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Prediction of linolenic and linoleic fatty acids content in flax seeds and flax seeds flours through the use of infrared reflectance spectroscopy and multivariate calibration

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ABSTRACT

Infrared spectroscopy was used for multivariate determination of linoleic (LA) and linolenic (ALA) acids in yellow and brown flax seed samples, using partial least square regression (PLSR). The models were developed by correlating near-(NIR) and mid-infrared (MIR) spectroscopic signals with the acid content determined by GC-FID. For the flax seed samples, the best models for both, LA ($R^2 = 0.90$, Standard Error of Prediction (SEP) = 1.61) and ALA ($R^2 = 0.86$, SEP = 0.63) were obtained by processing the NIR spectral data. For samples of flax seed flours, the best models for prediction of the ALA ($R^2 = 0.99$, SEP = 1.21) and LA content ($R^2 = 0.88$, SEP = 0.76) were developed by processing the NIR and MIR spectral region, respectively. This report demonstrates that NIR and MIR spectroscopies are efficient techniques for the determination and quantification of LA and ALA in flax seed and flax seed flours.

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1. Introduction

Several anthropological, genetic and nutritional studies have suggested that human beings evolved on a diet containing a ration of ω−6 to ω−3 fatty acids (FA) of about 1/1. However, nowadays Western diets have a ratio of 10/1 to 20–25/1, indicating that Western diets are deficient in ω−3 FA compared to the diet on which humans evolved (Simopoulos, 2011). Several decades ago, Burr and Burr (1998) demonstrated the importance of linoleic acid (LA) 18:2ω−6 and alpha-linolenic acid (ALA) 18:3ω−3 in restoring the effects caused by the fat-free diet in deprived animals. ALA and LA are important components of cell membranes. These two essential FAs are not interconvertible in the human body, are metabolically and functionally distinct, and often present important opposing physiological roles (Simopoulos, 2006). A diet rich in ω−6 FAs shifts the physiological state towards one that is prothrombotic and proaggregatory, with enhancement in blood viscosity, vasospasm, and vasoconstriction and decreases in bleeding time (Simopoulos, 2006). Deficiency of ALA is also known to increase incidence and severity of inflammatory/hyperproliferative diseases (Fan & Chapkin, 1998). Thus, a lower LA-to-ALA ratio dietary intake is necessary for the prevention and amelioration of chronic diseases. Seeds from the flax plant (*Linum usitatissimum* Linaceae) are known to be one of the richest sources of ALA (Prieto et al., 2012). Not surprisingly, flax seed consumption has been considered to help in disease prevention such as arthritis, diabetes and menopausal symptoms, besides reducing the risk of coronary heart diseases, stroke and cancer (Morris, 2007a).

The FA composition of oilseeds is usually determined by gas chromatography (GC). However, this method of analysis is destructive, time-consuming and expensive (Fassio & Cozzolino, 2004). In addition, GC requires a long time for sample preparation, derivatization, and analysis by highly-skilled personnel, besides not allowing analysis on-line (Cantarelli, Funes, Marchevsky, & Camina, 2009; Guy, Prache, Thomas, Bauchart, & Andueza, 2011; Prieto et al., 2012; Sinelli et al., 2010). Because of the demand for easy and fast analytical methods, both near infrared (NIR) and mid-infrared (MIR) spectroscopies have been considered as an interesting alternative to traditional analytical techniques, GC included (Casale, Zunin, & Cosulich, 2010; Zhang, Cheng, Liu, He, & Frost, 2011). NIR and MIR infrared spectroscopies offer a number of important advantages over methods traditionally used for chemical analysis. Infrared spectroscopy is non-destructive, rapid and can analyze large number of samples in small quantities, requiring minimal or no sample preparation. Moreover, infrared spectroscopy is less expensive, because no reagents are required, is environmentally friendly, because no waste is produced (Allendorf, Subramanian, & Rodriguez-Saona, 2011; Casale et al., 2010; Patil, Oak, Taware, & Tamhankar, 2010), and provides more information about the components present in the raw materials and formulated food products (Sundaram, Kandala, Holser, Butts, &

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Windham, 2010). Because of that, infrared spectroscopy has been used as an analytical tool to determine several constituents present in food like carbohydrates, proteins and lipids (Di Egidio et al., 2009; Sundaram et al., 2010).

There are two varieties of flax seeds used regularly in human diet: the yellow and brown flax seeds (Morris, 2007b; Pradhan, Meda, Rout, Naik, & Dalai, 2010). The fact that FA composition in flax seeds changes between varieties and also according to growth environment and seed processing (Daun, Barthet, Chornick, & Duguid, 2003) prompted us to search for a rapid, easy and less expensive analytical method, which also allowed analysis on-line, for the determination of LA and ALA in flax seeds. In this paper, we describe the development multivariate calibration models capable to predict LA and ALA contents, in yellow and brown flax seeds and flax seed flours, through the use of NIR and MIR reflectance spectroscopy.

2. Materials and methods

2.1. Materials

A total of 78 samples of flax seeds and flax seed flours were obtained from two local food-suppliers, Jasmine Limited (Curitiba, PR, Brazil) and Nutri House Foods Limited (Curitiba, PR, Brazil). The samples were divided into two groups: one group contained 12 yellow flax seed flour samples and 10 yellow flax seed samples, both from Jasmine Limited. The second group contained 14 yellow and 14 brown flax seed flour samples, and 14 yellow and 14 brown flax seed samples, all from Nutri House Foods Limited.

2.2. Lipid extraction

Total lipids were extracted by mixing 3 g of each sample with petroleum ether (Carlo Erba, Milan, Italy) for 5 h using a Soxhlet (Prodicil, Curitiba, PR, Brazil) solvent extractor, according to the American Oil Chemists' Society Official Method, Af 3–54 (AOCS, 2004).

