high pressure treatment of waxy maize starch resulted in lack of binding such odorants as methyl anthranilate and γ-decalactone. These authors also found that hexanol, guaiacol and methyl anthranilate that were slightly sorbed by native starches and those ones treated with high pressure, manifested the highest binding affinity to starch directly upon high pressure treatment at 650 MPa for 9 min, irrespectively on botanical origin of granules. However, the incorporation of odorants to starch directly under the high pressure conditions diminished average sorption of the aroma compounds.

Upon cryotexturization (moderate freeze-storing and freeze-thawing), biopolymers form cryosponge with specific porosity that may affect odorant sorption (Golovnya, Misharina, & Terenina, 1998; Wasserman et al., 2009). The results of various experiments have demonstrated that starch cryotexturizates demonstrated ability to bind odorants (Krikunova, Terenina, Ruchkina, & Misharina, 2006; Misharina et al., 2004; Terenina, Krikunova, & Misharina, 2002; Terenina, Misharina, Krikunova, & Golovnya, 2002). According to Terenina, Krikunova, et al. (2002), the process of binding of cyclic compounds and/or aliphatic ketones is mainly irreversible and included the formation of supramolecular complexes. An increase in sorption affinity of odorants to corn starch cryotexturizates was connected with formation of suitable places for sorption, due to noncovalent interaction of the odorants with the polymers (Golovnya et al., 1998).

The data on interaction of different starch systems with volatiles from the multicomponent mixtures are rather scarce (Błaszczak et al., 2007a; Pozo-Bayon, Biais, Rampon, Cayot, & Le Bail, 2008; Terenina & Misharina, 2005). The interaction of starch with flavor compounds was mostly studied using a mixture consisted of several components (Krikunova et al., 2006; Savary, Lafarge, Doublier, & Cayot, 2007; Tapanapunnitikul et al., 2008). Binding the odorants by starches from the multicomponent mixture was found to be related to the competitive sorption and synergistic effect that occurred between the odorant mixture components. As it was reported, the presence of strongly bound compounds in the mixture increased the sorption of odorants with low binding activity (Terenina & Misharina, 2005). Bearing in mind that high pressure treatment distinctly influences physicochemical properties of granules, it might be also expected that the nature of binding sites in starch would be modified by the treatment used what in turn affect the binding capacity of obtained matrices.

In view of the above, the objective of this study was to investigate 1) the sorption of odorants from the multicomponent mixture by selected starches varied in structure and physicochemical properties; 2) in which extent the physical treatment of starch granules (high hydrostatic pressure, cryotexturization) affect the sorption of different aroma compounds.

2. Materials and methods

2.1. Materials

The seeds of plant species *Amarantus cruentus* L. were donated by the Metro Industrial Centre "Szarłat" s.c. (Lomza, Poland). Sorghum (Sorghum bicolor (v. Rona 1)) grains were purchased from the Kutno-Centre for Sugar Beet Breeding in Straszkow, Poland.

Commercial maize starch was donated by the Department of Food Concentrates in Poznan, the Institute of Agricultural and Food Biotechnology, Poland.

The aroma mixture comprising 30 main compounds, including monoterpene and sesquiterpene hydrocarbons, alcohols, ketones, phenols and ester (Table 1), was chosen for this experiment regarding the fact that all of them are constituents of commonly applied seasonings, and widely occur in a number of food products. The aroma mixture was prepared by mixing the essential oils of black pepper (1 mL), caraway (1 mL), coriander (1 mL), oregano (1 mL) and ginger (1.5 mL). The essential oils were purchased from Plant Lipids, Ltd, Cochin, Kerala, India. The concentrations of the odorant mixture in all of the analyzed starch systems accounted for 50 mg of odorants per 1 g (d.m.) of starch.

2.2. Methods

2.2.1. Characteristics of essential oil mixture components

The quantitative content of the components in the essential oils (μg/50 mg) was determined by GC with internal standard – n-tridecane (Table 1). Some peaks appeared in the chromatogram were not identified but amount of unknown compounds was calculated and accounted for 5.302 mg. Since quantity of essential oil mixture was calculated as a ratio of all the peaks in automatic mode, the amount of unknown compounds was included, as well.

The hydrophobic properties of odorants were analyzed according to the method proposed by Griffin, Grant Wyllie, and Markham

Table 1
Composition of model essential oil mixture.

No	Compound	Hydrophobicity coefficient, log K_{ow}[a]	Dose[b] μg/50 mg
Monoterpene hydrocarbons			
1	Camphene		544
2	3-Carene	4.38	856
3	p-Cymene	4.10	2186
4	Limonene	4.38	7011
5	β–Myrcene		397
6	α–Phellandrene		78
7	α-Pinene	4.44	1769
8	β-Pinene	4.16	1046
9	Sabinene		1002
10	α–Terpinene	4.25	65
11	γ–Terpinene	4.36	717
12	α-Tujene		143
Alcohols			
13	Carveol	3.12	132
14	Linalool	3.50	6913
15	Terpinen-4-ol	3.26	70
16	α–Terpineol	3.28	114
Ketones, phenols			
17	Camphor	2.74	475
18	Carvacrol	3.49	5276
19	Carvone	2.74	5090
20	Thymol	3.30	284
Ester			
21	Neryl acetate	3.98	309
Sesquiterpene hydrocarbons			
22	β–Bisabolene		814
23	Caryophyllene	6.33	2623
24	Caryophyllene oxide		281
25	α–Cubebene		487
26	α–Curcumene		1141
27	β–Elemene		160
28	β–Selinene		260
29	β–Sesquiphellandrene		1415
30	Zingiberene		3040

[a] K_{ow} – coefficient for distribution of the substance between n-octanol and water.
[b] Content of the components (μg) in the essential oil mixture (50 mg) added to 1 g of starch.