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Analytical Methods

Non-destructive fraud detection in rosehip oil by MIR spectroscopy and chemometrics

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ABSTRACT

Rosehip oil (*Rosa eglanteria* L.) is an important oil in the food, pharmaceutical and cosmetic industries. However, due to its high added value, it is liable to adulteration with other cheaper or lower quality oils. With this perspective, this work provides a new simple, fast and accurate methodology using mid-infrared (MIR) spectroscopy and partial least squares discriminant analysis (PLS-DA) as a means to discriminate authentic rosehip oil from adulterated rosehip oil containing soybean, corn and sunflower oils in different proportions. The model showed excellent sensitivity and specificity with 100% correct classification. Therefore, the developed methodology is a viable alternative for use in the laboratory and industry for standard quality analysis of rosehip oil since it is fast, accurate and non-destructive.

1. Introduction

Vegetable oils play an important role as raw materials in many products such as nutraceutical foods, therapeutic oils, active ingredients in medicines, components in cosmetics, and biofuels, among other applications. Rosehip oil is one of the various oils used in cosmetics and in the food industry.

Rosa rubiginosa (*Rosa eglanteria* L.), known as rosehip, is a European species of the Rosaceae family. The seeds contain a little less than 10% w/w oil, with 40.5% and 16% of linoleic and oleic acids, respectively. This oil contains significant levels of trans retinoic acid, which has regenerative properties and is therefore commonly used in cosmetics and medical clinics in order to assist in the regeneration of skin following scarring (Ercisli, 2007; Franco, Sineiro, Pinelo, & Núñez, 2007).

Rosehip oil has antibacterial, antifungal, and anti-inflammatory properties and could also inhibit cancer cell proliferation (Olsson, Gustavsson, Andersson, Nilsson, & Duan, 2004; Silva, Vandenabeele, Edwards, & Oliveira, 2008). It contains high levels of vitamin C and carotenoids (lycopene, beta-carotene, and rubixanthin) (Franco et al., 2007; Silva, Vandenabeele, Edwards, & Oliveira, 2008). The seed contains vitamins A, B1, B2, E, and K and minerals such as K, Ca, Na, Fe, and Mg. Due to this composition, rosehip oil is also preferred in the food industry for processing jams, jellies, tea, and juices (Ercisli, 2007; Gonzalez-Sarrias, Larrosa, Garcia-Conesa, Tomas-Barberan, & Espin, 2013).

In recent decades, there has been a growing interest in natural products in many different areas. This interest may not be just a fad, but rather a reflection of the growing evidence of the effectiveness and safety of natural origin products by health authorities such the World Health Organization. Due to these factors, over time, the pharmaceutical and food industries have tended to increase the integration of natural extracts in their products.

Due to the low yield of the oil extraction process and its high added value, rosehip oil is often adulterated by the addition of vegetable oil of lower economic values, such as soybean, corn, or sunflower oil. This adulteration not only represents economic fraud, but can cause harm to human health, since it changes the nutraceutical properties of the product. However, this kind of adulteration is difficult to detect, since the oils have similar physical and chemical characteristics (Cserhati, Forgacs, Deyl, & Miksik, 2005). Thus, it is necessary to develop methods to detect the adulteration of rosehip oil.

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It should be noted that authenticity is an important matter for the food, pharmaceutical and cosmetics industries due to legal compliance, economic reasons, and the effective reduction of the nutraceutical properties presented by the authentic oil (Van Ruth et al., 2010). It is important to emphasize that the effectiveness of these products depends directly on the quality of the oil used in its manufacture. For all of these reasons, the analysis of oil quality is indispensable before sale to the relevant industries (Nunes, 2014).

The American Oil Chemists' Society (AOCS) has established a number of official methods (Official Methods and Recommended Practices of the AOCS) to analyze the quality of fats and oils. Many of these methods are relatively simple, but some are time-consuming, use expensive or harmful reagents, generate waste, or may be strongly dependent on rigorously following a standardized procedure to obtain good accuracy. However, these methodology standards have been adopted by various industries and inspection agencies (Nunes, 2014).

In this perspective, there are several studies in the literature involving alternative methods for analysis of the properties of various oils. Some of them are highlighted in Table 1.

As shown in Table 1, there are several studies in the literature proposing the use of MIR spectroscopy combined with chemometric tools. The wide applicability of MIR spectroscopy is due to the fact this is a non-destructive method regarding the sample, does not require prior sample preparation, does not involve the use of toxic or expensive reagents, can produce a response in real time, is considered a rapid methodology, and is reproducible and accurate. Additionally, MIR spectroscopy lower costs compared to conventional methods such as chromatography, mass spectrometry, and nuclear magnetic resonance (NMR).

