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Comparing the crystallization and polymorphic behaviour of saturated and unsaturated monoglycerides

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ABSTRACT

The crystallization and melting behaviour of pure monoglyceride standards and two types of commercial monoglycerides were analyzed by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Firstly, a series of saturated monoglycerides, ranging from monolaurin to monobehenin, were analyzed by DSC using a specific temperature program to obtain a complete image of the crystallization behaviour and polymorphism. The different crystallization and melting peaks were characterized by wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). Three polymorphic forms (sub-α, α and β) could be discerned for the shorter chain length saturated monoglycerides, while a second sub-α polymorph was observed for the longer chain length samples. Secondly, unsaturated monoglyceride standards were analyzed using the same methodology. These results reveal a less complex behaviour with the occurrence of only one polymorph. Finally, the analysis of two commercial monoglycerides revealed the importance of minor components for the crystallization of unsaturated monoglycerides.

1. Introduction

Monoglycerides and their derivatives are by volume the most commonly used polar lipids in food products (Krog, 2001). Their amphiphilic properties explain their well-known use as emulsifiers in margarines and other w/o emulsions (Davies, Dickinson, & Bee, 2001). Another important application is their use as bread improvers, more specifically as improvers of the fermentation stability and as delayers of the staling of bread by complex formation with starch present in the dough (Azizi, Rajabzadeh, & Riahi, 2003; Moonen & Bas, 2004). Further applications include their use in the development of healthy spreads (Batte, Wright, Rush, Idziak, & Marangoni, 2007), as part of an anti-atherosclerotic functional oil (Cho et al., 2006) and in pharmaceutical applications, e.g. as drug delivery system, solubilizer, absorption enhancer, etc. (Ganem-Quintanar, Quintanar-Guerrero, & Buri, 2000).

In a wide range of food and non-food products monoglycerides are introduced in combination with water as mesomorphic phases. These phases possess specific structuring properties, e.g. an α-gel with an ointment-like consistency could be formed under certain conditions which could be used in low-calorie food products. The α-gel phase is metastable and can transform into a crystalline coagel state with a more fat-like consistency, which also is able to incorporate large amounts of water (Heertje, Roijers, & Hendrickx, 1998). Especially saturated monoglycerides can form firm gels in water, which is due to network formation (Sein, Verheij, & Agterof, 2002; Van de Walle, Goossens, & Dewettinck, 2008a,b).

The phase behaviour and polymorphism of systems with monoglycerides and water used for different applications have been widely described in older (e.g. Lutton, 1965) and more recent studies (e.g. Batte et al., 2007). However, monoglycerides could also be present in water-free systems and, under certain conditions, they can behave similar to triglycerides present in regular fats and oils. Indeed, they also crystallize and melt at certain temperatures and they form different polymorphic forms depending on the temperature (Bailey, 1950; Hagemann, 1988; Krog, 2001). These crystallization and polymorphic properties are very important in determining the functional properties of monoglycerides in many food products, as mentioned by Krog (2001). For example, Moonen and Bas (2004) mention that for some applications the alpha form has some advantageous effects, such as easier dispersibility, improved aerating properties and increased emulsifying activity.

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Despite the importance of their crystallization and polymorphic behaviour, no recent studies can be found on these different properties of monoglycerides in detail. Most information about the polymorphism and crystallization of monoglycerides can be found in the reviews of Bailey (1950) and Hagemann (1988). Both reviews discuss especially the behaviour of pure saturated asymmetric monoglycerides (1-MGL). Three polymorphic forms do generally exist for these monoglycerides, namely sub-α, α and β. All polymorphs have a double chain length packing mode which is characterized by a long spacing of around 50 Å for 1-monostearin. Monoglycerides crystallize directly in an α polymorph which can transform into a more stable β polymorph during longtime storage at ambient temperatures. When monoglycerides, present in the α polymorph, are cooled 35–50 °C below the crystallization point of the α polymorph, they undergo a polymorphic transition to a reversible sub-α polymorph (Krog, 2001). The transition to the sub-α form was already observed microscopically by Lutton and Jackson. In their study they mention also that monostearin and monopalmitin are present in the sub-α form at room temperature.

A β′ polymorphic form is only formed through quick crystallization using specific solvents and is not observed by thermal analysis techniques such as differential scanning calorimetry (DSC) (Hagemann, 1988). For commercial monoglycerides, containing also small amounts of other components like diglycerides and triglycerides, no β′ polymorph could be found (Krog, 2001).

In contrast to the asymmetric 1-monoglycerides, different studies have described that the symmetric 2-monoglycerides (also called β-monoglycerides) are free of polymorphism and are only characterized by a melting point which is lower than the melting point of the corresponding asymmetric isomers (Bailey, 1950; Hagemann, 1988). Also the behaviour of unsaturated monoglycerides is not clearly mentioned in literature and is not straightforward: the observed number of polymorphic forms ranges from one polymorph to four polymorphs (Hagemann, 1988). Possibly the unsaturated monoglycerides are less studied because they are less used in food applications.

