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A new cost-effective approach for lavender essential oils quality assessment

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ABSTRACT

The existing methods used to evaluate the lavender oils quality, is related generally to the percentage abundance of the specific compounds (linalool, linalyl acetate). The strict monitoring of these products was considered mandatory, for all involved counterparts (producers, consumers, and control authorities). A new reliable approach for the quality of lavender oils assessment is presented in this work. For this purpose, 31 volatile organic compounds were quantified using GC/MS system in 32 lavender oil samples, purchased from local stores and autochthon producers. Cluster analysis split the samples set in two main clusters based on volatile components. These results combined with those obtained by applying linear discriminant analysis allowed the identification of four commercial samples which were adulterated by addition of lower quality oil. The quality grades for every product were achieved applying the new developed algorithm, using the correlation between two calculated indicators: percentage abundance of the linalool and linalyl acetate and sum of all volatile organic compounds peak areas. The new algorithm, confirmed with chemometric models, allowed the classification of lavender oils as high, medium or low quality, without using the time consuming and expensive techniques such as quantitative analysis. The new developed approach presented also a very good correlation with quantitative analysis in terms of linalool. Therefore, the proposed model, constitute a robust, economical and fast method for quality determination of lavender oils and offer the possibility to be extended to other essential oils.

1. Introduction

Essential oils are complex matrices, having a wide range of applications and containing more than 100 compounds, which need to be analyzed by different techniques in order to ensure quality control, consumer safety and fair trade (Lafhal et al., 2016; Xiao et al., 2017). Lavender (*Lavandula angustifolia* L.) oil has a great industrial significance with multiple applications in: cosmetics, perfumes, skin lotions, soaps (Bombarda et al., 2008; Dušková et al., 2016; Won et al., 2009), and also in aromatherapy as a relaxant (Ali et al., 2015; Nasiri and Mahmodi, 2018; Rafie et al., 2016). In the food industry these products are used as a natural flavouring for beverages, ice cream, candy, etc. (Calvo-Irabien, 2018; Da Porto et al., 2009; Özogul et al., 2017; Pistelli et al., 2017), especially nowadays when the consumers interest in high quality natural products is in an ongoing increase. Moreover, several therapeutic effects of lavender oil have been recently reported: sedative, relaxant, antioxidant, anti-depressive, anti-inflammatory, anticonvulsive, antiviral and antibacterial activities as well as for gastrointestinal, nervous and rheumatic disorders (Cavanagh and Wilkinson, 2002; Danh et al., 2012; Hassiotis et al., 2010, 2014; Jalali-Heravi et al., 2015).

In the oil industry the quality is extremely important from several points of view, i.e. the classification and labelling of essential oils, identification of adulterated products with essential oil from one cheaper hybrid, diluted oils labelled as being a higher-quality. The most common form of adulteration, widely observed among the producers, is made by mixing lavender authentic essential oils with those obtained from cheaper variety of lavandin (*Lavandula x Intermedia)*. Lavandin oil is considered to have a lower quality in part due to its relatively higher camphor content (Renaud et al., 2001). Considering the price of lavender essential oil, which is approximately 6–7 time higher than lavandin oil, and the lack of regulation in this industry, the attempts to adulterate these products are increasingly higher (Beale et al., 2017; Do et al., 2015).

The quality of the oil produced from lavender depends on many factors (i.e. soil, climatic conditions, harvesting, and oil production condition) and is characterised by high levels of linalool and linalyl acetate and very low to moderate amount of 1,8-cineole and camphor (Kara and Baydar, 2013; Shellie et al., 2002). The composition and the variability of volatile organic compounds (per cent) in essential oils, are very important regarding quality, and are analyzed by gas chromatography coupled with mass spectrometry (GC/MS). One of the best

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methods for quality assessment is the quantitative analysis which gives the precise concentration of every component present in the oil matrix. Unfortunately, this approach has some important drawbacks (De Godoy et al., 2011) mainly concerning the high cost of pure reference standards. Other weak points are the time consuming processes like construction of calibration curve with at least six different concentrations for each compound, set up the experiments and the results evaluation.

From our point of view, the quality of an essential oil is given not only by the percentage abundance of the specific compounds (linalool, linalyl acetate, camphor, 1,8 cineole), but also by the concentration of the entire product. A low concentration of the total volatile organic compounds would suggest either a dilution of lavender oil or a low quality product. In this context, for quality evaluation, is not enough to have only a simple GC/MS analysis and to calculate the percentage abundance of the compounds, like majority of the producer and testing laboratories do, but some complementary parameters should be used.

A method using mid infrared (MIR) and near infrared (NIR) spectroscopy in tandem with chemometric data analysis for quality control of lavender oil was reported by Tankeu et al. (2014). Their model was able to predict six major compounds for lavender oil samples, having a great contribution in this field.

In the context presented above, this study proposes a new algorithm, able to qualify oils from high to low quality grade, and to serve as routine quality control test for lavender oils. This new predictive model, for quality determination, is based on a combination of four factors: i) accurate determination of oil composition (percentage abundance of each constituent) by GC/MS; ii) the concentration of the oil, calculated by the amount of all peak areas of volatile organic compounds determined by GC/MS; iii) building a quality scale through correlation between the percentage abundance of each specific compound with concentration of the oil to establish a grade for each product (from one to ten); iv) chemometric models and quantitative analysis to demonstrate the suitability of the scale to assess the lavender oil quality.

