Food Chemistry 134 (2012) 1409–1417

Contents lists available at SciVerse ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Evaluation of high oleic-high stearic sunflower hard stearins for cocoa butter equivalent formulation

Miguel A. Bootello [a], Richard W. Hartel [b], Rafael Garcés [a], Enrique Martínez-Force [a], Joaquín J. Salas [a,*]

[a] Instituto de la Grasa (CSIC), Av. Padre García Tejero, 4, 41012 Sevilla, Spain
[b] University of Wisconsin–Madison, Department of Food Science, Madison, WI 53706, USA

ARTICLE INFO

Article history:
Received 25 October 2011
Received in revised form 6 February 2012
Accepted 7 March 2012
Available online 16 March 2012

Keywords:
Cocoa butter equivalents
High oleic-high stearic sunflower oil
Shea stearin
Isosolid diagram
Phase behaviour

ABSTRACT

Cocoa butter equivalents (CBEs) are produced from vegetable fats by blending palm mid fraction (PMF) and tropical butters coming from shea, mango kernel or kokum fat. In this regard, high oleic-high stearic (HOHS) sunflower hard stearins from solvent fractionation can be used in CBE production since their compositions and physical properties are similar to those found in the above-mentioned tropical butters. In this work, three sunflower hard stearins (SHS) ranging from 65% to 95% of disaturated triacylglycerols and a shea stearin (used as reference) were blended with PMF to evaluate their potential use in CBEs formulation. Isosolid phase diagrams of mixtures of PMF/SHS showed eutectic formation for SHS 65 and SHS 80, but monotectic behaviour with softening effect for SHS 95. Three CBEs from SHS and shea stearin were formulated according to phase behaviour diagrams and solid fat content data at 25 °C. Isosolid phase diagrams of mixtures of these CBEs with cocoa butter showed no eutectic behaviour. Therefore, CBEs elaborated from SHS exhibited full compatibility with cocoa butter.

1. Introduction

Cocoa butter (CB) is an important ingredient for chocolate and other confectionery products, having a major influence on their organoleptic and physical properties. CB, as the continuous phase in chocolate, supports the nonfat ingredients (Smith, 2001) and is responsible for much of the snap, gloss, appearance, mouthfeel, and flavour release typical of this product. At the same time, CB influences the shelf-life of chocolate and storage condition requirements (Bigalli, 1988). Cocoa butter contains three main fatty acids: palmitic, stearic and oleic acid (Gunstone & Hardwood, 2007). The saturated fatty acids, palmitic and stearic, are predominantly found in the *sn*-1 and *sn*-3 positions of the glycerol backbone, with the unsaturated oleic acid occupying the *sn*-2 central position. This distribution results in a triacylglycerol (TAG) composition rich in disaturated species, with 1,3-dipalmitoyl-2-oleoyl glycerol (POP), 1-palmitoyl-3-stearoyl-2-oleoyl glycerol (POSt) and 1,3-distearoyl-2-oleoyl glycerol (StOSt) being the most abundant TAG species. This TAG composition is responsible for the characteristic melting profile of cocoa butter, highly solid at 20 °C, sharp melting between 20 and 30 °C, and complete melting by 30–35 °C (Shukla, 1995). This melting profile is desirable for confectionery applications.

Among tropical fats, cocoa butter is one of the most valuable; however, its production is hampered by its difficult cultivation, low productivity and pest attacks. On the other hand, world cocoa prices have been increasing in recent years due to a strong demand in emerging countries, and changes in chocolate consumption towards higher cocoa content chocolate products (Afoakwa, 2010). For that reason, fats alternative to cocoa butter have been developed by food researchers (Lipp & Anklam, 1998). Cocoa butter alternatives can be classified into three groups: (1) cocoa butter substitutes (CBS), fats based on palm kernel oil or coconut oil, (2) cocoa butter replacers (CBR), non-polymorphic non-lauric fats based on partially hydrogenated oils, and (3) cocoa butter equivalents (CBE), polymorphic non-lauric fats that are defined as fat or fat blends with a similar melting profile, composition and polymorphism as CB, which should be compatible with CB without presenting any eutectic behaviour (McGinley, 1991).