Due to these reasons, MIR spectroscopy has been widely used as an analytical tool in many quality laboratories in various industries, such as agriculture, petrochemicals, textiles, pharmaceuticals and others (Alves, Henriques, & Poppi, 2014; Balabin & Smirnov, 2011; Cozzolino, 2014).

In this sense, this work proposes an efficient and viable methodology for the detection of adulterations in rosehip oil with lower economic value oils employing MIR spectrometry coupled with a supervised classification method, i.e. partial least squares discriminant analysis (PLS-DA).

2. Experimental

2.1. Acquisition of samples

Forty samples of rosehip oil (*Rosa canina* L.) were acquired commercially in the states of Minas Gerais and São Paulo. Samples of contaminants, including soybean oil (n = 24), corn oil (n = 24), and sunflower oil (n = 24), were purchased from supermarkets in cities in the state of Minas Gerais, Brazil.

2.2. Samples preparation

In this study, we used 40 authentic rosehip oils samples of different brands. From the authentic samples, 288 adulterated samples were prepared and for each adulteration was selected a random sample, so that all authentic samples were used. The adulterants used were corn oil (n = 96), soybean oil (n = 96) and sunflower oil (n = 96) in the following proportions: 5%, 10%, 15% and 20% (w/w).

2.3. Acquisition of spectra

The Fourier-transform mid-infrared (FT-MIR) spectra were recorded using a PerkinElmer Spectrum Two spectrometer equipped with a sampler device using horizontal attenuated total reflectance (HATR) containing a ZnSe crystal and detector deuterated triglycine sulfate (DTGS) in the range of 4000–600 cm^{-1}, with a resolution of 4 cm^{-1}, over 16 scans and repeated in quintuplicate. Between each spectrum, the horizontal ATR was cleaned with isopropyl alcohol and cotton (QUIMEX purity PA). Cleanliness was monitored using PerkinElmer Spectrum Software version 3.10 software with every insertion of a new sample. The baselines of the spectra were processed using the baseline algorithm available in SOLO 7.8 (Eigenvector Research). The initial data matrix consisted of 328 spectra with 2401 variables per spectrum.

2.4. MIR spectral pre-processing

Pre-processing techniques were essential in the multivariate analyses. The aim of preprocessing is to make the data suitable for statistical analysis by removing the extraneous sources of variation which are not related to the sample information. Usually, these sources of variance can increase the difficulty in modeling (Pielesz & Wesełucha-Birczyńska, 2000).

Different data pre-processing methods were tested in order to choose the one that provided the best model development using the PLS-DA algorithm. The tested pre-processing methods were: mean centering, standard normal variate (SNV), first derivative (Savitzky-Golay), mean centering and SNV, SNV and mean centering, mean centering and Savitzky-Golay, Savitzky-Golay and mean centering, Savitzky-Golay and SNV, and SNV and Savitzky-Golay. For this model, the best data pre-processing method was SNV and mean centering.

2.5. Data analysis

For the construction of the PLS-DA classification models, MATLAB R2007b (Mathworks Inc.) and SOLO 7.8 (Eigenvector Research) software were used. Before the construction of the models, two thirds of the samples from each group were randomly selected for the training set and the remaining samples were used

Table 1
Studies employing alternative techniques in the analysis of vegetable oils.

Techniques	References
UV–vis	Casale et al. (2012), Makky and Soni (2014), Luna, Silva, Pinho, Ferre, and Boque (2013)
MIR	Casale et al. (2012), Silva, Vandenabeele, Edwards, and Oliveira (2008), Tankeu, Vermaak, Kamatou, and Viljoen (2014), Rohman and Che Man (2011), Rohman, Riyanto, Sasi, and Yusof (2014), Wu, Sun, Zhou, and Leung (2008), Luna, Silva, Pinho, Ferre, and Boque (2013)
NIR	Javidnia, Parish, Karimi, and Hemmateenejad (2013), Casale et al. (2012), Silva, Vandenabeele, Edwards, and Oliveira (2008), Tankeu et al. (2014), Makky and Soni (2014), Luna, Silva, Pinho, Ferre, and Boque (2013), Wu et al. (2008)
Raman	Zahir, Saeed, Hameed, and Yousuf (2014)
Electrochemical	Apetrei (2012), Tormin, Cunha, Richter, and Munoz (2012)
HPLC	Salghi, Armbruster, and Schwack (2014)
Mass spectrometry	Alves, Borges Neto, Mitsutake, Alves, and Augusti (2010)
Fluorimetry	Silva, Filardi, Pepe, Chaves, and Santos (2015)