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Inhibition of lactose crystallisation in the presence of galacto-oligosaccharide

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ABSTRACT

The stabilization of lactose in the form of amorphous (i.e. non-crystalline form) is the basic requirement to maintain the quality of relevant food and pharmaceutical products. The physiochemical properties of amorphous lactose mixed with galacto-oligosaccharide (GOS) were investigated. Water sorption, glass transition temperature, and crystallisation behaviour of lactose in the present of GOS (1:1 w/w) were measured at various water activity (0.11–0.75 a_w, 25 °C) and lactose mutarotation was also evaluated. All of them were compared with the physiochemical properties of trehalose-lactose (1:1 w/w). The addition of GOS to lactose increased the hygroscopicity of the mixture, as well as slightly increased the glass transition temperature compared to lactose alone. The critical water activity (at 0.68 a_w) of lactose crystallisation was increased by the addition of GOS as compared to that of trehalose-lactose (1:1 w/w) (at 0.58 a_w) or lactose alone (at 0.44 a_w). The dramatical inhibition of lactose crystallisation with a lower crystallisation kinetic constant and the alternation of lactose crystal forms in the presence of GOS was observed as compared to the crystallisation behaviour of trehalose-lactose (1:1 w/w) and pure lactose at 0.68 and 0.75 a_w, 25 °C. Without affecting its T_g, the significantly delayed crystallisation of lactose in GOS-lactose mixture (1:1 w/w) was more likely due to the change of lactose mutarotation. As comparing to trehalose that is an effective inhibitor, GOS has a stronger ability to prevent lactose from crystallisation in hydrous matrices.

1. Introduction

Lactose is the main constituent of breast milk. It is commonly used as an ingredient in various food products and as an excipient and tableting agent in pharmaceutical products (Carpin et al., 2016). In many products, lactose amorphous state and crystallisation during storage cannot occur (Hartel, 1991). The tendency of amorphous lactose to form crystals is the leading cause of decreased powder flowability, caking of dairy powder (i.e. amorphous caking and humidity caking), and diminished rehydration properties (Fitzpatrick et al., 2007). The crystallinity of lactose, as an additive of drug tablets, is important for drug solubility and bioavailability. Dried solids containing amorphous compounds have a faster dissolution rate than solids containing crystals, as bonding between the amorphous molecules is weaker as compared to the crystalline regions (Hancock & Parks, 2000). Drug solubility is one of the key determinants of bioavailability. Additionally, lactose is an important type of microencapsulation wall materials. The amorphous form of lactose is essential for the entrapment and protection of active or non-compatible components in microencapsulation (Miao & Roos, 2010). In the research and development of food and drug products, it is important to use certain technologies and processes to ensure the amorphous structure of lactose and to postpone the undesirable crystallisation to improve product quality.

The mechanism of α-monohydrate lactose crystallisation in solution and the main influencing factors have been studied in great detail. Kinetic models for each of the different steps of mutarotation, nucleation, and crystal growth have been developed. At a low concentration of lactose (≤0.6 g/g H_2O), the rate of growth of lactose crystals is predominantly governed by the lactose mutarotation, which is the reversible transition between two anomeric forms of lactose (α-form with low solubility and β-form with high solubility) and α-lactose supersaturation. A rapid conversion of β-lactose to α-lactose could decrease the solubility of lactose and increase α-lactose supersaturation, which could provide a strong driving force to increase the rate of the

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crystallisation process. At a high concentration of lactose (> 0.6 g/g H_2O), the rate of lactose crystallisation is dependent on the degree of α-lactose supersaturation and the crystal surface area (Mimouni, Schuck, & Bouhallab, 2009). Lactose crystallisation is also significantly influenced by pH and temperature. In solid matrices, lactose mutarotation (or the proportion of α- and β-lactose) and its molecular mobility are two major influences governing water sorption-induced lactose nucleation formation and crystal growth (Champion, Le Meste & Simatos, 2000; Heljo et al., 2012; Miu & Tag, 2010; Timmermann, Steckel, & Trunk, 2006; Zhou, Zhang, Law, Grant, & Schmitt, 2008).

Prevention or delay of lactose crystallisation can be achieved by the addition of impurities, such as mineral salts, proteins, milk fats and carbohydrates (Ame & Roos, 2007; Fan & Roos, 2016b; Kelly, 2009; Miao & Roos, 2010; Potes, Kerry, & Roos, 2012). The effects of different additives on the inhibition of crystallisation of lactose vary. Many kinds of mineral salts, such as LiCl, $MgSO_4$ and K_2HPO_4, inhibit lactose crystallisation by altering lactose solubility and/or formation of the complex between lactose and the mineral salt (Haase & Nickerson, 1966; Omar & Roos, 2007; Wong & Hartel, 2014). Milk fat is an effective inhibitor as it acts as a hydrophobic barrier that limits the diffusion of hydrophilic lactose and the growth of lactose crystals (Kelly, 2009). Delayed crystallisation of lactose in the presence of whey protein has been described (Fan & Roos, 2016). Whey protein isolates may increase the solubility of lactose crystals by changing the proportion of the α- and β-lactose anomeric forms and limiting the molecular diffusion of lactose during crystal growth (Fan & Roos, 2016; Mimouni et al., 2009). Carbohydrates have diverse structure with pronounced differences in molecular weight between monosaccharides and polysaccharides. Carbohydrates with different molecular sizes and structures can influence lactose crystallisation accordingly. Their addition can inhibit or promote lactose crystallisation in dried solids (Li, Roos & Miao, 2017a,b; Potes et al., 2012). The effect of various carbohydrates on the behaviour of lactose crystallisation mainly depends on the molecular mobility of composite systems, which is influenced by the solubility of lactose, mutarotation associated with solid-solid transformation, molecular size-related steric hindrance, and effects of glass transition temperature (T_g) (Biliaderis, Lazaridou, Mavropoulos, & Barbayiannis, 2002; Li, Roos & Miao, 2017; Potes et al., 2012). As carbohydrates differ markedly in their physicochemical properties, the effect of carbohydrates on the lactose crystallisation could vary from different type of carbohydrates.

