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Surfactant-free solid dispersion of fat-soluble flavour in an amorphous sugar matrix

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ABSTRACT

A solid dispersion technique to homogeneously disperse hydrophobic ingredients in a water-soluble solid without using surfactant was examined as follows: first, freeze-dried amorphous sugar was dissolved in an organic medium that contained a soluble model hydrophobic component. Second, the mixed solution of sugar and the model hydrophobic component was vacuum dried into a solid (solid dispersion). Methanol and six fat-soluble flavours, including cinnamaldehyde, were used as organic media and model hydrophobic components. The retention of flavours in the solid dispersion during drying and storage under vacuum was evaluated. The amorphised disaccharides dissolved in methanol up to 100 mg/mL, even temporarily (20 s to 10 days) and could be solidified without any evidence of crystallisation and segregation from flavour. The solid dispersion, prepared using α-maltose usually showed 65–95% flavour retention during drying (and storage for cinnamaldehyde), whereas ⩾50% of the flavour was lost when the flavour was O/W emulsified with a surfactant and then freeze-dried with sugar.

1. Introduction

Most food products are mixtures of both fat-soluble and water-soluble ingredients. The homogenisation of hydrophobic and hydrophilic ingredients in the liquid phase is usually performed by emulsification in the presence of a surface-active component. The stability and physicochemical characteristics of the resulting emulsions can vary substantially, depending on the emulsification conditions, including the emulsifying intensity (Baby, Santoro, Velasco, & Serra, 2008; Floury, Desrumaux, & Lardières, 2000; Thiebaud, Dumay, Picart, Guiraud, & Cheftel, 2003), emulsifier type and content (Benita & Levy, 1993; Capek, 2004; Tadros, Izquierdo, Esquena, & Solans, 2004), and so on (Benita & Levy, 1993).

The liquid mixtures of hydrophobic and hydrophilic components are often turned into a solid form. One of the methods used to solidify a liquid mixture is to remove the solvent from the emulsified suspension (Corveleyn & Remon, 1999; Desai & Park, 2005; Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007; Gibbs, Kermasha, Alli, & Mulligan, 1999; Gouin, 2004; Porter, Charman, Williams, Bakalova, & Charman, 1996; Shimada, Roos, & Karel, 1991). In addition, in the solidification of emulsions, the conditions used in the process can have a dramatic effect on the homogeneity and stability of the dried mixture (Anwar & Kunz, 2011; Nakayama et al., 2015). However, designing an emulsification process so as to optimise the stability of an emulsion both in the liquid and solid phases can be a complicated process.

On the other hand, the amorphous state of a material can be regarded as a liquid in which the constituent molecules largely lose their mobility. Therefore, if an insoluble substance is amorphised and dispersed in a poor solvent, it follows that it would eventually become dissolved in that solvent even for a short period of time. It has been reported that highly hydrophobic drugs could temporarily be dissolved in water up to much higher concentrations than the solubility of the drug (Hancock & Parks, 2000). The opposite is true, namely, that hydrophilic substances also can be dissolved in a hydrophobic solvent by amorphisation. Flores, Naraghi, Engasser, and Halling (2002) reported that amorphised sucrose was enzymatically esterified with fatty acids in an organic medium to a greater extent than the crystalline compound by increasing the concentration of sucrose in the mixture.

Here, when hydrophobic and hydrophilic substances coexist in an organic solvent, even temporarily, the following novel solid dispersion technique (Imamura et al., 2014) is possible: (i) the hydrophilic substance is amorphised and (ii) added to an organic solvent that contains hydrophobic components dissolved in it, followed by

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homogenisation. (iii) The homogenised solution is then desolvated to produce a solid (solid dispersion) before the hydrophobic and hydrophilic phases become segregated. In the resulting solid dispersion, hydrophobic and hydrophilic substances would be expected to be mixed at a molecular level without using surfactant. This solid dispersion technique may possibly increase the stability of a product with respect to the segregation of hydrophobic and hydrophilic components and improve the solubility and thus the bioavailability of hydrophobic components when taken up by the human body.

In this study, we first demonstrate, using our newly developed strategy, that it is possible to produce a surfactant-free solid dispersion, in which hydrophobic substances were embedded. One of the typical hydrophobe/hydrophile mixed systems in the food industry is a flavouring powder that encapsulates volatile aromas. Hence, six types of well-known flavouring agents, such as cinnamaldehyde, were employed as hydrophobic components, and several types of sugars were used as hydrophilic glass-forming agents. Methanol was used as an organic solvent. Second, the retention of the flavour in the surfactant-free solid dispersion during desolvation (drying) and storage under vacuum was investigated and the results were compared with that for a dried O/W emulsion system. The characteristics of several types of sugars in the dissolution in an organic solvent and the preservation of flavour in the dried matrix were also investigated.

