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Optimization of frying oil composition rich in essential fatty acids by mixture design

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A B S T R A C T

Studies have shown that the n-6/n-3 fatty acids (FA) ratio intake has risen dramatically, which is associated with the development of inflammatory diseases. Mixtures of vegetable oils may modify the FA profile so that lowering n-6/n-3 ratio and contributing to balance the intake of these fatty acids. Additionally, oil stability over frying may be enhanced. In this context, a multivariate mixture design was used to formulate frying oil mixes with high content of essential FA and low n-6/n-3 ratio from soybean, safflower and flaxseed oils. Among the mixtures ($n = 185$), 3 were selected for stability (180 days), application in food (French fries) and sensory acceptance studies, and the contents of FA, sterols, and tocopherols were determined in the formulations and French fries. The formulation containing soybean, flaxseed and safflower oil (75:20:5 g.100 g^{-1} v/v) showed a higher stability than pure soybean oil, was rich in essential fatty acids, phytosterols, tocopherols, and presented a reduced n-6/n-3 ratio. French fries processed with this mix had an increase in the content of these substances, and a sensory acceptance similar to that of soybean oil processed samples. Thus, the oil mixes might boost the nutritional quality of French fries and contribute for a healthier diet.

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1. Introduction

Polyunsaturated fatty acids (PUFAs), such as linoleic and linolenic acids, are fatty acids essential (EFAs) for human health and cannot be synthesized by mammalian cells, it being necessary to be obtained from diet (Harauma et al., 2017). They are precursors of long-chain polyunsaturated fatty acids (PUFA-CL) such as n-6 and n-3 fatty acids. Their metabolic products are essential for maintaining under normal conditions cell membranes, brain function, transmission of nerve impulses, atmospheric oxygen transfer to the blood plasma, hemoglobin synthesis and cell division (Aguiar et al., 2011; Newton, 2001; Pickens, Sordillo, Zhang, & Fenton, 2017). PUFAs also have effects on the reduction of low-density lipoprotein cholesterol, total cholesterol and triglycerides. Because of these metabolic functions, the ingestion of foods containing EFAs is extremely important for the maintenance of health (Santos et al., 2017).

The main EFAs sources in the human diet are fish, some vegetables, cereals and, legumes. In the post-industrialization period, the consumption of vegetables and seafood has been reduced, causing the increase of linoleic acid intake in relation to linolenic acid. The ratio varied between 1:1 and 1:2 for the levels from 20:1 to 50:1 (Bhardwaj, Verma, Trivedi, Bhardwaj, & Shukla, 2016; Newton, 2001). As the metabolic pathway of both is similar, a competition between the metabolism of these acids occurs, determined by enzyme affinities, it being necessary to maintain an appropriate relationship between the intake levels (Alashmali, Hopperton, & Bazinet, 2016).

The increased intake of n-6 fatty acids may raise the risk of

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inflammatory and neurodegenerative diseases (Bhardwaj et al., 2016). On the other hand, protective effects of n-3 fatty acids supplementation against neurodegenerative diseases have been demonstrated in experimental animal models, ratifying the need to increase fatty acids intake containing three unsaturation, lowering the n-6/n-3 ratio (Dong, Xu, Kalueff, & Song, 2017). For this reason, efforts have been made by research groups to find the most appropriate ratio of n-6/n-3 EFAs (Alashmali et al., 2016; Bhardwaj et al., 2016; McDaniel, Ahijevych, & Belury, 2010; Newton, 2001; Organization, 2008, pp. 10–14; Simopoulos, 2002).

The findings are as follows: 5:1 ratio controlled the symptoms of asthma, and 4:1 ratio reduced by 70% the risk of death in patients with cardiovascular disease. Regarding ratio between 2 and 3:1, inflammation resulting from rheumatoid arthritis has been minimized (Bhardwaj et al., 2016). Ratio below 1:1 is not recommended since it may slow blood coagulation (Newton, 2001). Studies conducted on 52 subjects show that the most suitable ratio is between 1:1 and 4:1 (McDaniel et al., 2010).

Fried foods are widely consumed all over the world because of their unique sensory properties and soybean oil is widely used for such foods. Among the widely consumed fried foods, French fries have stood out, mainly in Europe, due to great sensory acceptance by consumers of all age groups. Furthermore, French fries are used as accompaniment for various culinary dishes (Giovanelli, Torri, Sinelli, & Buratti, 2017; Omayio, Abong, & Okoth, 2016).

Safflower and flaxseed oils have been investigated because they show positive effects on human health. Among these effects, it was proven that safflower oil intake reduces blood pressure, might provide neuroprotection against cerebral ischemia/reperfusion injury through its antioxidant action and, decrease low-density lipoprotein cholesterol (LDL) levels (Nie, Zhang, Zhang, Rong, & Zhi, 2012; Upadya, Devaraju, & Joshi, 2015). Regarding flaxseed oil, studies have correlated the high concentration of fatty acids containing 3 unsaturation with efficiency in slowing ovarian cancer (Ansenberger et al., 2010), and increased plasma levels of eicosapentaenoic and docosahexaenoic acids, indicating its cardioprotective potential (Bhardwaj et al., 2016; Harper, Edwards, DeFilipis, & Jacobson, 2006).

