



Effect of konjac glucomannan addition on aroma release in gels containing potato starch



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ABSTRACT

The present study aimed to measure the retention of aroma compounds (ethyl acetate, ethyl hexanoate and carvacrol) in dispersions based on konjac glucomannan and/or potato starch, and to highlight the influence of konjac glucomannan on the mechanisms involved in aroma retention. Publications on the effect of konjac glucomannan on aroma release are scarce. Konjac glucomannan is a polysaccharide used as a food additive for its viscous and emulsifying properties. Retention of aroma compounds in dispersions was calculated from partition coefficients which were measured using the phase ratio variation method. This method, consisting of analyses of the headspace at equilibrium, enables the determination of the partition coefficient of volatile compounds in a gas/liquid system without external or internal calibration. The three aroma compounds chosen for this study behave differently toward amylose. Prior to the release study, the complexing behavior of carvacrol with starch, hitherto unknown, was investigated by X-ray diffraction: V_{041} amylose complexes were formed with carvacrol. Our results showed no specific interaction between ethyl hexanoate and potato starch or konjac glucomannan. Ethyl acetate retention seemed to be due to trapping in the complex network of polysaccharides and to the density of this network. Retention of carvacrol was influenced by the nature of polysaccharides present in the dispersion, and was mainly governed by specific interaction with starch. Additionally, the addition of konjac glucomannan to potato starch dispersions decreased the retention of volatile compounds complexing starch, but had little effect on the retention of the other aroma compounds.

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1. Introduction

Polysaccharides, when used as thickening and stabilizing agents in food formulation, are commonly known to reduce flavor release due to an increase in viscosity and/or molecular interaction with flavor compounds (Arvisenet, Le Bail, Voilley, & Cayot, 2002).

Among polysaccharides used in the food industry, starch is one of the most important food hydrocolloids. It is used not only as a main ingredient of staple foods but also as a thickener, gelling agent, stabilizer and fat replacer in processed food products. Starch may interact with small molecules such as aroma compounds and lipids. Additionally, to avoid negative effects such as syneresis which may occur during storage, other hydrocolloids are often added to starch to maintain overall product quality throughout the shelf-life. Synergistic interaction between starch and the added hydrocolloid may modify the texture,

improve moisture retention and control water mobility (Alam, Siddiqui, Lutfi, & Hasnain, 2009; Takahiro et al., 2005).

Konjac glucomannan (KGM) is one of these polysaccharides. KGM is an essentially linear polysaccharide composed of blocks of β -1,4-linked mannose and glucosyl residues with approximately 5–10% acetylation (Khanna & Tester, 2006; Yoshimura, Takaya, & Nishirani, 1997). KGM was reported by diverse authors to interact synergistically with carrageenan, xanthan, and gellan gum, and with starches of various botanic origins: maize (Khanna & Tester, 2006; Yoshimura, Takayab, & Nishinarib, 1998; Yoshimura et al., 1997), wheat (Takahiro et al., 2005; Zhou, Wang, Zhang, Du, & Zhou, 2008), potato (Khanna & Tester, 2006), tapioca (Muadklay & Charoenrein, 2008), and rice (Charoenrein, Tatirat, Rengsutti, & Thonggam, 2010; Huang, Kennedy, Li, Xiao, & Xie, 2007). All these authors found that the high water holding capacity of KGM prevented syneresis occurring in starch gels and slowed down the retrogradation rate of starch during storage. Due to its technological properties when combined with other ingredients, KGM can also be used as a 'fat analog' in the formulation of reduced/low-fat food products (Delgado-Pando, Cofrades, Rodríguez-Salas, &

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Jiménez-Colmenero, 2011; Jimenez-Colmenero, Cofrades, Herrero, Solasb, & Ruiz-Capillas, 2013).

To our knowledge, publications on the effect of konjac glucomannan on aroma release are scarce. Though the addition of a small amount of KGM to starch matrices might be useful to control the texture and extend the shelf life of food products, it might also affect the interactions between aroma compounds and starch, and, as a consequence, affect flavor retention and release.

