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Determination of Trigonelline in Seeds and Vegetable Oils by Capillary Electrophoresis as a Novel Marker for the Detection of Adulterations in Olive Oils

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A capillary electrophoresis method with UV detection was developed for the first time for the determination of the pyridine betaine trigonelline (*N*-methylnicotinic acid) in seeds and vegetable oils. Analytical characteristics of the method showed its good performance in terms of linearity ($r > 0.999$), precision (relative standard deviations < 5%), and limits of detection (up to 0.9 μM or 1 ng/g for oils). The developed method was applied to the analysis of soy and sunflower seeds, three varieties of olives, and sunflower, soy, and extra virgin olive oils. Trigonelline was determined in soy and sunflower seeds and their respective oils, whereas it was not detected in olives or olive oils. Different mixtures of extra virgin olive oil with seed oils were analyzed, detecting up to 10% of soy oil in olive oil. As a consequence, trigonelline is proposed in this work as a novel marker for the detection of adulterations of olive oils with other vegetable oils such as soy and sunflower oils.

KEYWORDS: Capillary electrophoresis; stacking; trigonelline; soy; sunflower; vegetable oils; olive oils

INTRODUCTION

Trigonelline (*N*-methylnicotinic acid, M_w = 137.14, CAS Registry No. 535-83-1) is an alkaloid belonging to the group of pyridine betaines possessing a quaternary amino group. Several health-promoting properties of trigonelline such as hypoglycemic, hypocholesterolemic, antitumor, antimigraine, or antiseptic effects have been reported (*1*). In addition, betaines are natural osmoregulators of many plants and are present in a high number of foods. Moreover, betaines have also been the subject of several investigations in view of their potentially positive biological effects in humans. In fact, they can act as osmolytes of kidney cells (*2*) and may have a role as a possible therapy in lowering the plasma concentration of homocysteine in homocystinuria (e.g., glycine betaine, proline betaine) (*3*, *4*).

Several methods have been reported for the determination of trigonelline, most of them employing a derivatization step. Thus, UV spectrophotometry (*5*), mass spectrometry (MS) (*6*), high-performance thin layer chromatography (HPTLC) with UV detection (*7*), high-performance liquid chromatography (HPLC) with UV detection (*8*−*18*) including methods with a previous derivatization with 2-naphthacyl trifluoromethane sulfonate (*12*, *15*) or phenylisothiocyanate (PITC) (*10*, *11*, *17*), HPLC coupled to MS (*19*, *20*), and capillary electrophoresis (CE) with UV detection and derivatization with *p*-bromophenacyl ester (*21*) have been employed. The described methods were applied both to plants (*7*, *9*, *19*, *21*) and to foods (*5*, *6*, *8*, *10*−*18*, *20*).

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In foods (as fruits, grains, vegetables, beverages, meat, seafood, or dairy products), trigonelline was found at low concentrations (e.g., chocolate) or it was not detected (e.g., olive oil sample), whereas it was found at high concentrations in coffee beans, lentils, and chickpeas (*12*, *15*). This was corroborated in other papers, where the content of trigonelline in edible lentil and garden pea seedlings was determined (*10*, *11*). What is more, in coffee beans, which present the highest content of trigonelline, it has been determined widely (*6*, *8*, *13*, *14*, *16*, *18*, *20*). Finally, trigonelline was also found in a considerable quantity in soy seeds and seedlings (*5*, *17*).

Although the presence of trigonelline in seeds was confirmed, there is no literature aimed to study the traceability of this compound from seeds to their oils. However, it is worth to noting that among oil minor components, peptides and proteins from seeds or fruits may be transferred to the edible oil together with fats (*22*).

The extra virgin olive oils are expensive oils that may become the object of adulterations for economical purposes. The most common method for adulteration is doping olive oils with cheaper oils such as seed oils, sunflower or soy oils being the most widely employed for this purpose. However, according to European regulations, the definition of virgin olive oils excludes "mixture with oils of other kinds" (*23*), and, on the other hand, at a national level (in Spain), it is specified that the mixture of olive oils with vegetable seed oils is forbidden (*24*). Thus, many powerful techniques for the detection of adulteration of virgin olive oil by edible oils have been described. They can be divided into "physical" and "chemical" methods. The first group is based on the total chemical makeup of the oil using spectrometric techniques such as fluorescence, nuclear magnetic resonance (NMR), Fourier transform Raman (FT-Raman), FT-infrared (FT-IR),

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