Galacto-oligosaccharide (GOS) is a non-digestible food ingredient with health-promoting benefits for some species of gut bacteria. Thus, GOS can be considered to be prebiotics. Their health benefits and favourable physiochemical properties, including high solubility, colourless appearance, and mild sweetness, have spurred innovative efforts to utilise health-promoting compounds in commercial food and pharmaceutical products. GOS comprises a mixture of oligomers. Purified GOS (97% w/w) is predominantly composed of trisaccharides (47% w/w) and tetrasaccharides (42% w/w), with the minor presence of pentasaccharides (8% w/w) (Torres, Bastos, Goncalves, Teixeira & Rodrigues, 2011). The stabilising effect of GOS could be expected on the basis of their high T_g, ability to form amorphous matrices of high viscosity and low molecular mobility (Potes et al., 2012; Torres, Bastos, Gonçalves, Teixeira, & Rodrigues, 2011). GOS might stabilise lactose, which could prevent lactose crystallisation in solid matrices.

This study examined lactose crystallisation in the presence of GOS in dehydrated mixtures. The two major influencing factors (i.e. lactose mutarotation and molecular mobility) were investigated by testing the physicochemical properties of GOS and lactose mixtures. Trehalose was used for comparison, as it is an effective inhibitor and is a popular component in many food and pharmaceutical formulations. The characterisation of physicochemical properties of GOS-lactose mixtures will allow for the prediction of stability and quality changes during storage of related products.

2. Materials and methods

2.1. Materials

α-Lactose monohydrate was obtained from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China), D-(+)-trehalose dihydrate (purity > 99%) from Aladdin Industrial Corporation (Shanghai, China) and GOS (purity approximately 78%) from Yuanye Biotechnology Co., Ltd., (Shanghai, China). GOS was confirmed to be free of lactose by high-performance liquid chromatography analysis conducted in our laboratory. LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, NaBr, KI, NaCl and P_2O_5 were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of freeze-dried powders

Fifteen grams of α-lactose monohydrate (lactose), GOS and trehalose or the mixtures of GOS-lactose and trehalose-lactose at a mass ratio of 1:1 were completely dissolved in 85.0 g of distilled water to obtain 15% (w/w) solutions. A 30-min treatment in an ultrasonic water bath (Jielite Ultrasonic Cleaner Co., Ltd., Shenzhen, China) facilitated complete dissolution. The resulting solutions were individually frozen at −80 °C for 12 h and then freeze-dried for 48 h under a pressure (p) < 0.2 mbar using an Alpha 1–4 LD plus device (Marin Christ Gefriertrocknunsanlagen, Germany). Freeze-dried materials were quickly crushed into powder and kept over phosphorus pentoxide (P_2O_5) in a Vaseline-sealed desiccator to avoid future moisture uptake from the surrounding environment.

2.3. Methods

2.3.1. Initial water activity and water content of freeze-dried powders

The initial water activity (a_w) of freeze-dried powders was determined at 25 °C using an AQUA LAB 4 TE apparatus, (Decagon Devices, Pullman, WA, USA). The water content (m) was measured using a model DE 401 rapid moisture analyser (Shenzheng, Yuanya Technology Co., Ltd.) and was expressed as the difference of tested sample weight before and after heating at 160 °C for 40 s.

2.3.2. Water sorption

Freeze-dried powders were placed into vacuum desiccators containing saturated solutions (LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, NaBr, KI and NaCl) to maintain a relative humidity (RH) of 11%, 23%, 33%, 44%, 58%, 68% or 75%, respectively (Greenspan, 1977). The $a_w = p/p_o$ = RH/100, with the assumption that the ratio of vapor pressure (p) in food and that of pure water (p_o) equals a_w at a steady state (Roos, 1995). Approximately 1.0 g of freeze-dried powder was placed into a 30 mm-diameter pre-weighted petri dish. The total weight of each petri dish containing freeze-dried powder was determined at 0, 3, 6, 9, 12 and 24 h and every 24 h thereafter up to 288 h at 25 °C. The absorbed m value at each time point was obtained as the difference of the sample before and after incubation under various RHs (11–75%) at 25 °C. The total m value was the sum of the initial water content and the absorbed water content.

The Guggenheim-Anderson-de Boer (GAB) equation (1) was used to predict the m of non-crystalline material at any given water activity at a certain temperature (Torres, Bastos, Goncalves, Teixeira & Rodrigues, 2011).

$$\frac{m}{m_m} = \frac{CKa_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)} \quad (1)$$

The GAB isotherm parameters were determined by plotting a_w/m against a_w (equation (2)). The total m of freeze-dried powder and its a_w were used to calculate the constant values of α, β and γ. The GAB isotherm parameters C, K and m_m (g/100 g of solids) were obtained from equations (3)–(5).