In this context, the present study aimed to measure the retention of aroma compounds in dispersions based on konjac glucomannan (KGM), potato starch (PS) and a dispersion of konjac glucomannan and potato starch (SK) and highlighted the influence of the konjac glucomannan on the mechanisms involved in aroma retention.

Three aroma compounds with different physicochemical properties, functional groups and behavior toward starch were chosen: ethyl hexanoate, ethyl acetate and carvacrol. Ethyl hexanoate and ethyl acetate are two aroma compounds frequently used in food research. Ethyl hexanoate can induce V_{611} amylose but ethyl acetate is non-complexing with amylose (Biais, Le Bail, Robert, Pontoire, & Buléon, 2006). Carvacrol is a phenolic compound and a natural antioxidant of great interest for the food industry because of its inhibitory effect on the growth of various microorganisms and its capacity to protect organisms and cells from damage induced by oxidative stress (Ben Arfa, Combes, Prezosi-Belloy, Gontard, & Chalier, 2006; Burt, 2004). The complexing properties of carvacrol with amylose are unknown. X-ray analysis was used in the present study to verify its complexing behavior: V_{611} amylose complexes were formed with carvacrol.

The retention (or release) of the three aroma compounds in complex matrices can be measured using the gas/dispersion partition coefficient $K(=C_g/C_m)$ at equilibrium under infinite dilution conditions. No specific interaction was found between the ethyl hexanoate and the different polysaccharides. Ethyl acetate retention seemed to be due to trapping in the complex network of polysaccharides and to the density of this network. Retention of carvacrol was influenced by the nature of polysaccharides present in the dispersion, and was mainly governed by specific interactions with starch. Additionally, the addition of konjac glucomannan to potato starch dispersions decreased the retention of volatile compounds complexing starch, but had little effect on the retention of the other aroma compounds.

2. Materials and methods

2.1. Material

Potato starch (PS) (Sigma Aldrich) and purified konjac glucomannan (KGM) (kindly given by Georges Szrednick (UNSW, Sidney)) were used. Aqueous dispersions of potato starch (PS), of konjac glucomannan (KGM), and of the starch – konjac glucomannan dispersion (SK) were made using deionized MilliQ water.

Ethyl acetate (CAS number: 141-78-6, $\log P_{oct-w} = 0.73$, molecular weight = $0.088 \text{ kg}\cdot\text{mol}^{-1}$, boiling point = 77°C , vapor pressure at $25^\circ\text{C} = 13105 \text{ Pa}$, water solubility at $25^\circ\text{C} = 0.082 \text{ kg}\cdot\text{L}^{-1}$, non complexing with amylose (Biais et al., 2006)) and ethyl hexanoate (CAS number: 123-66-0, $\log P_{oct-w} = 2.83$, molecular weight = $0.144 \text{ kg}\cdot\text{mol}^{-1}$, boiling point = 170°C , vapor pressure at $25^\circ\text{C} = 240 \text{ Pa}$, water solubility at $25^\circ\text{C} = 0.00048 \text{ kg}\cdot\text{L}^{-1}$, V_{611} -type complexes with amylose (Biais et al., 2006)) were supplied by Aldrich (Saint-Louis, USA).

Carvacrol (CAS number: 499-75-2, $\log P_{oct-w} = 3.49$, molecular weight = $0.150 \text{ kg}\cdot\text{mol}^{-1}$, boiling point = 237°C , vapor pressure at $25^\circ\text{C} = 3 \text{ Pa}$, water solubility at $25^\circ\text{C} = 0.00125 \text{ kg}\cdot\text{L}^{-1}$, V_{611} -type complexes with amylose (Biais et al., 2006)) was supplied by SAFC (Saint-Louis, USA). The purity of the three aroma compounds was greater than 98%.

Propylene glycol (Aldrich, purity 99.5%, food grade, CAS number: 57-55-6, $\log P_{oct-w} = -0.92$, molecular weight = $0.076 \text{ kg}\cdot\text{mol}^{-1}$,

boiling point = 155°C , vapor pressure at $25^\circ\text{C} = 39 \text{ Pa}$, water solubility at $25^\circ\text{C} = 0.811 \text{ kg}\cdot\text{L}^{-1}$, V_{61} -type complexes with amylose (Biais et al., 2006)) was used as a dispersion solvent to prepare a stock solution of aroma compound.