CBEs are usually prepared by blending a fat rich in POP, usually palm mid fraction (PMF), and StOSt-rich fats, which come from exotic species like shea, kokum or mango kernel. Shea butter is the most common StOSt source, but it contains elevated level of 1-stearoyl-2,3-dioleoyl glycerol (StOO), which considerably softens the oil. For that reason, shea butter needs to be fractionated to obtain a high melting point stearin suitable for CBE formulation (Brench, 2002; Bup, Kapseu, Matos, Mabiala, & Mouloungui, 2011; Lipp & Anklam, 1998). However, these tropical fats come from trees growing in the rainforest and their availability from year to year can change substantially (Talbot, 2004). In this regard,

* Corresponding author. Tel.: +34 954611550x264; fax: +34 954616790.
E-mail address: jjsalas@cica.es (J.J. Salas).

0308-8146/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodchem.2012.03.040

new sunflower oils with altered fatty acid composition can be a reliable source of stearate-rich fats since this oil crop can be cultivated in large areas with temperate climate (Martínez-Force & Garcés, 1999).

High oleic-high stearic (HOHS) sunflower has been developed by techniques of breeding and mutagenesis (a non-genetically modified ingredient) and its oil contains about four times more stearic acid than common sunflower oil, ranging from 17% to 25% of stearate. The oleic acid content is about three times higher than common sunflower oil, with 60–70% of total fatty acids. Furthermore, HOHS displays very low amounts of polyunsaturated fatty acids and about 4% of very long chain fatty acids in the form of arachidic (20:0) and behenic acids (22:0) (Fernández-Moya, Martínez-Force, & Garcés, 2005). The content of disaturated TAGs (SUS) of HOHS sunflower oils is very low compared with SUS-rich fats like CB. In fact, the melting profile shows a solid fat content far from that necessary for the production of CBEs, making it necessary to fractionate HOHS to obtain a stearin rich in disaturated TAGs. The dry and solvent fractionations of HOHS have been investigated in previous works (Bootello, Garcés, Martínez-Force, & Salas, 2011; Salas, Bootello, Martínez-Force, & Garcés, 2011). Solvent fractionation is more efficient than dry fractionation and produces a higher enrichment of disaturated TAGs in a single step. This technique is usually applied in the production of valuable fractions used in CBEs or confectionary formulation.

The aim of the present work was to evaluate the potential use of HOHS sunflower hard stearins (SHS) for CBEs formulation in blends with PMF by studying fat compatibility by means of isosolid plots. Then, some CBEs were formulated according to phase behaviour diagrams and solid fat content data at 25 °C, and mixed with CB from different origin to study fat compatibility and functionality as CBEs.

2. Materials and methods

2.1. Oil materials

HOHS sunflower hard stearins were produced by solvent fractionation with acetone. The initial oil was a HOHS sunflower soft stearin containing 30% of SUS. This soft stearin was obtained by dry fractionation of refined, bleached, deodorized, and partially dewaxed HOHS sunflower oil provided by Nutrisun Business (Mar del Plata, Argentina) as described by Bootello et al. (2011). The solvent fractionation was carried out in a mini-pilot plant at temperatures between 15 and 17 °C and oil/solvent ratios ranging from 1/2 to 1/4. The resulting stearins were vacuum filtered and washed with fresh acetone, followed by vacuum distillation to remove the solvent. Three hard stearins with 65%, 80% and 95% of SUS were produced depending on fractionation conditions. The palm mid fraction was provided by Lípidos Santiga (Barcelona, Spain). Shea stearin used as reference fat was provided by Loders Croklaan (Wormerveer, The Netherlands) and cocoa butter samples from Ivory Coast and Ecuador by ADM Cocoa (Milwaukee, WI, USA).

