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Monte Carlo simulation based prediction of blended oil composition containing mustard, rapeseed and soybean oil

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ABSTRACT

High erucic acid rapeseed and mustard seed (HEARM) oils are popular cooking oil in various southeast Asian countries (e.g. Nepal, India, Bangladesh) due to the preference of the local consumer for its strong pungency. Low erucic acid rapeseed (LEAR) oil having lower pungency is frequently mixed with the pungent HEARM oil to increase its sensory appeal to the local consumer. Moreover, these oils are also prone to be adulterated with the cheaper oil available in the local market like soybean oil for economical reasons. In order to detect this fraud in a quick and easy manner, a Monte Carlo simulation based approach was developed for the estimation of blend composition using only the fatty acid composition of the sample. The limits of detection (LODs) of soybean oil in HEARM oil and LEAR oil were 14% and 13%, respectively. The LODs of LEAR oil in HEARM oil and soybean oil were 11 and 9%, respectively. Similarly, the LODs of HEARM oil in LEAR oil and soybean oil were 9% and 3%, respectively. The prediction from the developed method was evaluated both in real oil blends (prepared in the laboratory) and in theoretically simulated blends. The method was applied on forty-nine samples (labeled as mustard/rapeseed oil) collected from the Nepalese market. Among them, twenty-seven samples were found to be adulterated with soybean oil. The predicted adulteration was further supported by their δ-tocopherol content and *trans* fatty acid content, as an indicator for the adulteration with refined oil. The developed Monte Carlo simulation method is based on a single analytical run of determining the fatty acid composition of the suspected oil blend and thus useful for a quick segregation of samples in routine analysis.

1. Introduction

Mustard and rapeseed are close relatives, belonging to the genus *Brassica*. The traditional varieties of rapeseed (*Brassica campestris*) and mustard (*Brassica juncea*) are widely grown in Bangladesh, India, Nepal and other southeast Asian countries. The oil from these varieties contains high amounts of erucic acid (Mortuza, Dutta, & Das, 2006; Przybylski, Mag, Eskin, & McDonald, 2005). Hereafter, these traditional varieties will be grouped together as high erucic acid rapeseed and mustard (HEARM) varieties. Various low erucic acid rapeseed (LEAR) varieties (e.g. *Brassica napus*) have been developed by breeding practices. Among them, canola is the most well-known variety and is widely produced in the world. The canola type low erucic variety grown in Europe is simply called rapeseed (Shahidi, 1990).

Based on the latest Food and Agriculture Organization (FAO) statistics, Nepal is the largest producer of mustard seed in the world (FAO, 2011). In the Indian subcontinent including Nepal, undeodorized crude oil from HEARM variety is one of the most popular oil and is widely used as a liquid cooking oil because of the high preference of the local consumer for its strong pungency. On the other hand, the oil from LEAR varieties does not have a strong flavor and taste like that from HEARM varieties, and thus cannot compete in the local market (Przybylski et al., 2005). Although the prices of HEARM and LEAR oils are comparable, there is an increasing tendency to mix LEAR oil with some HEARM oil, so as to increase its pungency and hence consumer acceptance (Przybylski et al., 2005). Such a practice would contaminate LEAR oil with erucic acid. Blending of any edible oil can be considered as fraudulent activity, unless both the qualitative and quantitative information are properly communicated in the label. In addition, adulteration with cheaper and easily available oil (for economical reason) has been an ever increasing problem on the Nepalese market. Soybean oil is one of the cheapest and most widely available in the local market and hence, has been frequently used as an adulterant. Other common vegetable oils like sunflower oil and corn oil have a market price comparable to the mustard/rapeseed oil and hence, are not commonly used for adulteration. The Department of Food Technology and Quality Control (Government of Nepal) has frequently observed the adulteration of mustard seed oil with soybean oil during industry inspection (Himalayan News service, 2011). Therefore, there is an immediate necessity for a simple and rapid method for the estimation of blended oil composition containing HEARM oil, LEAR oil and soybean oil.

Abbreviations: HEARM, high erucic acid rapeseed and mustard; LEAR, low erucic acid rapeseed; CDA, canonical discriminant analysis; LOD, limit of detection; TAG, triacylglycerides; FA, fatty acid.

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The estimation of the concentration of an individual oil in a blend is typically carried out by applying chemometric approaches based on analytical data. The impossibility of physical separation of the individual oils from the blended oil creates complication on the accurate estimation (van Vliet, van Kempen, Reinders, & de Ridder, 2005). Various methods were used in the past for discrimination of different oils and for estimation of oil adulteration. The linear discriminant analysis along with the back propagation artificial neural network method was studied to authenticate Italian extra virgin olive oil varieties (Marini et al., 2004). Furthermore, the counter propagation neural network method was found to be useful for the classification of different vegetable oils on the basis of the fatty acid composition (Brodnjak-Voncina, Kodba, & Novic, 2005). However, it remained confined to the classification and it did not allow the estimation of the oil blend composition. Afterwards, van Vliet et al. (2005) introduced the strategies that could be adopted for the qualitative and quantitative estimations of oil blend composition. In addition, the study on the use of an electronic nose for the detection of maize oil adulteration in camellia seed oil and sesame oil was carried out later. This study showed that linear discriminant analysis was more effective than principal component analysis (PCA) in adulterant discrimination (Hai & Wang, 2006). A recent study on the adulteration of extra virgin olive oil with other oils has used the partial least squares (PLS) method for multivariate calibration based on Fourier transform infrared spectroscopy (FTIR) (Maggio, Cerretani, Chiavaro, Kaufman, & Bendini, 2010). In another study, dielectric spectroscopy data has been used to predict the adulteration of olive oil applying the PLS method (Lizhi, Toyoda, & Ihara, 2010). Recently, blend prediction of sunflower and olive oils using different chemometric tools based on fatty acid data has also been described (Monfreda, Gobbi, & Grippa, 2012).