2.2. Preparation of carvacrol – amylose complexes

The preparation procedure was designed to favor the formation of complexes. Twenty eight grams of distilled water was stirred for 10 min with a bubbling of nitrogen to prevent further oxidation, and was put in an aluminum flask. Potato starch was gently added and the resulting PS dispersion (5% w/w) was stirred to avoid sedimentation. In the case of the SK dispersion, KGM was added to the PS dispersion, very slowly but with strong stirring. Then the dispersion was placed in the RVA apparatus (Newport Scientific, Jessup, USA) at 50°C for 1 min and carvacrol (1 cm^3) was added. The dispersions were heated to 90°C at a constant rate of $10^\circ\text{C}\cdot\text{min}^{-1}$, kept at this temperature for 15 min and finally cooled to 20°C at the same rate. At the beginning of the pasting profile, the dispersion was stirred at 960 rpm for the first 10 s to ensure the uniformity of the dispersion. Afterwards, a constant stirring of 160 rpm was applied.

After cooling, water content of samples was adjusted at $a_w = 0.75$ by desorption over saturated NaCl solution.

2.3. X-ray diffraction analysis

Fifty milligrams of sample equilibrated at $a_w = 0.75$ was sealed in a copper ring between two adhesive tape sheets to prevent any change in water content. The sample was examined by Wide Angle X-ray Scattering. Measurements were performed using a D8 Discover spectrometer with GADDS detector and cross-coupled mirrors from Bruker-AXS (Madison, USA), working at 40 kV and 40 mA, with a copper monochromator ($\lambda = 1.54059\cdot 10^{-10} \text{ m}$) and sample alignment by microscopic video and laser. Data were monitored by a 120° curve detector for 10 min and normalized between 3 and 30° (2θ).

2.4. Preparation of konjac glucomannan and potato starch dispersions

Aqueous dispersions of potato starch (PS, 5% w/w), of konjac glucomannan (KGM, 0.2% w/w), and of the starch – konjac glucomannan dispersion (SK, 0.2% w/w of konjac glucomannan and 5% w/w of potato starch) were prepared using a Rapid ViscoAnalyser (RVA) Super 4 apparatus (Newport Scientific, Jessup, USA) with the “STD1” thermal program. The dispersions were kept at 50°C for 1 min, heated from 50°C to 95°C at a constant rate of $12^\circ\text{C}\cdot\text{min}^{-1}$, kept at 95°C for 3.5 min, cooled to 60°C at the same scanning rate and then kept at 60°C for 3 min. The agitation speed was fixed at 960 rpm for the first 10 s at 50°C then for 10 s at 60°C (during cooling) to ensure the uniformity of the dispersion, and finally at 160 rpm until the end of the process. A stock solution of aroma compound was prepared by dissolving a given amount of aroma compound in propylene glycol at 25°C while stirring in order to obtain a final concentration of 2 mmol of volatile compound per glucose equivalent in the polysaccharide gel. The stock solutions were stored at 4°C . One hundred microliters of stock solution was added either before heating (early ligand addition: ELA), or after cooling (30 s after the start of the plateau at 60°C , late ligand addition: LLA). Resulting concentrations of aroma compounds in polysaccharide gel are as follows: carvacrol $77.1 \text{ mg}\cdot\text{L}^{-1}$; hexanoate $65.4 \text{ mg}\cdot\text{L}^{-1}$ and $41.3 \text{ mg}\cdot\text{L}^{-1}$ ethyl acetate. Distilled de-ionized water (STD) was used as the control and underwent the same preparation procedure. Finally, for each aroma compound, height samples in triplicate were made: STD-ELA, STD-LLA, PS-ELA, PS-LLA, KGM-ELA, KGM-LLA, SK-ELA, and SK-LLA.

Viscosity profiles were recorded for all of the systems. Three parameters were taken from the RVA curves: pasting temperature ($^\circ\text{C}$)

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