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Physicochemical properties of lard-based diacylglycerols in blends with lard

Rikke Miklos [a], Hong Zhang [b,1], René Lametsch [a,*], Xuebing Xu [b]

[a] Department of Food Science, University of Copenhagen, Rolighedsvej 30, DK-1958 Frederiksberg C, Denmark
[b] Department of Engineering, Aarhus University, Gustav Wieds Vej 10, DK-8000 Aarhus C, Denmark

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ABSTRACT

The objective of the study was to investigate how blending of triacylglycerols and diacylglycerols affected the melting and crystallisation properties in a solid fat system. Lard-based diacylglycerols (DAGs) were blended with lard in various concentrations (0%, 1%, 5%, 10%, 20%, 50%, 60%, 70%, 80%, 90%, and 100%). The melting and crystallisation properties were investigated by the determination of dropping point (DP), solid fat content (SFC), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). In general, the effects of DAGs were found to be dependent on concentration. The DP was significantly ($P < 0.0001$) decreased when DAGs were added to the lard from 5–50%, whereas the DP was increased ($P < 0.0001$) when the blends contained more than 60% DAGs. The DSC thermograms showed that DAGs changed the melting and crystallisation profiles of lard. The crystallisation onset point increased ($P < 0.05$) with increasing the DAG concentrations (10–100%). The melting peaks and off-set points generally shifted slightly towards higher temperatures as the content of DAGs increased above 50%. DAG content of 5% and 10% resulted in lowering of the off-set point. The lard contained both β and β′ crystals. The β form was more pronounced in the blends with high concentrations of DAGs. Blending of TAGs and DAGs may serve as a solution to achieve specific functional properties in products containing solid fats.

1. Introduction

Diacylglycerols (DAGs) are esters of glycerol with two of its hydroxyl groups esterified with fatty acids. DAGs are found as a natural minor component of various fats and oil and have been reported in levels up to 10% (w/w) (Lo, Tan, Long, Yusoff, & Lai, 2008). With hydrophilic hydroxyl group in the molecular structure, DAGs exhibit interfacial properties and surface activity which make them suitable for use as emulsifiers. At the same time they are widely used particularly in the food and cosmetic industries (Macierzanka et al., 2009). DAGs can be produced both chemically (Yang, Zhang, Mu, Sinclair, & Xu, 2004; Zhong et al., 2010) and enzymatically (Kahveci, Guo, Ozcelik, & Xu, 2010; Lo et al., 2008) and the development of the latter during the last decades has resulted in the commercial production of high quality DAGs that enables the use of DAGs as a major component in food products. Recently DAGs have generated interest in the food industry as a functional food with beneficial health effects on aspects related to lipid metabolism as lowering the postprandial lipid level (Flickinger & Matsuo, 2003) and suppression of accumulation of body fat (Maki et al., 2002; Murase, Aoki, Wakisaka, Hase, & Tokimitsu, 2002). The safety of DAG when used as an edible oil for human consumption has been verified in a number of human and animal studies reviewed previously (Morita & Soni, 2009). A DAG oil is commercially manufactured from soy bean and canola oil and is marketed in Japan and USA as a functional cooking oil (Xu, Kristensen, & Zhang, 2007).

Beside the perspectives of the nutritional benefits of the uses of DAGs in the food industry, the physio-chemical properties of DAGs due to the existing of the free hydroxyl group is an interesting aspect that gives DAGs a potential as a new parameter to modify the properties of the fat. DAGs have different melting points, melting and crystallisation properties and interfacial properties compared to TAGs (Nakajima, Fukasawa, & Shimada, 2008). These properties are all of critical importance in the determination of the application of a given fat as they are directly related to the macroscopic properties of the end product such as texture, mouth feel and spreadability (Narine & Marangoni, 1999).

In relation to crystallisation, DAGs constituents have been studied in various fats and oils such as milk fat (Wright & Marangoni, 2002), palm olein TAGs (Siew & Ng, 1996), palm oil (Siew & Ng, 1999), trilaurin (Smith & Povey, 1997) and lard blends with rapeseed oil (Cheong, Zhang, Xu, & Xu, 2009) and are widely reported as inhibitors of the crystallisation processes. Information about DAGs as a major component in fat blends is still limited but they have been studied in lard-rapeseed-oil blends (Cheong et al., 2009) and in blends with palm oil (Saberi, Lai, & Toro-Vázquez,

* Corresponding author. Tel.: +45 35333483; fax: +45 35333341.
E-mail address: rla@life.ku.dk (R. Lametsch).
[1] Curreny address: Wilmar (Shanghai) Biotechnology Research & Development Center Co., Ltd., China.

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2011). However, to the best of our knowledge, no information concerning the physical properties of DAGs in purely animal-based fat blends has been published. The objective of this study was thus to provide information about the physiochemical properties of lard-based fat blends containing DAGs in concentrations between 0 and 100 percent. Thereby the study includes information about DAGs as both a minor and major constituent of a fat. The results provide useful information in cases where the application of DAGs as a functional ingredient is taken into consideration.

