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Plant polyphenols to enhance the nutritional and sensory properties of chocolates

Shaun Y.J. Sim [a], Jun Wei Ng [b], Wai Kiong Ng [b], Ciarán G. Forde [a], Christiani Jeyakumar Henry [a,c,*]

[a] Clinical Nutrition Research Centre, Singapore Institute for Clinical Sciences, Singapore, Singapore
[b] Crystallisation and Particle Science, Institute of Chemical and Engineering Sciences, A*STAR, 1 Pesek Road, Jurong Island, Singapore 627833, Singapore
[c] Department of Biochemistry, Yong Loo Lin School of Medicine, National University of Singapore, Singapore, Singapore

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ABSTRACT

A relatively unexplored method to enhance the sensory and nutritional properties of chocolate is to use plant polyphenols. In this study, a low cost agricultural waste product – mangosteen (*Garcinia mangostana* Linn.) pericarp – was added as powder in graded amounts (1%, 2% and 3% w/w) to dark and compound chocolates during the mixing stage and evaluated. The particle size distributions of the chocolates were mostly within 30 μm and the chocolates displayed a homogeneous morphology. The polyphenols (procyanidins and xanthones) in mangosteen pericarp powder were also stable to simulated chocolate processing. The 3% pericarp powder concentration significantly expanded the bioactive profile and total phenolic content (13% in dark chocolates and 50% in compound chocolates) compared to their plain counterparts without affecting sensory qualities. Such low cost plant polyphenols could enhance the bioactive and flavor profile of chocolates, especially in low cocoa content compound chocolates.

1. Introduction

Polyphenols are the most abundant antioxidants found in foods and have been extensively studied in the last 20 years (Scalbert, Johnson, & Saltmarsh, 2005; Tomas-Barberan & Andres-Lacueva, 2012). Cocoa in particular is rich in flavonoids that mainly consists the monomeric (−)-epicatechin and catechins, and polymeric procyanidins (Steinberg, Bearden, & Keen, 2003). Procyanidins form the most abundant phytochemicals in cocoa and chocolate products (Kim et al., 2014; Wollgast & Anklam, 2000). Besides antioxidative and anti-inflammatory properties, cocoa polyphenols have demonstrated beneficial cardiovascular, metabolic, antiradical and anti-skin ageing effects (Andújar, Recio, Giner, & Ríos, 2012; Hooper et al., 2012; Kim et al., 2014).

The cocoa phenolic content is largely dependent upon the cultivar, origin, agricultural and postharvest practices, with major losses during processing (Andres-Lacueva et al., 2008; Wollgast & Anklam, 2000). A low polyphenol concentration was found to be crucial for flavor development during the roasting stage (Misnawi, Jinap, Jamilah, & Nazamid, 2004; Noor-Soffalina, Jinap, Nazamid, & Nazimah, 2009), yet paradoxically, a high phenolic content is desirable in the final product for its nutritional benefits. There have been some approaches to balance and maximize both flavor development and phenolic content (Afoakwa, Ofosu-Ansah, Budu, Mensah-Brown, & Takrama, 2015; Bordiga et al., 2015; Ioannone et al., 2015; Payne, Hurst, Miller, Rank, & Stuart, 2010), but they are limited to the scope of cocoa cultivation and processing. A relatively less explored approach to expand both flavor and phenolic profile of chocolates is to add naturally derived polyphenolic compounds from plant sources. This includes plant polyphenols from red raspberry leaves (Belščak-Cvitanovic et al., 2012), ginseng (Chung, Lee, Kyung Rhee, & Lee, 2011), green tea and fruit extracts such as red grape and acai berries. This approach is restricted, however, by cost and must not be detrimental to taste and consumer acceptability.

