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Compositional and thermal characteristics of palm olein-based diacylglycerol in blends with palm super olein

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ABSTRACT

Palm olein-based diacylglycerol (POL-DAG) was blended with palm super olein (POoo) in various concentrations (10–90%), with increments of 10% (wt/wt) POL-DAG. The physical and chemical characteristics, i.e., iodine value, acylglycerol content, fatty acid composition, melting and crystallization profiles and solid fat content, for POL-DAG, POoo and their binary blends were evaluated. The mid-infrared FTIR was used to determine the absorption bands of the different concentrations of the oil blends. Only slight differences of FAC and IV were observed. POL-DAG:POoo blends showed significant changes ($p < 0.05$) in DAG content and decreases in TAG content with increasing POL-DAG content. The DSC thermograms showed that the addition of different concentrations of POL-DAG changed the melting and crystallization behavior of the oil blends (POL-DAG:POoo). The crystallization onset point increased ($p < 0.05$) with an increasing POL-DAG concentration (10–90%). POL-DAG has the same absorption bands as POoo, with the exception of several minor peaks that appeared at (I) 2954 cm^{-1}, (II) 1267 cm^{-1}, (III) 1199 cm^{-1}, (IV) 1222 cm^{-1} and (V) 966 cm^{-1}. This study will provide essential information for the palm oil industry to identify the most suitable POL-DAG blends with desirable physicochemical properties for food application purposes.

1. Introduction

A novel application of DAG (diacylglycerol) emerged in the late 1990s as a healthier form of oil, with a focus on the nutritional properties provided by the glyceride structure of DAG. DAGs are digested and metabolized differently from other oils, which significantly reduces the risk of obesity. DAGs consist of a glycerol backbone esterified with two fatty acids (FA). DAGs have two isomeric forms, the sn-1, 3-DAG and the sn-1, 2(2, 3)-DAG, with a natural isomeric ratio of approximately 7:3. DAGs are found as minor components of various edible oils (D'Alonzo, Kozarek, & Wade, 1982). Notably, DAG has the same bioavailability and physiological fuel value as TAG (Flickinger & Matsuo, 2003). There are two main health benefits of DAGs. First, the regular consumption of DAG oil in the diet has been shown to affect body weight and body fat in both animals and humans (Maki et al., 2002; Murase, Aoki, Wakisaka, Hase, & Tokimitsu, 2002; Murase et al., 2001; Nagao et al., 2000). Second, DAG oil has been shown to lower serum triglyceride (TG) levels when compared with conventional oils (Hara et al., 1993; Tada, Watanabe, Matsuo, Tokimitsu, & Okazaki, 2001; Taguchi et al., 2000). Consequently, oils with high concentrations of DAG have drawn attention as useful oils for use in various food applications. The safety issues of DAG oil have been evaluated by the Japanese Ministry of Health and Welfare, and DAG oil has been classified as a "Food for Specified Health Use"; moreover, the FDA in the United States classified the oil as GRAS (Generally Regarded as Safe). Healthier DAGs can be applied in O/W emulsions, such as mayonnaises and salad dressings, and in W/O emulsions, such as margarines, spreads, creamy fillings, confectionary foods, shortening, fried products (potato chips, fried cakes, and doughnuts), icings and ice creams (Lo, Tan, Long, Yussof, & Lai, 2008). Recently, DAG has been marketed as functional cooking oil in Japan and in United States (Flickinger & Matsuo, 2003). The production of DAG usually results in a mixture containing MAG, DAG, and TAG through an enzymatic and purification process. In addition, the free hydroxyl group and nutritional benefits of DAG allow for many product possibilities, such as the use of DAG in foods, cosmetics, dietary supplements, and pharmaceuticals.

Palm olein-based diacylglycerol oil (POL-DAG) is a pale yellowish liquid fraction obtained from the dry fractionation of palm oil after crystallization under a controlled temperature. The purified POL-DAG appears in semisolid form at room temperature. POL-DAG is less saturated than palm oil. To produce POL-DAG, palm oil undergoes a two-step glycerolysis process, and the purified product contains 35.6% C16:0, 46.5% C18:1 and 12.2% C18:2 (Saberi, Beh, Lai, & Miskandar,

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2011). POL-DAG can be blended with other vegetable oils to suit various fat applications. Furthermore, palm oil has many applications in the food industry, and many healthful solid fat products can be produced from palm-based DAG.

