Talanta 144 (2015) 363–368

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Spectroscopic determination of the photodegradation of monovarietal extra virgin olive oils and their binary mixtures through intelligent systems

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ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form
11 June 2015
Accepted 17 June 2015
Available online 24 June 2015

Keywords:
Extra virgin olive oil
Chlorophyll
Carotenoids
Pigments
Spectroscopy
Artificial neural networks

ABSTRACT

A common phenomenon that takes place in bottled extra virgin olive oil (EVOO) is the photooxidation of its pigments, especially chlorophyll, which acts as a singlet-oxygen sensitizer. This translates into a severe decrease of quality, potentially leading to oxidized and rancid olive oils by the time they reach to the consumers. In this current research, the photochemical degradation has been monitored for 45 days in binary mixtures of four monovarietal EVOOs (Arbequina, Hojiblanca, Cornicabra, and Picual) through UV–Visible spectroscopy. A multilayer perceptron-based model was optimized to estimate the photodegradation suffered by the samples, in terms of photodegradation time, relying on the spectroscopic information gathered and attaining an error rate of 2.43 days (5.3%) in the determination of this parameter.

1. Introduction

Extra virgin olive oil (EVOO) is one of the key components of the Mediterranean diet [1,2], and it presents a series of traits that make it beneficial for health due to its characteristic composition [1,3], which is typically divided into two main fractions: the saponifiable fraction (comprising 98–99% of the weight of EVOO) and the non-saponifiable fraction (containing the remaining 1–2%) [1]. The first one consists of triglycerides, diglycerides, monoglycerides, and free fatty acids, while the non-saponifiable fraction is formed by minor components, such as pigments, volatile compounds, polyphenols, tocopherols, and sterols [1,3]. It is important to remark the role of the pigments, particularly chlorophylls and carotenes, which provide its characteristic color to EVOO [2,4]. Additionally, they have been found to be somewhat more than colorful molecules, as pigments have shown a relation with the mitigation of the effects of certain degenerative diseases, as well as possessing anticarcinogenic and antimutagenic qualities [5,6].

Moreover, pigments play an essential part in the oxidation and degradation of EVOO due to the effect of both light and temperature [5,6]. In the case of chlorophylls, the demetalation and loss of the magnesium atom in the center of the tetrapyrrole macrocycle is the first step of its degradation mechanism, and transforms these molecules into pheophytins (Fig. 1) [7]. Although this first stage does not involve any change of color, there is a light-favored pathway that leads to the photolytic cleavage of the chromophore of pheophytin through its photooxidation, generating a colorless molecule as a product [6].

It has been observed that chlorophyll pigments act as photosensitizers as they can transfer energy from electromagnetic radiation to triplet oxygen, thus producing singlet oxygen, a highly oxidative species [8], which would eventually react with the unsaturated fatty acids of EVOO, degrading the oil and lowering its quality [8].

On the contrary, carotenoids (which are mainly represented in EVOO by lutein and β-carotene, Fig. 2) have a remarkable antioxidant activity, protecting the oil against photooxidation by acting as singlet oxygen-quenchers and light filters [5,6,9].

Although the pigment-related compounds are the major responsible molecules of the photooxidation process that takes place in EVOO, the loss of organoleptic characteristics and quality affects the whole product. Therefore, it is crucial during bottling, packaging, transportation, and storage to limit the exposure of the EVOO to light and changes in temperature to ensure that the initial high quality bottled oil reaches the consumer in these same (or almost same) conditions [10].

As the EVOO photodegradation process leads to a cascade of

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http://dx.doi.org/10.1016/j.talanta.2015.06.042
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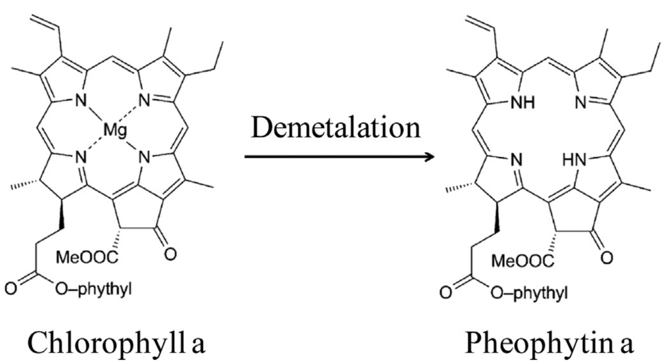

Fig. 1. Demetalation of the chlorophyll molecule (pheophytinization).

