Food Hydrocolloids 39 (2014) 215–222

Contents lists available at ScienceDirect

Food Hydrocolloids

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

Comparison of volatile release in hydrocolloid model systems containing original and regio selectively carboxylated β-glucans

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ARTICLE INFO

Article history:
Received 4 July 2012
Accepted 8 January 2014

Keywords:
β-Glucan
Regio selectively carboxylation
Release
Interaction
Hydrocolloid
Hydrophobicity

ABSTRACT

The release of 13 volatile compounds in hydrocolloid model systems containing original or regio selectively carboxylated β-glucan at different pHs was analyzed using static headspace gas chromatographic analysis. There was significant difference in the release of most compounds, except for butyl propionate, 2-propanol, and 2,3-butanedione, in both the original and carboxylated β-glucan hydrocolloid model systems. However, the effects of pH in the hydrocolloid systems were not significant for most compounds studied, except for butyl propionate, ethyl caproate, 3-methyl-1-butanol, 2,3-butanedione. In particular, the release of 2,3-butanedione was considerably decreased at pH 10 compared to pH 4 and 7. In addition, the partition coefficient of each ethyl ester compound was measured to investigate the release of aroma compounds using the phase ratio variation (PRV) method. The difference in the partition coefficients of short and medium chain-ethyl esters between the reference solution and the original/carboxylated β-glucan solutions was not significant. In contrast, the release of relatively long chain-ethyl esters (ethyl caprylate and ethyl nonanoate) from both the original and carboxylated cellulose solutions was decreased compared to that in reference solution.

1. Introduction

The perception of flavor in foods, which is strongly related to their acceptance, is influenced by the headspace composition of volatile components above the food matrix (Shiota, Isogai, Iwasawa, & Kotera, 2011; Taylor, 1996). Headspace composition is also affected by diverse factors, such as the concentrations of volatile compounds in the food matrix, temperature, pH, water activity, and the physicochemical properties of the volatile compounds (i.e., molecular weight, boiling point, solubility, hydrophobicity, and interaction with other components of the food matrix including proteins, fats, and polysaccharides) (Lo, Lee, Richter, & Dill, 1996).

Polysaccharides are used as thickening agents to modify the texture and appearance of beverages, sauces, salad dressings, soups, mayonnaise, and ice cream, and as a fat replacer in calorie-reduced foods (Charles, Rosselin, Beck, Sauvageot, & Guichard, 2000; Hwang & Shin, 2011). The polysaccharides used in foods modify the rate and intensity of flavor release through specific or non specific bindings of flavor molecules and by physically entrapping flavor molecules within the food matrix (Boland, Buhr, Guannouli, & Van Ruth, 2004; Carr et al., 1996). In particular, the effects of polysaccharides on flavor release in aqueous food systems have been studied extensively by applying polysaccharides to hydrocolloid systems (Goubet et al., 2001; Hansson, Andersson, & Leufvén, 2001; Jouquand, Ducruet, & Giampaoli, 2004; Landy, Druaux, & Voilley, 1995; Roberts, Elmore, Langley, & Bakker, 1996; Yven, Guichard, Giboreau, & Roberts, 1998). It was obvious that the diverse polysaccharides added could affect the release of flavor components in both static and dynamic states. However, the general release patterns of various components in different hydrocolloid systems could not be predictable and clearly explained.

The increasing interest in the importance of dietary fiber has led to its supplementation to various food products. In particular, β-glucan is one of major dietary fibers that have many health benefits, such as lowering the serum cholesterol level, impeding postprandial blood glucose, and reducing the risk of coronary heart disease; this is achieved by reducing the absorption of lipids and glucose at the intestinal surface (Bhatty, 1992; Tosh et al., 2010). β-Glucan is found in the bran of cereals such as barley, oat, rye, and wheat. Its structure contains an unbranched chain with (1 → 3)-linked cellotriosyl and cellotetraosyl units arranged randomly, comprising about 70% β-(1 → 4) and 30% β-(1 → 3)-linkages (Wang, Wood, Huang, & Cui,

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http://dx.doi.org/10.1016/j.foodhyd.2014.01.010

2003). It forms worm-like cylindrical molecule containing up to about 250,000 glucose residues that produce cross-links between regular areas with consecutive cellotriose units (Beer, Wood, & Weisz, 1997). However, β-glucan has the drawback of low solubility in water (i.e., soluble below a concentration of 1% at room temperature). Diverse methods have been developed to overcome this drawback. For example, β-glucan was converted to a monosaccharide or oligosaccharide by decomposing the polysaccharide linkage, but this either reduced or completely removed its original functional and physiological activities (Vaikousi, Biliaderis, & Izydorczyk, 2004). Other studies have also been performed to increase the solubility of polysaccharides by oxidization. Cross et al. (2001) reported on the biological activity of β-glucan oxidized by 2,2,6,6-tetramethyl-1-piperidine oxoammonium (TEMPO). However, these studies revealed the non specific and random carboxylation of polysaccharide, which led to loss of their original function and structure. On the other hand, Chang and Robyt (1996) employed specific carboxylation to improve the water-solubility of polysaccharide, thus conserving the original polysaccharides linkage. They found that the water solubility of the oxidized products greatly improved, and their functionality and biological activity could be preserved by selective oxidation of polysaccharides.

Recently, there have been numerous studies on the flavor release using static and dynamic headspace methods (Goubet et al., 2001; Hansson et al., 2001; Jouquand et al., 2004; Landy et al., 1995; Langourieux & Crouzet, 1995; Nahon, Harrison, & Roozen, 2000; Roberts et al., 1996; Yven et al., 1998). Although the dynamic headspace methods could more closely reflect the release of flavor components in our mouths during eating, the headspace methods could be applied to observe the effect of polysaccharides on the release of volatiles, in particular, being related to the partition coefficients.