According to Dubois, Breton, Linder, Fanni, and Parmentier (2007), soybean oil has n-6/n-3 ratio around 6 and 7. Since flaxseed oil stands out for containing high levels of n-3, and safflower oil stands out for introducing high n-3 values, the mixture of these oils may result in a mix with higher concentrations of polyunsaturated fatty acids and different n-6/n-3 ratios.

Recent studies have been demonstrated that mixtures of vegetable oils might modify the fatty acid profile and improve the stability of soybean oil (Wang et al., 2016). Moreover, the transference of bioactive compounds from vegetable oils rich in EFAs has been reported (Ramírez-Anaya, Samaniego-Sánchez, Castañeda-Saucedo, Villalón-Mir, & de la Serrana, 2015).

Therefore, the objective of this study was to use a mixture design to prepare one oil formulation for frying with high concentrations of linoleic (18:2 n-6) and linolenic (18:3 n-3) acids and n-6/n-3 ratio between 2 and 5. For this purpose, three oil formulations and French fries obtained with these formulations were studied and compared with soybean oil regarding stability, costs, chemical composition (fatty acids, tocopherols, and sterols) and sensory acceptance.

2. Material and methods

2.1. Samples

Initially, different brands of soybean (n = 3), safflower (n = 2) and flaxseed (n = 3) oils, sold in supermarkets of Campinas, Brazil, were investigated regarding the fatty acids content. From these results, a database was established for optimizing formulations.

Soybean oil (10 liters), flaxseed oil (5 liters) and safflower oil (5 liters) were used to prepare the formulations. All oils were purchased from companies of Rio Grande do Sul and São Paulo, Brazil, after processing and free of any additives. The safflower and flaxseed oils were unrefined while soybean oil was refined.

Regarding frying studies, were used ten kilos of pre-cooked French fries, frozen and from the same batch, acquired in Campinas, Brazil.

2.2. Reagents

Analytical standards of fatty acid methyl esters, α, β, γ and δ tocopherol were purchased from Supelco (St. Louis, USA). 23:0 methyl ester, butylated hydroxytoluene (BHT), stigmasterol, campesterol, β sitosterol and cholesterol were obtained from Sigma-Aldrich (St. Louis, USA). Methanol, isopropanol and acetic acid were obtained from J.T. Backer (Goiania, Brazil) and hexane from Macron Fine Chemicals™ (Center Valley, USA), all in chromatographic grade. Ethyl ether, acetic acid, chloroform, methanol, hexane, isopropanol, ethyl alcohol, phenolphthalein, potassium iodide, sodium thiosulfate, starch, NaOH, KOH and sodium sulfate were purchased from Synth (Diadema, Brazil); boric acid from Ecibra (Santo Amaro, Brazil); BF_3 12% from Merck (Darmstadt, Germany); NaCl from Allkimia (Campinas, Brazil) and TBHQ was kindly donated by Danisco Brazil Ltda (Cotia, Brazil). The water used in experiments was purified by the Milli-Q system from Millipore and the solutions were filtered through PVDF membranes with porosity 0.22 from Millipore (Billerica, USA).

2.3. Optimization of formulations and application to foods

2.3.1. Multivariate optimization of formulations

Through the analysis of the fatty acid composition in commercial samples of safflower, linseed and soy bean we obtained a database about the composition of fatty acids and the ratio of n-6/n-3. The concentration of fatty acids was used to optimize the composition of the formulations, with the purpose of obtaining oil mixtures with the ratio of n-6/n-3 between 2 and 5, different concentrations of EFAs and at the lowest cost. The costs were determined based on three estimates for each sample and taking into account the period of May 2017.

Initially, a simplex–lattice mixture design with concentrations of safflower, linseed and soy bean varying from 0 to 1 was performed, however, this one did not present adequate models adjustment. For this reason, the formulations were studied using pseudo-component multivariate models. Through the desirability function of Derringer and Suich (1980), several combinations of different mixtures by EFAs composition, n-6/n-3 ratio and cost were obtained. Among these, three formulations were chosen (A, B and C) with different characteristics, for studies of stability, sensory acceptance, composition of fatty acids, phytosterols and tocopherols. The models were treated through the Design Expert 6.0.10 software (Minneapolis, USA) and validated by Analysis of Variance ($p < 0.05$).

2.3.2. Stability of the formulations

To study the stability of formulations tert-Butylhydroquinone (TBHQ) was added to the oils at levels of 45% and 90% of maximum concentration permitted by Brazilian legislation (i.e. 0.02 g.100 mL^{-1}) (CNS, 1988). The assessment of stability was performed through induction assay with oxygen using Rancimat, following the method proposed by American Oil Chemists' Society (AOAC, 1990, pp. 8–53). The same analyses were also conducted in

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