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Authenticity of olive oil: Mapping and comparing official methods and promising alternatives

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ABSTRACT

Trade standards are continuously updated to give plausible solutions to situations created by fraudsters who apply the most sophisticated procedures to their objectives of olive oil adulteration. Clustered inside targeted and profiling approaches, methods based on spectroscopic, isotopic and chromatographic techniques are reviewed. Chromatographic methods, most of them being official methods, compete with newer methods based on spectroscopic, isotopic and trace element techniques for ensuring that the pace of research in the detection of malpractices is rapid enough.

The speed of the analyses, the need of statistical interpretation of the results, the quality parameters of the methods, limit of detection of the adulterants, and the applicability range among others are on the basis for the absolute and comparative analyses of the most known methods, which results are unpacked in the paper. The new frontiers of research in the field of olive oil authenticity are also dissected together with the challenges for the near future.

The extensive and deep analysis of the methods for quantifying the chemical compounds responsible for olive oil authenticity will contribute to a better comprehension of the complex analytical world of olive oil for the analyst working with this food product for the first time, as well as for experienced professionals.

1. Introduction

The high price of olive oil and its reputation as a healthy and delectable oil makes it a preferred target for fraudsters. Thus, adulteration may take place not only by accidental contamination during the stages of oil processing but even more often by deliberate mislabeling of less expensive olive oil categories or by the addition of less expensive edible oils to virgin olive oil for the purpose of financial gain.

Numerous adulterants have been found in virgin olive oil, and they vary from refined olive oil, deodorized virgin olive oils, raw olive-pomace oil and synthetic olive oil–glycerol mixtures to almost all seed oils (e.g. maize, cottonseed, hazelnut, rapeseed and sunflower). In fact, the admixtures of expensive olive oils with less expensive and lower-grade oils have been traditionally more than a potential problem in countries that manufacture seed oils and import olive oils. This procedure is harmful for new consumers who buy olive oil for its health benefits and strict purity control and are surprised receiving oil that does not fulfill their expectations (García-González, Aparicio-Ruiz, & Aparicio, 2009).

Several international institutions (e.g. International Olive Council – IOC – and Antifraud Unit of the European Union – OLAF – among others) are actively involved in anti-fraud regulations, which are focused on tighter control of producing and importing countries, clear definitions for olive oil products, uniform labeling regulations, and rapid, easy and accurate instrumental techniques and analytical methodologies. The final objective is to avoid any image of a hypothetical uncontrolled distribution of adulterated olive oil into the market and to ensure fair trade as well as the safety and consumer protection.

Advances in knowledge and technology, which have been needed in the detection of malpractices by fraudsters, have required a considerable investment although no rapid and universal method has been officially recognized for all the authenticity issues yet; e.g. adulteration, mislabeling, and misleading among others.

At this point, the most accepted definition for the genuineness of a food product is: "A product is authentic as long as it is firstly described accurately by the label and secondly complies with the current legislation in force in the country where it is marketed or sold" (Lees, 1998). An authentic food is, in consequence, one which is truly derived from a specified source where the term source must be clearly defined (e.g. a particular category of olive oil). The ample number of olive oil categories, which are clearly defined by current regulations (EC, 2013; IOC, 2011), and the numerous edible oils that can be used in adulterations require of a plethora of analytical techniques and methods for carrying out a strict olive oil authenticity control.

This work is not a systematic revision of methods and instrumentation used in the authenticity of olive oil. There are several interesting works already published for this purpose (Aparicio & Aparicio-Ruiz,

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2000; Aparicio, Aparicio-Ruiz, & García-González, 2007; Aparicio, Conte, & Fiebig, 2013; Aparicio et al., 1998; Ben-Ayed, Kamoun-Grati, & Rebai, 2013; Dais & Hatzakis, 2013; Frankel, 2010; García-González, Baeten, Fernández-Piernas, & Tena, 2013). In contrast to these reviews, this work presents an extensive and deep analysis of the most relevant compounds used as targeted analytes for virgin olive oil characterization and authentication, the analytical problems derived from their determination by targeted and profiling methods, and a critical approach of their utility today, and future trends.

2. Discussion

2.1. Official standards and promising alternatives: the state-of-the-art

Three are the different ordinances and legal sources that have traditionally ruled olive oil production and international trading although there are also regulations in force in some producer states (e.g. Australia, California). IOC trade standards have traditionally helped to design and improve the other ordinances with which it shares much more than 90%. Particular regulations exist within the European Union (EU) to control its olive oil market which represents 72% of the world production. As olive oils are subjected to worldwide trade, a further level of regulation is needed, and this is provided by the Codex Alimentarius Commission. EU regulations are in force for EU countries while IOC trade standards and Codex standards are agreements that signatory countries voluntarily have accepted to comply. They establish the limits for each quality and purity criterion, including the precision values of the applied methods, although IOC trade standards are more specific than the Codex Alimentarius standards in, for instance, the labeling aspects (IOC, 2011).

