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Articles

Analytical Methods

Bioactive Constituents

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Capillary Electrophoresis of Free Fatty Acids by Indirect Ultraviolet Detection: Application to the Classification of Vegetable Oils According to Their Botanical Origin

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ABSTRACT: A method for the determination of fatty acids in vegetable oils by capillary electrophoresis with indirect UV−vis detection has been developed. The separation of fatty acids was optimized in terms of Brij surfactant nature and concentration and organic modifier (2-propanol) percentage. The optimal background electrolyte consisted of 10 mM *p*-hydroxybenzoate, 5 mM Tris at pH 8.8, 80 mM Brij 98, 40% acetonitrile, and 10% 2-propanol. Under these conditions, vegetable oils from five botanical origins (avocado, corn, extra virgin olive, hazelnut, and soybean) were analyzed and the fatty acid contents established. Linear discriminant analysis (LDA) models were constructed using fatty acid peak areas as predictors. An excellent resolution among all category pairs was obtained, and all samples were correctly classified with assignment probabilities of >95%.

KEYWORDS: botanical origin, CE, fatty acid, linear discriminant analysis, vegetable oils

INTRODUCTION

Authentication of edible quality oils is of great importance from the viewpoints of commercial value and health impact. The organoleptic properties, high nutritional value, and health benefits of quality oils are related to the presence of many components, such as fatty acids, the concentration profiles of which differ according to fruit variety. A relevant aspect of oil authenticity is the adulteration of quality oils by mixing them with oils of lower quality. Then, the evaluation of fatty acid profiles could be an excellent tool to assess oil authenticity.

Traditionally, analysis of fatty acids has been performed spectroscopically[1−3] and chromatographically.[4−8] The chromatographic technique most widely applied to determine fatty acid profiles of lipids has been gas chromatography,[4,5] in which long-chain fatty acids are analyzed as methyl or trimethylsilyl esters in polar columns. On the other hand, high-performance liquid chromatography (HPLC) has been also used to determine fatty acids in lipid matrices, where several UV-absorbing derivatives have been usually employed, such as phenacyl[9] or naphthacyl[10] esters and 2-nitrophenylhydrazides.[11] However, derivatization reactions often produce incomplete conversion of the analyte and undesirable interfering side products.

In the past decade, capillary electrophoresis (CE) has been proposed as an interesting alternative for the analysis of underivatized long-chain fatty acids.[12−28] However, one of the major concerns in analyzing fatty acids by CE has been their limited solubility in aqueous electrolyte systems. To solve this problem, CE separation has been described by using background electrolytes (BGEs) containing organic solvents, such as methanol,[15,16] ethanol,[26] acetonitrile (ACN),[22,25,27] 1-octanol,[25,27] and methylformamidedioxane.[19] In addition, the use of additives to the BGE, such as cyclodextrins[16,22,24,26] or surfactants (sodium dodecyl sulfate[24,26] and polyoxyethylene 23 lauryl ether (Brij 35)[19,21,25,27,28] among others), has been described to modify selectivity on analyte separation. On the other hand, fatty acids do not possess strong chromophores in their structures, which makes difficult their sensitive detection in direct photometric mode. Then, direct UV or fluorescence detection was only employed when a previous derivatization step was performed, although the use of indirect UV and indirect fluorescence detection[29] was preferred. The chromophoric agents used include *p*-anisate,[15,16] diethylbarbiturate,[30] adenosine monophosphate,[29] dodecylbenzenesulfonate,[19,21,25,27,28] and *p*-hydroxybenzoate,[24] among others.

In this work, a CE method with an alkaline buffer in the presence of an anionic chromophore (*p*-hydroxybenzoate) for the indirect UV detection of fatty acids was developed. The separation of fatty acids was optimized in terms of Brij surfactant nature and concentration and organic modifier (2-propanol) percentage. The fatty acid content present in different vegetable oil samples was obtained. Moreover, the fatty acid profiles observed were used to construct linear discriminant analysis (LDA) models to classify oil samples according to their botanical origin.

MATERIALS AND METHODS

Reagents and Samples. The following analytical grade reagents were used: acetonitrile (ACN), methanol, ethanol, 1-propanol, 2-propanol (Scharlau, Barcelona, Spain); tris(hydroxymethyl)aminomethane (Tris, Fluka, Buchs, Switzerland); polyethylene glycol dodecyl ether (Brij 30, $C_{12}EO_4$; EO = number of ethoxylate groups), polyoxyethylene 23 lauryl ether (Brij 35, $C_{12}EO_{23}$), polyoxyethylene (20) oleyl ether (Brij 98,

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