2. Materials and methods

2.1. Essential oil samples

Twenty two lavender oil samples (AS1 – AS22) were collected from various Romanian local producers from Transylvania area. Additional eight samples (CS1–CS8) were purchased from local stores, representing the main commercial oils present in Romanian market. According to their label, all the oil samples used in this study were obtained from the flowers of *Lavandula angustifolia* through steam distillation. Another two essential oil samples (L1, L2) obtained from Lavandin flowers (*Lavandula x Intermedia)* were also collected from local producers, as control samples, in order to establish the possibility of oil adulteration. All the samples were diluted in hexane (0.01%) and stored at 4 °C prior to GC/MS analysis.

2.2. Chemicals

High purity reference standards of alpha-pinene, camphene, beta-pinene, limonene, gamma-terpinene, linalool, borneol, alpha-terpineol, were purchased from Ultra Scientific (North Kingstown, RI, USA). Hexane (HPLC grade) was supplied from Sigma-Aldrich (Saint Louis, MO, USA).

2.3. Gas chromatography–mass spectrometry analysis

GC/MS analyses were performed on a Trace GC Ultra gas chromatograph from Thermo Scientific (Bremen, Germany) coupled with Thermo Electron Polaris Q mass spectrometer. The separation of volatile organic compounds was performed using a DB-5MS (30 m x 0.25 mm ID, 0.25 μm film thickness) capillary column (5% diphenyl, 95% dimethylpolysiloxane). The injection volume of each oil sample was 2 μL. The oven temperature program was: 40 °C for 3 min, increased from 40 to 300 °C with 10 °C min^{-1}, and kept at 300 °C for 10 min. The injector and transfer line were 250 °C, and 300 °C, respectively. The carrier gas was helium with a flow rate of 1.5 mL min^{-1}.

The volatile constituents of the samples were identified and confirmed based on three different approaches: i) the comparison of their retention times (RT) with those of pure reference standards; ii) linear retention indices (LRIs) determined relatively to a series of n-alkanes (C8–C20) and iii) by comparison of the mass spectra with those available in the commercial libraries (NIST 2011). Calibration curves for the used reference standards of alpha-pinene, camphene, beta-pinene, limonene, gamma-terpinene, linalool, borneol, alpha-terpineol were realized by plotting peak area versus analyte concentration (0.625, 1.25, 2.5, 5, 10, and 20 μg mL^{-1}). The linear regression equations were calculated with $y = ax \pm b$, were x was concentration and y was the peak area of each analyzed compound. The obtained calibration curves and the correlation coefficients (R^2) for analyzed compounds were presented in Figure S1 (Supplementary Data). Instrumental precision was determined on the same day with two different concentrations (0.625 and 20 μg mL^{-1}) (six replicate injections each) and by repeated injections for four different days. All the results (RSD%) obtained for the retention times and for the peak areas have been summarized in Table S1 (Supplementary Data).

The linear retention indices (LRIs) were calculated using Van den Dool and Kratz's equation and compared with those reported in the literature (Da Porto et al., 2009; Hassiotis et al., 2014; Méndez-Tovar et al., 2016; Pistelli et al., 2017; Shellie et al., 2002).

2.4. Statistical analysis

Chemometric models were applied in order to check the samples authenticity (according to their labels) and to demonstrate the suitability of the proposed algorithm to quality oil evaluation. Analytical data were processed using SPSS Statistics version 24 (IBM, USA). The results obtained using GC/MS analytical technique, meaning 31 volatile organic compounds, analyzed in 30 lavender oil samples and two lavandin oil samples, represented the matrix used for further chemometric interpretation. The first method which was applied to this matrix was cluster analysis, which is an unsupervised method used for samples or descriptors grouping, based on similar characteristics within the same group, and different characteristic between distinct groups. In this specific case, cluster analysis was applied using Ward method as a clustering procedure with Euclidian distance as a similarity measure. Another powerful classification method is represented by linear discriminant analysis (LDA). Comparing with cluster analysis, this supervised method aims to provide a classification model, which comprises linear combination of significant descriptors (measured variables), which should be able to maximize the variance between groups (previously defined), and minimize the variance within one specific group. The validation of obtained model is assessed by "leave-one out procedure", which tests each sample as a new one. The higher percent obtained in this step, the stronger the model is.

2.5. Quantitative analysis

Quantitative analysis of linalool was performed in order to demonstrate the suitability of the proposed model in lavender essential oil quality assessment, and to verify the correct distribution of the samples on the quality scale. For this approach three samples were selected, with similar percentage of linalool content, one from each quality group: AS12 from high quality group (23.80% linalool), AS14 from medium quality group (23.77% linalool) and AS21 from low quality group (26.55% linalool). Stock solution (400 μg mL^{-1}) of linalool was prepared in n-hexane. The working solution was successively diluted to obtain the appropriate concentrations: 0.625, 1.25, 2.5, 5, 10, and 20 μg