Mangosteen (*Garcinia mangostana* Linn.), often considered "the queen of fruits" for its pleasant flavor, is a tropical fruit from the Guttiferae family (Morton, 1987). It is commonly grown in Thailand, Malaysia and Indonesia and has a worldwide production of about 150,000 tons per year (Ramage, Sando, Peace, Carroll, & Drew, 2004). It consists of a sweet edible milky white pulp and a dark red pericarp. The pericarp makes up about two-thirds the whole fruit weight and is often discarded as agricultural waste. The pericarp however is rich in bioactive compounds such as anthocyanins, xanthones and procyanidins (Du & Francis, 1977; Fu, Loo, Chia, & Huang, 2007) and has been long used in traditional Thai medicine for treating diarrhea, wounds and skin infections

* Corresponding author at: Clinical Nutrition Research Centre, Singapore Institute for Clinical Sciences, 14 Medical Drive #07-02, MD 6 Building, Singapore 117599, Singapore.
E-mail address: jeya_henry@sics.a-star.edu.sg (C.J. Henry).

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(Peres & Nagem, 1997). There are also health benefits associated with consuming the pericarp (Ohno et al., 2015; Xie, Sintara, Chang, & Ou, 2015). The incorporation of this low cost agricultural waste product could potentially expand the bioactive profile of chocolates.

Compound chocolate differs from regular chocolates in that the cocoa butter fat source is partially or fully replaced with cheaper vegetable and tropical fats of similar melting characteristics, such as palm kernel oil (Beckett, 2000). The lower cocoa content in compound chocolate also results in lower polyphenol content and a poorer flavor profile. Due to strict EU regulations on what constitutes chocolate (2000/36/EC directive), compound chocolates finds itself mainly in confectionery use such as ice cream coatings. The recent surge in chocolate demand and cocoa butter prices have led to a boom in compound chocolate production and are especially fueled by Asian and Eastern European markets (Nieburg, 2014). As more people consume compound chocolates, the addition of plant polyphenols presents an opportunity to increase the nutritional and organoleptic qualities of compound chocolates.

Conventional chocolate processing involves roasting, nib grinding, mixing, refining, conching, tempering and molding (Wollgast & Anklam, 2000). In previous studies, the polyphenols were added either as powder to melted chocolate, or during the molding stage of chocolate processing. While high temperatures and long roasting time may be detrimental to the quantity and quality of these polyphenols (Bordiga et al., 2015; Ioannone et al., 2015; Wollgast & Anklam, 2000), it was found that total polyphenol content was not significantly reduced with conching time (Bordin Schumacher et al., 2009). Polyphenols could therefore be added somewhere in between these two stages, such as during the mixing stage.

This study therefore aims to explore incorporating a low cost agricultural waste product with high bioactive content such as mangosteen pericarp powder, as a plant polyphenol source, in graded amounts to dark and compound dark chocolates and to determine the resultant physical, bioactive and sensory properties.

2. Materials and methods

2.1. Chemicals

Folin–Ciocalteu reagent was purchased from Merck (Darmstadt, Germany). Anhydrous sodium carbonate was purchased from Thermo Fisher (Singapore). Gallic acid was purchased from Acros Organics (Singapore). HPLC grade hexane was purchased from JT Baker (Pennsylvania, USA).

2.2. Preparation of mangosteen pericarp powder

Mangosteen pericarp powder (*Garcinia mangostana* Linn.) was obtained from a global supplier of botanical ingredients, NP Nutra. The mangosteens were grown and harvested in Thailand. Fresh mangosteens were cleaned, sun dried or tray dried at 68 °C for 8 h, milled to powder, sieved (with greater than 95% through 80 mesh size) and packaged. Quality control checks were made during the processing to ensure the appearance, taste, odor and safety aspects conform to standards. The powder physical and nutritional information is shown in Supplementary data.