Palm oil is one of the 17 major oils and fats that are produced and traded worldwide. Palm oil can be fractionated into many components containing liquid fractions such as oleins, super oleins and top oleins, which can be used as cooking and salad oils (Gibon, 2006). Palm super olein (POoo) is a softer type of olein that is obtained by fractionation of the regular palm olein, which has a higher IV. The IV of POoo ranges from 60 to 67.5 g iodine/100 g sample; the slip melting point ranges from 13 to 17 °C; and the SFC ranges from 0 to 26% at 10 °C. The major fatty acids in POoo are palmitic acid (35%), oleic acid (45%) and linoleic acid (13%). POoo was chosen to blend with POL-DAG to enhance the market acceptability in terms of melting point depression and shelf life. POoo is mostly used to improve the plasticity of products in the confectionery and bakery industry. The blending of oils has been encouraged recently to improve the nutritional properties of oils. Additionally, oil blending is the simplest method for modifying oils and fats for specific applications (NorAini, Embong, Aminah, Ali, & Che Maimon, 1995). Blending does not result in the chemical modification of the triacylglycerol composition. The physical and chemical characteristics substantially influence the uses of oils and fats by controlling the final characteristics of the derived products. The complicated interactions between DAGs and TAGs in blended oils must first be understood to achieve desirable properties. Information about DAGs as a major component in fat blends is still limited, but DAGs have been studied in lard-rapeseed-oil blends (Cheong, Zhang, Xu, & Xu, 2009) and in blends with palm oil (Saberi, Lai, & Toro-Vázquez, 2011). Moreover, there are fewer processing functions in foods made with POL-DAG oil and POoo compared with those made with traditional edible plant fats and oils. Furthermore, the utilization of DAG in blends with the same source of oil would be useful because this increases the functionality of the oil and the stability of the fat while also lowering the cost of production.

Hence, it is important to understand the relationships between the specific properties of oil blends and the composition of oil blends to modify the blends for use in certain food products. However, little is known concerning the effect of blending POL-DAG with the same source of oil, POoo, on the basic physicochemical properties of the resulting blends an important aspect for the food application. Therefore, the main objectives of this study were to evaluate the effect of blending palm olein-based diacylglycerol oil with palm super olein at different ratios on the physicochemical properties, namely, the fatty acid composition, acylglycerol content, solid fat content and thermal behavior, of the resulting blends. In addition, the Fourier transform infrared (FTIR) technique was used as a qualitative method to determine the functional groups of the oil blends and serve as a fingerprint method for the oil blends.

2. Materials and methods

Palm super olein (POoo) and palm olein (POL) were provided by Sime Darby Sdn. Bhd. (Banting, Selangor, Malaysia). Commercial immobilized lipase from *Candida antarctica* (Novozymes 435) was purchased from Novozymes A/S (Bagsvaerd, Denmark). Fatty acid methyl ester (FAME) standards were purchased from Sigma-Aldrich (St Louis, MO, USA). Sodium methoxide was purchased from Fisher (Pittsburgh, PA, USA). All other chemicals used were either of high-performance liquid chromatography (HPLC) or analytical grade and were obtained from Merck (Darmstadt, Germany).

2.1. Preparation of oil blends

Eleven blends with various ratios of palm olein-based diacylglycerol (POL-DAG) to palm super olein (POoo) were prepared based on the percentage of the total weight (wt.%) and labeled as blends A–K as shown in Table 1. The concentration of POL-DAG ranged from 0% to 100%, while the concentration of POoo ranged from 100% to 0%, in 10% increments (wt/wt). All blends were prepared in three independent replicates and stored at −20 °C before further analysis to ensure the stability of the molecules prior to the analysis. All binary blends of POL-DAG:POoo were melted at 70 °C, stirred vigorously for 5 min, and then blended using low rotation speed for 2 min to destroy any crystals that were present. POL-DAG (100% w/w) and POoo (100% w/w) were considered to be control samples. The blends were homogenized using a magnetic stirrer.

2.2. Pilot plant production and purification of POL-DAG oil

POL-DAG was produced by enzymatic glycerolysis using Novozyme 435, as described by Saberi, Beh et al. (2011), in a pilot packed bed bioreactor (PBR) consisting of a 10 l reaction vessel and a 6 l filtration vessel. Purification of the DAG oil was carried out in two steps using short path distillation (SPD) with the KD6 system (UIC, Alzenau-Hoerstein, Germany) to separate DAG from MAG, TAG, glycerol and free fatty acid (FFA). Glycerol, FFA and MAG can be easily separated from the reaction mixture and were separated in the first purification step, while DAG was separated from the TAG and collected from the distillate vessel during the second purification step (Saberi, Beh et al., 2011). The product was stored at −20 °C between the steps and after the final purification.