2.3. Analysis of fatty acids

Total fatty acids (FA) were extracted and converted into their methyl ester derivatives. Briefly, 10 mg of total lipids from flax seeds and flax seed flours was dissolved in 1 mL of *n*-hexane (Mallinckrodt Chemicals, Saint Louis, MO, U.S.A.). Then, the solution was derivatized with diazomethane for approximately 120 min, according to the manufacturer's recommendation (Sigma-Aldrich Co., Saint Louis, MO, U.S.A.). The composition of the derivatized FAs was determined by gas chromatography–mass spectrometry (GC–MS) and their content was determined by gas chromatography-flame ionization detection (GC-FID), as described below.

2.4. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analysis was performed using a Varian-450 gas chromatograph combined with a Varian-320 Mass Spectrometer (Agilent Tecnologies, Oxford, U.K.) according to Yang et al. (2010), with modifications. For the gas chromatography, a CP 8944 capillary column (30.0 m × 0.25 mm × 0.25 μm) (J&W Scientific, Agilent Technologies, Santa Clara, CA, U.S.A) was used. All of the parameters used for the GC–MS runs were optimized during this study. Oven temperature program: the column was held initially at 190 °C for 1 min. Then, the temperature was increased to 200 °C, at 10 °C/min and held for 2 min at 200 °C. Afterwards, the temperature was increased to 310 °C at 3.5 °C/min. Then, the temperature was held for 1.57 min at 310 °C. The injector temperature was 315 °C. Helium was used as carrier gas at a flow rate of 0.8 mL/min and split ratio 1:50. Injection volume was 1 μL. Mass spectrometry conditions were: ionization energy at 70 eV, ion source temperature at 330 °C and mass range at 32–380 amu.

FA methyl esters were identified by their characteristic electron impact MS spectra (NIST library, National Institute of Standards and Technology, Gaithersburg, MD, U.S.A.) and retention times (R_t), which were compared with those of methyl esters of primary standards (Sigma-Aldrich Chemical Co., St. Louis, MO, U.S.A.) and Supelco™37 standard FAME Mix (Supelco Inc., Bellefonte, PA, USA).

2.5. Gas chromatography (GC)

GC analysis was performed using a Shimadzu GC 14B gas chromatography equipped with a flame ionization detector (FID) (Shimadzu Co., Kyoto, Japan) and a DB-23 capillary column (60 m × 0.25 mm × 0.25 μm) (J&W Scientific, Agilent Technologies, Santa Clara, CA, U.S.A), according to Petrović, Kezić, and Bolanča (2010), with modifications. All of the parameters used for the GC run, described below, were optimized during this study. The injector and detector temperatures were 235 and 260 °C, respectively. Inlet pressure was 250 kPa, linear gas velocity was 14.5 m/s and split ratio was 1:63. Nitrogen was used as a carrier gas at a flow rate of 0.71 mL/min, with injection volumes of 1 μL and 2 μL, respectively for flax seed flours and flax seeds FA methyl esters. Baseline separation was achieved at an oven temperature of 220 °C and running time of 11 min. FA esters were quantified in GC runs by comparison with the retention times of methyl esters of primary standards (Sigma-Aldrich Chemical Co., St. Louis, MO, U.S.A.) and Supelco™37 standard FAME Mix (Supelco Inc., Bellefonte, PA, USA). Quantification was carried out by normalization and the data obtained were converted to a percentage of the total FAs measured.

2.6. Infrared reflectance spectrometry

The reflectance spectra of yellow and brown flax seeds in the near- (NIR) and mid-infrared (MIR) range were measured on flax seeds and flax seed flours. Four gram samples were scanned, in the reflectance mode, in the 9000–4000 cm^{-1} range for the NIR spectra, while 1 gram samples were scanned, in the 4000–750 cm^{-1}, range for the MID spectra using a Tensor 37 FTIR spectrometer system (Bruker Optics, Ettlingen, Germany) equipped with an integrative sphere. OPUS software (v. 6.0 Bruker Optics, Ettlingen, Germany) was used for spectral acquisition and instrumental control. Reflectance data were recorded, at a nominal resolution of 4 cm^{-1}, accumulating 128 scans, for both NIR and MIR spectra.

2.7. Multivariate calibration

The NIR and MIR spectral data and the FAs content data were organized in matrices using the Origin Pro 8.0 software (OriginLab., Northampton, MA, U.S.A.). Principal Components Analysis (PCA) was carried out through the use of PLSR-Toolbox 3.0 (Eigenvector Research Inc., Manson, WA, U.S.A.) in MATLAB (v 7.0, The MathWorks Inc., Natick, MA, U.S.A.) software, using NIR and MIR spectral data from the whole set of samples, i.e. 38 seed samples and 40 flour samples. For both, the NIR and MIR regions, differences were found for lipid content of flour and seed samples. For the NIR region, the first Principal Component (PC1) explained 75.60% of the variation among samples. For the MIR region, the second principal component (PC2) explained 20.34% of the variation. Because of the above mentioned differences in lipid content found for flour and seed samples, we decided to develop multivariate calibration models specific for flours and seeds.

In order to optimize the calibration accuracy, different combinations of scattering corrections and mathematical pre-treatments were used to reduce systematic noise, such as baseline variation. The most effective pretreatments for the spectral data were Multiplicative Scatter Correction (MSC) plus Normalization, MSC plus Smoothing and Normalization, Standard Normal Variate (SNV) plus Detrend, and MSC plus Smoothing and First Derivate (Savitzky–Golay's method, gap size = 11 data points).

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