In this study, the release of different volatiles was investigated in the hydrocolloid systems containing original and regio selectively carboxylated β-glucans using static headspace gas chromatographic (SH-GC) analysis.

2. Materials and methods

2.1. Materials

β-glucan (curdlan-type from *alcaligenes faecalis*), ethyl acetate (purity 99.8%), methyl propionate (purity 99%), ethyl propionate (purity 99%), ethyl butyrate (purity 99%), butyl propionate (purity 99%), ethyl caproate (purity 99%), ethyl caprylate (purity 99%), ethyl nonanoate (purity 97%), 2-propanol (purity 99%), 3-methyl-1-butanol (purity 99%), 2,3-butanedione (purity 97%), *trans*-2-hexenal (purity 98%), *cis*-4-decenal (purity 80%), and ethyl alcohol (purity 99.5%) were purchased from Aldrich (Milwaukee, WI, USA). The physicochemical properties of these volatile compounds are listed in Table 1. The water used in this study was distilled and purified using a Millipore Q system (Millipore, Billerica, MA, USA).

2.2. Procedure to modify β-glucan by regio selective carboxylation

The regio selectively carboxylated β-glucan was obtained using the process described below. First, 10 mmol of β-glucan (3.566 g) was dispersed in 100 mL of water and stirred. Oxidation was then initiated by the addition of TEMPO (0.1 mmol, 16 mg), sodium bromide (0.5 g), and 31.5 mL of 1.389 mol/L sodium hypochlorite solution. The reaction was conducted within 0.05 °C of 25 °C and pH 10.8. The pH was monitored and controlled with 0.5 mol/L sodium hydroxide using the pH-stat device (Metrohm, Hensau, Switzerland). After 1 mmol hydroxide per 1 mmol of primary alcohol was added, oxidation of β-glucan was quenched by the addition of 2.5 mL of n-propanol per 100 mL of solution, followed by neutralization with 4 mol/L hydrochloric acid. The oxidized product was precipitated by the addition of 2 volumes of n-propanol. The precipitate was washed using 5–6 volumes of n-propanol and dried in vacuo at 45 °C to give a dry power. The primary hydroxyl group of β-glucan was thus oxidized to a carboxylic group by oxidation and reduction catalysts (i.e., TEMPO, sodium hypochlorite, and sodium bromide).

Table 1
Physicochemical properties of aroma compounds.

Aroma compounds	Boiling point[a] (°C)	Molecular weight[b]	Log P^c
2-Propanol	82.5	60.1	0.16 ± 0.19
2,3-Butanedione	88	86.09	−1.33 ± 0.33
Methyl propionate	79.7	88.11	0.71 ± 0.20
Ethyl acetate	77	88.11	0.71 ± 0.20
Ethyl propionate	99	102.13	1.24 ± 0.21
3-Methyl-1-butanol	113–114	88.15	1.22 ± 0.19
Ethyl butyrate	120–121	116.16	1.77 ± 0.21
trans-2-Hexenal	–	98.14	1.58 ± 0.28
Butyl propionate	146.8	130.18	2.30 ± 0.21
Ethyl caproate	166–167	144.21	2.83 ± 0.21
cis-4-Decenal	–	154.25	3.77 ± 0.24
Ethyl caprylate	207–209	172.26	3.90 ± 0.21
Ethyl nonanoate	–	188.29	4.43 ± 0.21

[a] The Merck Index-An encyclopedia of chemicals, drugs, and biologicals (13th edition), published by Merck Research Laboratories Division of MERCK & CO., INC.(Whitehouse Station, NJ).
[b] http://webbook.nist.gov/chemistry/name-ser.html.
[c] Advanced Chemistry Development, Inc.(http://www.acdlabs.com/ilab).

2.3. Sample preparation

One-percent solutions of original and carboxylated β-glucans were prepared by dissolving in water at room temperature. The pH of each solution was then adjusted to 4, 7, or 10, and the solution was homogenized using a Vortex (Scientific Industries, Bohemia, NY, USA) at room temperature for 30 s.

The 13 volatile compounds (ethyl acetate, methyl propionate, ethyl propionate, ethyl butyrate, butyl propionate, ethyl caproate, ethyl caprylate, ethyl nonanoate, 2-propanol, 3-methyl-1-butanol, 2,3-butanedione, *trans*-2-hexenal, and *cis*-4-decenal) were dissolved in ethyl alcohol at a concentration of 1.7% (w/w). This stock solution was added drop-wise to water to obtain a final concentration of 420 mg/L for ester compounds and 1680 mg/L for other volatile compounds, and then diluted using water before use. Accordingly, the final concentrations of each of the volatile compounds and original/carboxylated β-glucan in hydrocolloid solutions were 84 mg/L for ester compounds, 336 mg/L for other aroma compounds, and 0.08% for original/carboxylated β-glucan. An aqueous solution without β-glucan was also prepared as a reference solution (the blank solution). The three different types of solutions (original β-glucan, carboxylated β-glucan, blank solution) containing all 13 volatile compounds were used for static headspace gas chromatographic analysis. All sample preparations were performed in triplicate.

2.4. Measurement of the release of volatile compounds from hydrocolloid model systems containing original and carboxylated β-glucans by static headspace gas chromatographic analysis

Static headspace gas chromatographic (SH-GC) analysis was performed using a gas chromatograph (CP 3800, Varian, Walnut Creek, CA, USA) equipped with a flame-ionization detector (CP 3800, Varian) and a static headspace autosampler (Headspace 7000, Tekmar Dohrmann, Cincinnati, OH, USA). The time required for equilibration between the liquid and air phases in the vial was