Although some studies provide data on the crystallization and polymorphic behaviour of monoglycerides, these studies are mostly quite old and give only a limited amount of data analysis. Krog (2001) gives more recent information about the polymorphic behaviour of monoglycerides, but only commercial monoglyceride data are presented and no information regarding the used methods and analyses of data is provided. Also the use of DSC to study the behaviour of bulk monoglycerides (in the absence of water) is not clearly mentioned in literature. Because of the importance of monoglycerides in food systems, the objective of this study was to provide a broad analysis and comparison of the crystallization and polymorphic behaviour of monoglycerides studied by DSC and X-ray diffraction (XRD). In a first phase saturated monoglycerides were studied, because these are the most important monoglycerides used in the food industry. Secondly the behaviour of unsaturated monoglycerides was studied and finally the crystallization and melting behaviour of commercial monoglycerides was compared with the behaviour of pure monoglyceride standards giving an idea of the impact of minor components present in commercial monoglycerides.

2. Materials and methods

2.1. Samples

A series of monoglyceride standards were analyzed which were provided by Nu-Chek Prep (Elysian, USA) and Larodan Fine Chemicals (Malmö, Sweden). Two commercial monoglyceride samples, namely SM90FHPos and UM90RSfo, were provided by Vandemoortele N.V. (Izegem, Belgium).

2.2. DSC-analysis

The different samples were analyzed by differential scanning calorimetry (DSC) to investigate their crystallization and melting behaviour. These experiments were performed with a TA Q1000 DSC (TA Instruments, New Castle, Delaware) with a Refrigerated Cooling System. The DSC was calibrated with indium (TA Instruments, New Castle, Delaware), azobenzene (Sigma–Aldrich, Bornem, Belgium) and undecane (Acros Organics, Geel, Belgium) before analyses. Nitrogen was used to purge the system. A sample (5–15 mg) was hermetically sealed in an aluminum pan using sample preparation procedure B as described by Foubert, Vanrolleghem, and Dewettinck (2003) and an empty pan was used as a reference. The monoglycerides were stored for sufficient time at −20 °C for the transition to their most stable polymorphic form. After this storage the following specific time–temperature program was applied for the monoglyceride standards to have a complete image of their crystallization and melting behaviour: equilibration at 20 °C (room temperature), heating at 5 °C/min to melt the stable polymorphic form of the sample, isothermal during 10 min, cooling at 5 °C/min (to give a complete crystallization), isothermal during 1 min, heating at 5 °C/min (remelting of the sample).

For the analysis of the commercial monoglycerides another time–temperature program was used which is more closely related to industrial applications: equilibration at 80 °C, isothermal during 10 min, cooling at 5 °C/min to 0 °C, isothermal during 3 min, heating at 5 °C/min to 80 °C.

2.3. WAXD-analysis

The wide angle X-ray diffraction (WAXD) of the samples, to analyze the lateral packing (short spacings) of the different crystal polymorphs, was performed at the Laboratoire de Chimie de la Biologie Structurale, Facultés Universitaires de Notre Dame de-la-Paix, Namur, Belgium.

The short spacings were measured on an X'pert Pro diffractometer (PANalytical, Almelo, The Netherlands) and an Anton Paar TTK-450 sample stage (Anton Paar Benelux, Sint-Martens-Latem, Belgium). An external water bath was then used to apply the same time–temperature protocol as used in DSC. The diffractometer was equipped with a sealed Cu-X-ray tube, 0.04 rad primary and secondary Soller slits (size 2 in.) and a Ni-filter that produces a Cu Kα1 X-ray beam ($\lambda = 1.541$ Å). The sample was scanned from 15°2θ to 27.7°2θ, increasing with a step size of 0.008°2θ.

The obtained WAXD patterns were smoothed, respectively, with a Fourier transformation by the X'pert High Score software (PANalytical, Almelo, The Netherlands). Spreadsheets were generated of each scan with the diffraction intensity as function of the incident beam angle. The relationship between incident beam angle (θ) and short spacings (d) is given by Bragg's law:

$$d = \frac{n'\lambda}{2\sin\theta} \quad (1)$$

in which n' is the order of diffraction and λ is the wavelength (Å) used. 2D-plots of the obtained results were drawn in SigmaPlot™ for Windows version 10.0 (SPSS Inc., Chicago, USA).

2.4. SAXS-analysis

The longitudinal packing of the different observed crystal polymorphs were analyzed using time-resolved synchrotron XRD measurements using the Dutch-Belgian (DUBBLE) beamline BM26B at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The experiments were performed at a fixed wavelength λ of 1.24 Å. A 2D multiwire gas-filled detector was used for