2. Materials and methods

2.1. Materials

Disaccharides, including sucrose, α-maltose, trehalose, α-lactose, and maltitol, were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Dextrans (MW *ca.* 1500, by enzymatic synthesis; MW *ca.* 40,000 from Leuconostoc sp.) were obtained from Sigma–Aldrich (St. Louis, MO). Cinnamaldehyde, anethole, citral, ethylvanillin, eugenol (Wako Pure Chemical Industry), and raspberry ketone (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) were employed as flavouring components. Methanol was obtained from Wako Pure Chemical Industry. Tween 20 as a representative surfactant was obtained from MP Biochemicals Inc., (Solon, OH). All of these chemicals were reagent grade and were used without further purification.

2.2. Preparation of freeze-dried amorphous sugar cake

Freeze-dried cakes of amorphous sugar were prepared by the same procedure as was used in our previous study (Imamura et al., 2008). Briefly, a 5-mL aliquot of an aqueous solution containing 100 mg/mL sugar was instantaneously frozen with liquid nitrogen and then freeze-dried for 24 h. The resulting sugar cakes were thoroughly dehydrated by storage over P_2O_5 in a vacuum desiccator for more than 3 days at 37 °C. Remaining water content after dehydration was confirmed to be below 0.002 g/g-dry matter by Karl-Fischer titration (Imamura, Iwai, Ogawa, Sakiyama, & Nakanishi, 2001).

2.3. Dissolution of amorphous sugar in an organic solvent

A 5-mL portion of methanol was added to a glass vial with 500 mg of thoroughly dehydrated amorphous sugar cake and the suspension stirred at 200 rpm with a 1.5-cm magnetic stirring bar at 25 ± 1 °C throughout the dissolution experiment. At appropriate intervals, aliquots of 100 μL of the sugar/methanol mixture were withdrawn and then filtered through a 0.2-μm syringe filter (Nihon Millipore K.K., Tokyo, Japan) to remove insoluble sugar aggregates. The filtrate was diluted 10–1000 fold with distilled water to give concentrations of 5–100 μg/mL and the sugar concentration was then determined by the phenol–sulphuric acid method (Dubois, Gilles, Hamilton, Repers, & Smith, 1956).

2.4. Preparation of surfactant-free solid dispersion of fat-soluble flavour and storage under vacuum

Each fat-soluble flavour was dissolved in methanol to give a final concentration of 10 mg/mL, and 500 mg freeze-dried sugar cake were suspended in 5 mL of the flavour-containing methanol, as described above. Immediately after the suspension, aliquots of 100 μL of the flavour/sugar mixture solution were vacuum-dried at approximately 1 Torr with a centrifuge at 25 ± 3 °C to produce the flavour-containing solid dispersions, using a TOMY Micro Vac MV-100 centrifugal concentrator (TOMY SEIKO Co., Ltd., Tokyo, Japan) for 2 h. During the vacuum drying, the remaining amount of methanol was measured at appropriate intervals by gravimetric measurement. Some of the resulting solid dispersions were stored in a vacuum desiccator (∼10 Pa) at 25 °C.

2.5. Preparation of emulsified fat-soluble flavour

Alternatively, 30 mg of flavour were added to 3 mL of an aqueous solution, containing 100 mg/mL α-maltose and 10 mg/mL Tween 20. The flavour suspension was emulsified into an oil-in-water (O/W) emulsion and then immediately freeze-dried in the same manner as in our previous study (Imamura et al., 2013). The dried emulsion samples were stored under the same conditions as described above (∼10 Pa, 25 °C).

2.6. Estimation of the flavour (cinnamaldehyde) retention in an amorphous sugar matrix

After vacuum drying and during storage, the flavour-containing solid dispersions or the dried emulsion samples were withdrawn from a vacuum storage container and suspended in a known volume (1–5 mL) of methanol. By stirring the methanol suspension sufficiently (for more than 15 s) using a vortex mixer, flavouring molecules that were contained in the solid dispersion were fully extracted into the methanol phase. The ultraviolet (UV) absorbance of the suspension supernatant due to the flavour was measured and converted into the flavour concentration. The measured wavelengths were 285 nm (cinnamaldehyde), 260 nm (anethole), 240 nm (citral), 230 nm (ethylvanillin), 235 nm (eugenol) and 225 nm (raspberry ketone).

2.7. Scanning electron microscopy

The solid dispersion samples were coated with a thin film (*ca.* 40 nm) by evaporating a platinum/palladium alloy using a Hitachi E-1030 ion sputter instrument (Hitachi High-Technologies Co., Tokyo, Japan). The resulting samples were observed by means of a KEYENCE VE9800 scanning electron microscope system (KEYENCE Co., Tokyo, Japan) at an accelerating voltage of 15 kV.

2.8. Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses of amorphous sugar matrices, obtained from methanol solutions, and the flavour-containing solid dispersions were conducted, using a TA Q2000 calorimeter (TA Instruments Co., New Castle, DE) equipped with RCS90 cooling system (TA Instruments Co.) as follows. Cinnamaldehyde was used as a representative flavouring agent. A 2.5–10 mg sample was hermetically sealed in a 20-μL aluminium pan and then scanned at a rate of 3 °C/min between 0 and