2.3. Formulation of pericarp powder enriched chocolates

The chocolates were made using a classical technological process in a confectionery factory (Aalst Chocolate, Singapore). 1%, 2% and 3% (w/w) of mangosteen pericarp powder were added to both dark chocolate (DC) and compound chocolate (CC) to give mangosteen pericarp powder enriched chocolates ($DC_{1\%}$ –$DC_{3\%}$ and $CC_{1\%}$–$CC_{3\%}$). Plain unenriched chocolates ($DC_{0\%}$ and $CC_{0\%}$) were also made. The powder concentrations were chosen based on sensory differences found in 3% samples during preliminary bench tasting. In addition, the concentrations are kept sufficiently low such that any sensory differences are less likely to be due to the reduction of the other ingredients. The formulations used for the production of chocolates are shown in Supplementary data.

For the dark chocolates, cocoa butter was pre-melted by heating between 40 and 50 °C and added to the cocoa liquor. Sugar, cocoa powder and mangosteen pericarp powder (for enriched chocolates) were added and mixed (Hobart, USA). For the compound chocolates, hydrogenated palm kernel oil was pre-melted between 40 and 50 °C and added to cocoa powder, sugar and mangosteen pericarp powder (for enriched chocolates) and mixed (Hobart, USA). In both cases, a minimum total fat content of 25% was achieved. The respective mixtures were then refined in a five-roll press (Buhler, Switzerland) and conched (BSA, Germany). The dark chocolates were conched for 8 h (6 h dry conche at 90 °C, and 2 h liquid conche at 45 °C) while the compound chocolates were conched for 4 h (2 h dry conche at 60 °C, and 2 h liquid conche at 45 °C). Emulsifier (lecithin E322), vanilla flavor and the remaining fat (natural vanilla and cocoa butter for dark chocolate, vanillin and hydrogenated palm kernel oil for compound chocolate) were added prior to liquid conching. The conched samples were kept in a dry cool room (18–23 °C) until analysis, where the dark chocolates were then hand tempered and both types of chocolates molded using plastic molds to form 4 × 3 cm neapolitans. The chocolates were transported in dry cardboard boxes.

2.4. Determination of physical properties of chocolate

2.4.1. Determination of particle size distribution

The particle size distribution (PSD) of the plain and enriched chocolate samples was determined using laser diffraction technique (Mastersizer 2000, Malvern Instruments Ltd., UK). The analysis was conducted in a wet dispersion mode (Hydro 2000S wet dispersion unit, Malvern Instruments Ltd., UK). About 5 g of each chocolate sample was dispersed in 50 mL of HPLC grade hexane at room temperature (25.2 °C). The samples were placed under ultrasonic dispersion for 2 min to ensure the particles were independently dispersed. All samples were measured in triplicate and the size distribution was quantified. PSD parameters (in μm) obtained included the largest particle size d(0.9), mean particle volume d(0.5), smallest particle size d(0.1), Sauter mean diameter (D [3,2]) and mean particle diameter (D [4,3]).

2.4.2. Microstructure visualization

The morphology of defatted and non-defatted chocolate samples were observed under JEOL JSM-6700F Field Emission Scanning Electron Microscope (FESEM) (JEOL Ltd, Japan) with a Gatan Alto 2500 cryotransfer system and a Gatan C1002 liquid nitrogen cold stage (*Gatan Inc.*, USA). The chocolate were placed on a brass holder and frozen in liquid nitrogen prior to scalpel fracturing to expose an internal structure. The sample was heated to −90 °C for 5 min to remove ice crystals through sublimation followed by a platinum sputter target coating in an argon atmosphere (60 s, 10 mA) at about −120 °C. Imaging was carried out at about −160 °C using an accelerating voltage of 5 kV under secondary electron imaging (SEI) mode.

2.5. Determination of bioactive properties of mangosteen pericarp powder and chocolates

2.5.1. Determination of total phenolic content (TPC)

2.5.1.1. Preparation of mangosteen pericarp powder. Mangosteen pericarp powder (1.0 g) was extracted with 60% ethanol (10 mL)