Today, most of the methods refer to ISO (International Standardization Organization) methods although some still refer to AOCS (American Oils Chemists' Society) methods. In fact, IOC is an official Liaison-Member of ISO/TC 34/SC 11 – Animal and vegetable fats and oils, which is a Subcommittee of ISO/TC-34 – Food products. Based on this relationship, IOC methods, which were developed for olive oil trade standards, have been able to be compared with already checked ISO methods that were developed for a wide number of fats and oils; sometimes, however, the peculiar characteristics of olive oils have allowed some IOC particular methods to be accepted as ISO norms. The consequence is that the IOC methods are applied worldwide for the analytical control of olive oils though alternative methods fostered by other associations should be taken into account as well; i.e. AOAC International, Federation of Oil Seeds and Fats Association (FOSFA) and International Union of Pure and Applied Chemistry (IUPAC).

In those days when the adulteration was very simple, the detection of adulterants was relatively easier than nowadays. The fraudulent practices, however, became more complex and ingenious as technology advanced and it was widely accessible to everybody. In the objective of determining chemical compounds that can be markers for olive oil authenticity, many modern techniques have been proposed by researchers and technologists. Thus, they have proposed methods based on gas, liquid, gas–liquid, quiral, silver-ion, mass, and supercritical fluid chromatographies, stable carbon isotope ratio analysis (SCIRA), excitation–emission fluorescence (EEFS) and total synchronous fluorescence (TSyF), pyrolysis–mass spectrometry (PyM), nuclear magnetic resonance spectroscopy (NMR), and infrared and Raman spectroscopy among others. However, any of those methods needs to be approved or recommended by international associations to become an official standard. In fact, most of those numerous proposed methods can only detect adulterations greater than 10%, which scarcely represent any advantage over current tests and official methods.

Conceptually the methods can be naturally divided into "targeted analyses" – based on definite information obtained from the fractionation of olive oil components – and "profiling or non-targeted analyses", which relies on the simultaneous contribution from many known or unknown analytes belonging to a predefined metabolic pathway (Baeten et al., 2005; Rezzi et al., 2005). The former analyses, which quantify and identify series of chemical compounds, analyte by analyte, search for compounds that do not appear, or only at trace levels, in genuine olive oils but do appear in adulterated ones. As these analyses reveal under what circumstances these analytes appear in the adulterated oils, the information can also be used to remove or diminish the amount of those selected markers in an improved adulteration process; e.g. adding desterolized seed oils that cannot be detected with methods based on the detection of sterols. This approach requires not only considerable investment in perfecting the classical methods, or in developing new methods, but also in ensuring that the pace of research in the detection of malpractices is rapid enough.

The profiling approach, which typically does not differentiate between analytes and sometimes neither quantify them, aims to rapidly determine the genuineness of olive oils based on information from multi-target screening methods, which are gaining popularity as alternative to targeted approaches based on gas liquid chromatography (GLC) or liquid chromatography (HPLC). In the case of profiling techniques, the fraudsters have no information since there is not a particular marker but the analysts may have problems interpreting the information because multivariate statistical procedures are needed to arrive at correct conclusions, in addition obviously of plausible chemical or biochemical explanations, if analysts want to avoid that the authenticity is not based on random parameters or noise.

The current limits for the physicochemical parameters involved in each purity or quality criterion (Tables 1a–1b) are results achieved, however, from the chromatographic techniques. It is so because of lower cost, rapid implementation and development, more versatility for quantifying diverse analytes, and superior reproducibility of the chromatography in comparison with other proposed techniques.

2.2. Targeted approaches

A standard method needs several years to be endorsed as official method from its submission to the regulatory institutions. The reasons for that period of time can be found, among others, in that the proposals are, in general, hyper-optimists due to a lax application of the statistical procedures, an inadequate selection of the validation samples or a casual relationship between the adulteration and the selected chemical markers.

The chemical compounds, whose contents allow determining the difference between genuine and adulterated olive oils with regard to their designations, are shown in Tables 1a–1b. The chemical composition of olive oil has been traditionally clustered into major and minor compounds; the former are, in large part, responsible for the olive oil main characteristics while the latter are markers for their peculiarities. This section, which has been structured around the series of chemical compounds that are currently used in olive oil authentication, analyzes the series from three viewpoints: a) the main reasons for analyzing them; b) the current standards, with practical comments and suggestions if possible, for quantifying them; and c) potential alternatives to official methods for determining them.

2.2.1. Fatty acids

Fatty acids are, with a few exceptions, the major components of any oil or fat. In small amounts they are present as free fatty acids but usually form esters, most often with glycerol, to produce glycerides (mono-, di- and tri-acylglycerols) and phospholipids but they can also form esters with aliphatic alcohols of linear structure (waxes) or terpenic structure (terpene and sterol esters).

2.2.1.1. Reasons for analyzing these compounds. The knowledge of the fatty acid composition has widely been used for characterizing edible oils since 1960s when seed oils with a modified fatty acid composition