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Distribution and competition between carvacrol and propylene glycol for trapping by amylose in aqueous suspensions based on potato starch and konjac glucomannan

Céline Lafarge [a], Elias Bou-Maroun [a], Bruno Pontoire [b], Nathalie Cayot [a, *], Patricia Le Bail [b]

[a] Univ. Bourgogne Franche-Comté, AgroSup Dijon, PAM UMR A 02.102, F-21000, Dijon, France
[b] UR1268, Biopolymères, Interactions, Assemblages, INRA, F-44300, Nantes, France

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ABSTRACT

The quantification and the distribution of carvacrol and propylene glycol between the continuous phase and the dispersed phase of aqueous suspensions based on potato starch and konjac glucomannan were investigated.

For this purpose, a series of potato starch suspensions with or without konjac glucomannan were prepared by hydrothermal treatment. Two different modes of adding ligands were used: either added before the heating of the suspensions or after the heating of the suspensions.

X-ray diffraction and differential scanning calorimetry studies confirmed the presence of carvacrol complexes in V_{6III} type. Propylene glycol did not create complex with amylose but promoted the formation of amylose-carvacrol complexes in the presence or not of konjac glucomannan. Differential scanning calorimetry study showed that low concentrations of konjac glucomannan (0.2%) seemed to disturb the establishment of amylose-carvacrol complexes. Results showed that the time of adding carvacrol to starch dispersions, i.e. prior or after the heating of suspensions, and the presence of konjac glucomannan influenced the location of carvacrol in the different phases. These results allow understanding how the location and the amounts of ligands in the biphasic suspension influence the retention of carvacrol.

By comparing the distribution of carvacrol on a period of 24H, the trapping by amylose was shown amplified with time. This demonstrated that the implementation of amylose - carvacrol interactions was highly dependent on the experimental conditions and on time.

1. Introduction

Starch is used not only as main ingredient of many staple foods but also as a thickener, gelling agent, stabilizer, and fat replacer in many processed food products. It is also used in the composition of delivery systems, for food flavour for example. To avoid negative effects such as syneresis which may occur during storage of aqueous starch suspensions, other hydrocolloids are often added 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; Funami et al., 2005). The products obtained are described as biphasic systems formed by a continuous phase containing the water soluble macromolecules and a dispersed phase composed of swollen starch granules. Konjac glucomannan (KGM) is one of these hydrocolloids. KGM is an essentially linear polysaccharide composed of β-1.4-linked D-glucosyl and D-mannosyl residues (in a molar ratio of 1.5:1) as main chain with branching β-1.4-glucosyl units. Degree of branching is about 8%. KGM contains acetyl group in the main chain, approximately 5–10% (Katsuraya, Okuyama, Hatanaka, Oshima, Sato, & Matsuzakic, 2003; Khanna & Tester, 2006). It was reported to interact with starches of various botanic origins: maize (Yoshimura, Takaya, & Nishinari, 1998), wheat (Funami et al., 2005; Zhou, Wang, Zhang, Du, & Zhou, 2008), potato (Khanna and Tester, 2006), tapioca (Muadklay & Charoenrein, 2008), and rice (Charoenrein, Tatirat, Rengsutti, & Thongngam, 2010; Huang, Kennedy, Li, Xu, & Xie, 2007). All these authors found the high

* Corresponding author.
E-mail address: nathalie.cayot@agrosupdijon.fr (N. Cayot).

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water holding capacity of KGM prevented syneresis occurring in starch gels and slowed down the retrogradation rate of starch during storage. Recently, Schwartz et al. (2014) demonstrated that the presence of KGM in potato starch suspension can affect the gelatinization and the retrogradation of potato starch. This phenomenon seems to appear at low concentrations of KGM. Several investigations concerning the use of KGM had shown its great potential as encapsulant of aroma compound (Yang, Xiao, & Ding, 2009) and KGM gel would be a promising choice to develop delivery systems and controlled release of molecules of interest (Alvarez-Manceñido, Landin, Lacik, & Martínez-Pacheco, 2008; Nakano, Takikawa, & Arita, 1979; Wen, Wang, Wang, Li, & Zhao, 2008; Zhang, Chen, & Yang, 2014).

It is well known that the amylose molecule of starch can form interactions (especially helical inclusion complexes) with a variety of small molecules such as aroma compounds (Conde-Petit, Escher, & Nuessli, 2006; Jouquand, Ducruet, & Le Bail, 2006). Two families of structures have been identified for these ligand - amylose complexes: V_6 and V_8 where 6 and 8 represent the number of D-glucosyl units per turn (Helbert & Chanzy, 1994). In the V_6 family, three types of crystalline packing V_{6I}, V_{6II} and V_{6III} (where I, II and III define unit cells of different size) may be obtained depending on the nature of the complexing molecule. The complexing molecule can be trapped either in the single helix only (V_{6I}) or both within and between amylose helices (V_{6II} and V_{6III}).