2.3. Fatty acid composition (FAC)

The fatty acid composition of the blended samples was determined by fatty acid methyl esters (FAME). The melted oil (100 mg) was dissolved with 5 ml of hexane, and 250 µl of sodium methoxide reagent was then added. The mixtures were vortex for 1 min, pausing every

Table 1
Total fatty acid composition of palm olein-based DAG (POL-DAG), palm super olein (POoo) and their binary blends[a]. Samples A to K represent the gradual increase of POL-DAG percentage from 0 to 100% in the binary blends.

FA (%)	A (0%:100%)	B (10%:90%)	C (20%:80%)	D (30%:70%)	E (40%:60%)	F (50%:50%)	G (60%:40%)	H (70%:30%)	I (80%:20%)	J (90%:10%)	K (100%:0%)
C:12:0	0.21 ± 0.01	0.22 ± 0.01	0.22 ± 0.01	0.23 ± 0.01	0.24 ± 0.01	0.24 ± 0.01	0.25 ± 0.01	0.26 ± 0.01	0.25 ± 0.02	0.27 ± 0.01	0.27 ± 0.01
C:14:0	1.01 ± 0.02	1.02 ± 0.01	1.02 ± 0.01	1.03 ± 0.02	1.03 ± 0.01	1.04 ± 0.02	1.05 ± 0.01	1.05 ± 0.01	1.06 ± 0.01	1.06 ± 0.01	1.06 ± 0.01
C:16:0	35.71 ± 0.02	35.83 ± 0.05	35.92 ± 0.07	36.09 ± 0.01	36.10 ± 0.05	36.35 ± 0.02	36.47 ± 0.02	36.58 ± 0.04	36.76 ± 0.04	36.90 ± 0.04	37.08 ± 0.07
C:18:0	3.86 ± 0.03	3.84 ± 0.01	3.84 ± 0.01	3.80 ± 0.06	3.83 ± 0.01	3.83 ± 0.02	3.84 ± 0.01	3.84 ± 0.01	3.84 ± 0.01	3.84 ± 0.01	3.84 ± 0.01
C:18:1	46.26 ± 0.03	46.20 ± 0.06	46.15 ± 0.10	45.98 ± 0.02	45.89 ± 0.05	45.74 ± 0.03	45.62 ± 0.02	45.51 ± 0.02	45.36 ± 0.06	45.26 ± 0.02	45.10 ± 0.08
C:18:2	12.31 ± 0.01	12.27 ± 0.02	12.25 ± 0.02	12.24 ± 0.01	12.28 ± 0.02	12.18 ± 0.01	12.16 ± 0.02	12.14 ± 0.02	12.12 ± 0.02	12.07 ± 0.02	12.06 ± 0.04
C:18:3	0.24 ± 0.01	0.25 ± 0.01	0.23 ± 0.02	0.24 ± 0.01	0.23 ± 0.01	0.23 ± 0.01	0.24 ± 0.02	0.25 ± 0.02	0.23 ± 0.01	0.23 ± 0.01	0.22 ± 0.02
C:20:0	0.39 ± 0.01	0.39 ± 0.01	0.37 ± 0.02	0.38 ± 0.01	0.39 ± 0.01	0.39 ± 0.01	0.38 ± 0.01	0.38 ± 0.01	0.38 ± 0.01	0.37 ± 0.01	0.37 ± 0.02
SAFA	41.19 ± 0.02	41.28 ± 0.06	41.37 ± 0.10	41.54 ± 0.03	41.59 ± 0.06	41.84 ± 0.04	41.98 ± 0.02	42.10 ± 0.03	42.28 ± 0.03	42.44 ± 0.03	42.62 ± 0.06
USAFA	58.81 ± 0.02	58.72 ± 0.06	58.63 ± 0.10	58.46 ± 0.03	58.41 ± 0.06	58.15 ± 0.03	58.02 ± 0.02	57.90 ± 0.03	57.72 ± 0.03	57.56 ± 0.03	57.38 ± 0.06
IV	61.89 ± 0.82	61.80 ± 0.50	61.60 ± 1.47	61.52 ± 2.02	60.63 ± 0.76	60.53 ± 2.10	60.36 ± 0.24	60.20 ± 2.25	60.05 ± 1.10	59.95 ± 1.83	59.79 ± 0.40

[a] Values are means of six determinations from three replicate experiments ± SD. All measurements were performed using peak area normalization. Abbreviations; A, POoo (100% w/w), B–J, oil blends containing (10–90% w/w) POL-DAG with POoo (90–10% w/w) and K, POL-DAG (100% w/w), respectively.