The development of a method for the estimation of blend composition of oil containing HEARM, LEAR and soybean oils was not previously described. Therefore, such method has been developed in this study by applying a Monte Carlo simulation approach using the fatty acid composition data. The simulation method is based on the universal mass balance principle. The developed method was applied to samples collected from the Nepalese market to evaluate the current adulteration status.

2. Materials and methods

2.1. Samples and chemicals

Forty nine oil samples of different brands (labeled as mustard/rapeseed) were collected from the Nepalese market. The samples were stored under freezing conditions below −18 °C until analysis. The seeds of five HEARM varieties and one LEAR variety were also collected from the Nepalese market.

Fatty acid standard (GLC 68D) was obtained from Nu-Check Prep. Inc. (USA). The *cis*/*trans*-isomers of linoleic acid methyl esters were obtained from Sigma Aldrich (Steinheim, Germany). Nonadecanoic acid (99.5 +%) was purchased from Fluka (Switzerland). Iso-octane (99.5 +%), methanol (99.8 +%), sodium sulfate (99 +%), sodium hydroxide (99 +%) and sodium chloride (99 +%) were obtained from Chem-lab (Belgium). Boron trifluoride in methanol reagent, isopropanol (99.9%) and a standard Calbiochem tocopherol set were supplied by Merck (Germany). HPLC grade hexane was purchased from Fischer Scientific (Belgium). Other chemicals and reagents were of analytical grade obtained from reliable commercial sources.

2.2. Analytical methods

2.2.1. Fatty acid analysis

The grounded seed powder (5 g) was homogenized with 40 ml chloroform/methanol (2/1, v/v) (containing 100 mg of internal standard (nonadecanoic acid) and 3 mg of butylated hydroxytoluene) using an ultra turrax homogenizer. After overnight standing in the dark, the mixture was filtered and washed with 20 ml of same solvent mixture. Afterwards, the filtrate was homogenized with 15 ml of acidified water (pH 2), and the resulting homogenate was centrifuged. The lower layer was evaporated to obtain the lipid fraction.

The boron trifluoride method was used for the preparation of fatty acid methyl esters (FAMEs) (AOCS, 1990). For the oil samples, 5 mg of internal standard was added to 50 mg of oil. Afterwards, transesterification to FAMEs was carried out applying the same procedure. FAMEs were analyzed on a gas chromatograph using the method described previously (Shrestha, Gemechu, & De Meulenaer, 2013).

2.2.2. Tocopherol analysis

Tocopherol content of the oil sample was analyzed on an Agilent 1100 series HPLC (USA) using a fluorescence detector as described previously (Shrestha, Stevens, & De Meulenaer, 2012).

2.2.3. Peroxide value

The peroxide value (PV) was determined using an iron based spectrophotometric method (Shantha & Decker, 1994). Calibration curve was constructed using a standard iron (III) chloride solution as described in the same method. Calibration was done using six concentrations in duplicate in the range of 5 to 30 μg of iron (III). The multiple R-squared value was more than 0.99 for the calibration. Such calibration curve was constructed just before the measurement of the peroxide value of the sample, each day.

2.3. Monte Carlo simulation and statistical analysis

The canonical discriminant analysis (CDA) and Pearson's correlation were calculated using Spotfire S + 8.1 software (TIBCO software Inc.). Normality of the data was accessed using the quantile–quantile plot and Kolmogorov–Smirnov test using the same software. Monte Carlo simulation was carried out using @Risk for Excel software (version 5.7.1, Palisade Corporation). The simulation settings were as follows: 100,000 iterations using Latin hypercube sampling type with a mersenne twister generator applying random initial sampling speed. The simulated fatty acid compositions were used as @Risk inputs and calculations were based on mass balance equations. The details of such simulations have been shown in Fig. 1 and the stepwise development of such simulation has been described below (Section 3.1).

3. Results and discussion

3.1. Development of a Monte Carlo simulation based method for the prediction of blend composition

The schematic representation of the different steps followed during the development of a Monte Carlo simulation based method for the prediction of blend composition has been shown in Fig. 1. The method development part (step 1 to 6) will be discussed in this section.

At first, fatty acid composition databases were prepared (step 1 of Fig. 1). Table S1 (in Supplementary data) demonstrates the sixty-four sources of information collected to set-up the fatty acid composition database. The fatty acid compositions of HEARM varieties (*B. juncea* and *B. campestris*) obtained from neighboring countries like India and Bangladesh were collected from literature data, as no data from Nepal could be obtained from literature. Seed samples collected from the Nepalese market were additionally analyzed for their fatty acid composition and added to the database (Table S1). The fatty acid composition data of LEAR varieties (*B. napus*) and soybean oil were also collected from the literature (Table S1). The fatty acid compositions of low erucic acid rapeseed collected from the Nepalese market and the soybean oil available on the Belgian market were analyzed and also added to the database. In addition, the maximum, minimum and mean values of fatty