2.2. Binary fat mixtures

Mixtures (w/w) of the two components in 10% increments were prepared from 0% to 100%. Samples were melted in an oven at 65 °C for 30 min to ensure that all crystal memory was erased before blending. The appropriate amounts of the different fats were weighed into a glass vial and mixed with a vortex. Two groups of mixtures were constructed; the first consisted of blends of PMF with each type of HOHS sunflower hard stearin described in Section 2.1, and with shea stearin as reference, since this is a common ingredient of commercial CBEs. The second group of mixtures was prepared by blending CBs from different origins and CBEs formulated from selected mixtures of the first group.

2.3. TAG analysis by GLC

The composition of TAGs of the different oil fractions was determined by GLC in an Agilent 6890 gas chromatograph (Palo Alto, CA) equipped with a chromatography column Quadrex Aluminium-Clad 400-65HT (30 m length, 0.25 mm i.d., 0.1 μm film thickness; Woodbridge, CT, USA) and a flame ionisation detector. Hydrogen was used as the carrier gas at a linear gas rate of 50 cm/s and split ratio 1:80. The injector and detector temperatures were 360 and 370 °C, respectively, the oven temperature was 335 °C, and a head pressure gradient from 100 to 180 kPa was applied. The relative response of the FID was corrected according to the method of Carelli and Cert (1993).

2.4. Analysis of fatty acid methyl esters

The fatty acid composition was determined by GLC by derivatizing 5 mg of the oil fractions to their corresponding fatty acid methyl esters with 1.5 mL of methanol/toluene/sulphuric acid (88/10/2; v/v/v) for 1 h at 80 °C. Fatty acid methyl esters were extracted with 1 ml of heptane and analysed by GLC using an Agilent 6890 gas chromatograph (Palo Alto, CA). The column was a Supelco SP-2380 fused silica capillary column (30 m length; 0.25 mm i.d.; 0.20 μm film thickness: Bellefonte, PA). Hydrogen was used as the carrier gas at 28 $cm\,s^{-1}$. Detector and injector temperatures were 200 °C, whereas oven temperature was kept at 170 °C. The different methyl esters were identified by comparison with known standards.

2.5. Solid fat content (SFC) by p-NMR

The solid fat content was determined by pulsed nuclear magnetic resonance using a Bruker Minispec unit, equipped with on-board software for data processing (Bruker, Milton, Ontario, Canada). Nuclear magnetic resonance tubes with a 10 mm diameter were filled with approximately 2.0–2.5 g of completely melted fat. Samples were tempered according to AOCS official method Cd 16–81 for stabilizing confectionery fats, which includes melting and storing for 15 min at 100 °C, then at least 5 min at 60 °C, followed by 90 min at 0 °C, 40 h at 26 °C, 120 min at 0 °C and finally 60 min at each chosen temperature. SFC was measured in 5 °C increments from 0 to 50 °C. Isosolid diagrams of fat mixtures were constructed using OriginPro 8.0 software (OriginLab Crop., Northampton, USA) based on NMR data for each temperature and for each mixture previously described in Section 2.2.

2.6. Calorimetric analysis by DSC

Thermal profiles of different oils and fat mixtures were obtained with a Q2000 V23.5 differential scanning calorimeter (DSC) (TA instruments, New Castle, Delaware, USA) with a refrigerated cooling system. The results were processed using the TA analysis software provided by the manufacturer. The instrument was calibrated prior to use with indium, azobenzene and undecane purchased from Sigma–Aldrich (Madrid, Spain). Nitrogen was used to purge the system. About 6–8 mg of the melted samples were weighed using a Sartorius M2P electronic microbalance (Sartorius AG, Goettingen, Germany) and hermetically sealed into an aluminium pan with an empty pan serving as reference. To study the melting profiles, samples were tempered with the same method as for SFC determination prior to measurement. The sample temperature was decreased to −20 °C at 100 °C/min followed by heating from −20 to 60 °C at 5 °C/min to generate melting curves.