2. Materials and methods

2.1. Materials

Lard was supplied by Danish Crown AmbA (Horsens, Denmark). The fatty acid composition (FAC) was C14:0,1.5; C16:0, 27.3; C16:1, 2.3; C17:0, 0.4; C18:0, 16.6; C18:1, 36.6; C18:2, 9.4; C18:3, 0.7; C20:0, 0.2; C20:1, 0.6; C20:2, 0.4; C22:1, 0.2; others: 3.7 (Cheong et al., 2009). Glycerol (99.5% pure) was purchased from VWR International Ltd., (Albertslund, Denmark). Novozym 435, a commercially available *Candida antarctica* lipase B (CALB) immobilised by physical adsorption onto a macroporous hydrophobic polymethyl methacrylate (PMMA) matrix, was donated by Novozymes A/S (Bagsværd, Denmark). All other reagents and solvents were of analytical grade.

2.2. Production of DAGs

The production was carried out in two steps: enzymatic glycerolysis and purification by short-path distillation. In between the two steps and after purification the product was stored at −20 °C.

Enzymatic glycerolysis of lard was performed in a 1 kg batch scale reactor as described previously (Zhang et al., 2000). The process was published in another paper (Cheong et al., 2009). The end product had a purity of >90% DAGs and the fatty acid composition was not significantly different from lard (Cheong et al., 2009).

2.3. Blends preparation

A series of blends of lard and lard-based DAGs was prepared by completely melting the lard and DAGs at 70 °C for 30 min and subsequently blended in different ratios so the final concentrations of DAGs were 1, 5, 10, 20, 50, 60, 70, 80 and 90 wt.% of the final blend weight. The blends were prepared in duplicates and stored at −20 °C before further analysis.

2.4. Solid fat content (SFC)

SFC was measured by low-resolution NMR using a Bruker Minispec mq 20 pulse nuclear magnetic resonance (pNMR). From each sample, 3 ml were transferred to an NMR tube. For determination of SFC as a function of temperature the tubes were placed at 70 °C for 30 min to destroy any crystal history. The completely melted samples were crystallised at 0 °C overnight before the initial SFC was measured. SFC was measured after 30 min at the following temperatures: 5, 10, 20, 30, 35 and 40 °C. Melting, crystallisation and holding of the samples were carried out in water baths. The measurements were performed in duplicates.

2.5. DSC

Melting and crystallisation profiles were measured on a Pyris 6 DSC (PerkinElmer, Boston, MA). From each fat mixture 8–12 mg was weighed into an aluminum pan. The pan was sealed and placed in the DSC auto sampler for measurements. The following temperature program was run to record the melting and crystallisation profile of the samples: From 20 °C the samples were heated to 90 °C by 20 °C/min. To destroy any crystal history the samples were held at 90 °C for 5 min. Before cooling to −60 °C by 5 °C/min. During this cooling process the crystallisation profile was recorded. The samples were held at −60 °C for 5 min before heated to 80 °C to determine the melting profile. For reference an empty aluminum pan was used. Samples were run in duplicates.

2.6. Dropping point (DP)

DP was determined by use of the AOCS Official Method Cc 18–80 (AOCS, 1998).

2.7. X-ray analysis

An Ẋpert Pro X-ray diffractometer (PANalytical, The Netherlands) with Cu-tube and wavelength of 2.29 Å was used. The sample holder was filled with fat sample (approximately 20 mg) and heated in the apparatus to 70 °C and held for 10 min to destroy any crystals. The samples were cooled to 5 °C with a cooling rate of 5 °C/min). X-ray spectra were recorded at 20 °C and 5 °C after a holding time of 10 min. The spectra were analysed with the software "Ẋpert data collector". Polymorphic forms were determined by short spacing by use of following information: The α form is a 2θ of about 21°, which is equivalent to a short spacing of 4.15 Å. The β′ form is a 2θ at 20.8° and 23.0°, which are equivalent to short spacings of 4.2 and 3.8 Å. The β crystal had a peak at 4.6 Å, which is a 2θ of approximately 19.1°.

2.8. Statistical analysis

One-way analysis of variance was carried out with the Statistical Analysis System version 9.1 (SAS Institute Inc., Cary, NC, USA). The GLM procedure was applied when calculating least squares means (LSM) and standard errors (SE) and the option PDIFF was used for calculating significant differences between LSM. Differences with *P*-values <0.05 were considered to be significant.

3. Results and discussion

3.1. Raw material

The lard used in this study had a natural content of 2.1% DAG consisting of the sn-1,2 and sn-1,3 isomers in around 1:1. The DAG had a purity of 95.8% and the isomers sn-1,2 and sn-1,3 were present in the relation of 1:3.5 respectively (Cheong et al., 2009). The blends used in this study were prepared irrespective of the fact that the lard and lard-based DAGs were not 100% pure TAGs and DAGs respectively.

The melting behaviour of acylglycerols depends on their fatty acid composition, acyl glycerol composition, crystals and tempering history. The enzymatic glycerolysis process did not change the fatty acid composition (FAC) of the acylglycerol fractions (Cheong et al., 2009), and the crystallisation history of the samples were destroyed before all analysis as described in the methods and material section. Thereby it can be assumed that the observed changes in the physiochemical properties were due to the changes in acylglycerols structure rather than the differences in the chemical composition.

3.2. Dropping point

DP is defined as the temperature at which the sample passes from a semi-solid to a liquid state under the specific test