Carvacrol and propylene glycol were chosen in the present study as they were known as ligands for starch. Carvacrol was chosen as volatile odorant compound. It 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 V_{6III} type (Le Bail et al., 2013). Propylene glycol was chosen as carrier solvent of carvacrol. In fact, propylene glycol (1,2-propanediol, PG) is one of the most widely used solvent for flavour carriage because it has a broad range of applications and is relatively inexpensive. PG is also known to be a complexing ligand of amylose in V_{6I} type (Pozo-Bayon, Biais, Rampon, Cayot, & Le Bail, 2008).

In a previous study, Lafarge et al. (2014) reported that the retention of carvacrol solubilized in PG by potato starch suspensions was governed mainly by the inclusion complexes with starch. This retention was more important when mixture carvacrol-PG was added at the end of heating, i.e. when amylose was leached out of the starch granules and available to interact. They also reported that the addition of KGM to the potato starch suspensions decreased the retention of carvacrol. Nevertheless, the influence of KGM on the formation of inclusion complexes of carvacrol by starch is not fully understood. Some hypotheses must be verified: is there any competitive effect between carvacrol and PG for amylose complexation; is there any effect of KGM on the amount of solubilized amylose able to interact with carvacrol and PG ?The inclusion of aroma compounds is similar to the one of fatty acids (Le Bail et al., 2015). The mode of addition of fatty acid (i.e. prior to heating or after heating) would also influence the structural properties of starch fatty acid system. X-ray diffraction studies revealed that the degree of crystallinity exhibited by the starch samples was dependent on the mode of fatty acid addition (Chang, He, & Huang, 2013, Exarhopoulos & Raphaelides, 2012; Vasiliadou, Raphaelides, & Papastergiadis, 2015). It is conceivable that crystalline and less crystalline complexes differ in the retention of the volatile compound.

The objective of the present study was to understand the mechanisms of carvacrol trapping by amylose, in presence of PG and KGM. The applicative aim of the study is to determine the best practice to achieve sufficient yields of amylose-carvacrol interactions. To achieve this goal, some points must be clarified: the competitive effect between carvacrol and PG (i), the effect of KGM (ii) and the effect of the moment of addition of ligands (iii) on the trapping of carvacrol by amylose in the suspensions.

For that purpose, the distribution of carvacrol and PG in the different phases of polysaccharide suspensions was studied.

Due to huge differences of concentration of carvacrol and PG in the different phases, some of the methods were adapted to each case.

The different analyses done on samples are schematically represented in Fig. 1.

2. Materials and methods

2.1. Materials

Potato starch does not contain any internal lipid interfering with the formation of the inclusion complex to be studied. It was obtained from Sigma Aldrich. Purified KGM was kindly given by Georges Srzednick (University of New South Wales of Sydney, Australia). All suspensions were made using deionized MilliQ water.

Carvacrol (SAFC, CAS n 499-75-2, and purity 98%) and propylene glycol (PG, Aldrich, CAS n 57-55-6, purity 99.5%, and food grade) have the following physicochemical characteristics at 25 °C (estimation program EPI suite™):

- Carvacrol ($C_{10}H_{14}O$), Log $P_{octanol\text{-}water}$ = 3.49, vapour pressure = 3.09 Pa, solubility in water = 1.25 g/L.
- PG ($C_3H_8O_2$), Log $P_{octanol\text{-}water}$ = −0.92, vapour pressure = 38.80 Pa, solubility in water = 811 g/L.

Dichloromethane (Carlo Erba, CAS 75-09-2, purity 99.8%, stabilized with amylene), sodium chloride (VWR, CAS 7647-14-5), and anhydrous sodium sulfate (VWR, CAS 7757-82-6) were used for Liken-Nickerson extraction. A mixture of ethyl acetate (Sigma, CAS 141-78-6, purity 99%) and absolute ethanol (Sigma, CAS 064-17-5) (3:1, v/v)) were used for liquid-liquid extraction.

Linalool (Fluka, CAS 78-70-6, purity 99%, prepared at 4 g/L in absolute ethanol) was used as extraction standard for quantification of carvacrol and PG. Ethyl octanoate (Aldrich, CAS 106-32-1, purity 98%) was used as chromatographic standard for quantification of carvacrol (prepared at 2 g/L in dichloromethane) and of PG (prepared at 4 g/L in the mixture ethyl acetate/ethanol (3:1, v/v)).

2.2. Preparation of samples

2.2.1. Preparation of starch and konjac-glucomannan aqueous suspensions

Aqueous suspensions containing potato starch (PS samples: 25 g of water plus 1.25 g of potato starch per batch), or both starch and KGM (SK samples: 25 g of water plus 1.25 g of starch and 0.05 g of KGM per batch) were prepared using a Rapid Visco Analyzer™ (model RVA super 4, Newport Scientific, Australia) equipped with the Thermocline™ software. The mixture was put in the aluminium flask and manually stirred to avoid sedimentation. Then, the mixture was held at 50 °C for 1 min, heated to 95 °C at a constant rate of 12 °C/min, held at 95 °C for 3.5 min and finally cooled to 60 °C at the same rate and held at this temperature for 3 min. A constant stirring of 160 rpm was applied, except at the beginning of the pasting profile when the mixture was stirred at 960 rpm for the first 10 s at 50 °C and during cooling step for 10 s at 60 °C to ensure a good homogeneity. Viscosity profiles were recorded to check