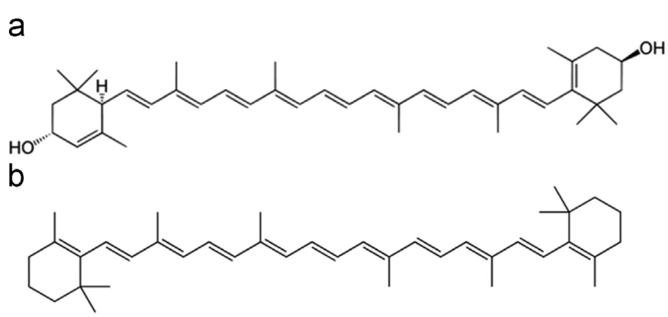

Fig. 2. Chemical 2D structure of lutein (a) and β-carotene (b).

physicochemical changes that affect the chromophore molecules, it can be supervised and registered by optical techniques. More specifically, these modifications could be detected through UV–Visible absorption spectroscopy, as the monitored compounds are active in this area of the electromagnetic spectrum. In fact, several methods that rely on this technique to control the degradation of EVOO have been already reported: the determination of the thermal degradation of olive oil [11], the analysis of the compositional changes that take place during the storage of EVOO [10], the study of the kinetics that govern the thermal degradation of the pigments in olive oil [6], or even the objective authentication of monovarietal EVOOs [12]; thus showing that the employment of this spectroscopic technique is useful to determine compositional and quality-related changes in EVOO over time due to the degradation of its pigments.

On the other hand, using UV–Visible absorption spectroscopy provides a relevant amount of data points, making necessary the use of mathematical and statistical procedures to process and adequate the data, such as principal components analysis (PCA), linear discriminant analysis (LDA), or soft independent modeling of class analogy (SIMCA) [13–15]. Nevertheless, sometimes these linear procedures do not offer the expected results and more sophisticated models are required. One of these advanced mathematical tools are artificial neural networks (ANNs), non-linear models which can determine relationships between independent and dependent variables within databases through non-linear interpolation [16]. They have been already employed in the study of olive oil and the olive sector, offering accurate estimations [17,18].

As the EVOO is photodegraded, it loses its organoleptic characteristics as well as quality grade, so the product that is provided to the consumers may not possess the initial nutritional nor healthy effects mentioned before if the product is not handled adequately. Therefore, the goal of this work is to offer a user-friendly and straightforward procedure to estimate the photodegradation time of four monovarietal EVOOs (Arbequina, Hojiblanca, Cornicabra, and Picual) and their binary mixtures by measuring their UV–vis absorption spectra and using ANNs to carry out the data treatment, providing a tool that is able to evaluate whether the product has been satisfactorily treated during distribution or not.

2. Materials and methods

In the following subsection, the samples considered, the preparation steps applied, the analytical procedures followed, and the mathematical tools employed are described.

2.1. Sample preparation

Four monovarietal EVOOs have been used to prepare the samples analyzed: Arbequina, Hojiblanca, Cornicabra, and Picual, all of which are within their expiration date, and stored in the dark at room temperature. A total of 22 samples were prepared: four of them corresponding to the single monovarietal EVOOs, and the rest, to binary mixtures of 25%, 50%, and 75% (v/v), leading to six samples for each possible mixture of olive oils. Once prepared, the samples were exposed to indirect sunlight for a total of 45 days.

2.2. UV–vis absorption measurements

The samples and a reference (stored in the dark) were daily measured five times per week (Monday through Friday) for a period of 45 days, in order to monitor the changes experimented by the pigment profile due to the presence of sunlight, thus evaluating the extent of the photodegradation suffered by the different pigments of the samples of EVOO. A total of 30 data points per sample were obtained.

The absorption spectra of the samples were collected between 350 and 800 nm using a UV–vis spectrophotometer (Varian Cary 50 Conc). The samples were introduced in a quartz cuvette of 1 cm path length and the samples were analyzed three times in order to obtain an averaged spectrum of each one. This led to spectra containing one absorption value per wavelength, which originates 450 potential variables.

The first phase of the mathematical treatment of the spectra was reducing the dimensionality of the system. This approach enables the elimination of redundant and/or non-informative variables (absorbance–wavelength pairs). In the case considered, the calculation of the areas under the curve (AUCs) of the different absorption bands observed was the procedure selected to both reduce the number of independent variables and extract the useful spectroscopic information from the bands, as a combination of AUCs might contain more information than absorption peaks at discrete wavelengths [19].

The mathematical treatment of the data was performed with OriginPro 8.0 and Matlab 2013 software packages.

2.3. Database

The final database contains a total of 658 spectra (after discarding two defective measurements which qualified as outliers in the preliminary analysis), corresponding to the measurement of the different mixtures of EVOO over time. The information gathered within the database possesses compositional, spectroscopic, and chronological data regarding the different samples analyzed.

2.4. Artificial neural networks

ANNs were the selected mathematical tool to assist in the estimation of the degradation time of the samples. These algorithms are able to determine non-linear relations between dependent and independent variables within databases through non-linear