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Maria Francesca Riccio [a b], Alexandra C. H. F. Sawaya [a c], Patrícia V. Abdelnur [a], Sergio A. Saraiva [a], Renato Haddad [a], Marcos N. Eberlin [a] & Rodrigo R. Catharino [a b]

[a] ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, University of Campinas - UNICAMP, Campinas, Brazil

[b] Department of Clinical Pathology, School of Medical Sciences, University of Campinas - UNICAMP, Campinas, Brazil

[c] Institute of Biology, University of Campinas - UNICAMP, Campinas, Brazil

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Mass Spectrometry

EASY AMBIENT SONIC-SPRAY IONIZATION MASS SPECTROMETRIC OF OLIVE OILS: QUALITY CONTROL AND CERTIFICATION OF GEOGRAPHICAL ORIGIN

Maria Francesca Riccio,[1,2] Alexandra C. H. F. Sawaya,[1,3] Patrícia V. Abdelnur,[1] Sergio A. Saraiva,[1] Renato Haddad,[1] Marcos N. Eberlin,[1] and Rodrigo R. Catharino[1,2]

[1]*ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, University of Campinas – UNICAMP, Campinas, Brazil*
[2]*Department of Clinical Pathology, School of Medical Sciences, University of Campinas – UNICAMP, Campinas, Brazil*
[3]*Institute of Biology, University of Campinas – UNICAMP, Campinas, Brazil*

Herein, we show that easy ambient sonic spray ionization mass spectrometry in the negative ion mode [EASI(-)-MS] of water:methanol extracts of olive oil samples from 5 different countries (Portugal, Italy, Spain, Lebanon, and Greece) provides very characteristic profiles of chemotaxonomic markers, that is, free fatty acids and phenols. These EASI(-)-MS fingerprints, acquired with great speed and simplicity after minimal sample preparation, permits secure identification of the samples as olive oils via their unique profiles of fatty acids plus phenolic constituents as well the certification of geographical regions via characteristic features of the profiles of phenolic constituents.

Keywords: Easy ambient sonic spray ionization mass spectrometry; Fatty acids; Virgin olive oil

INTRODUCTION

Olive oil, the major fat component of the Mediterranean diet, is highly appreciated worldwide due to its beneficial effects on human health, and these effects are often associated with the content of phenolic compounds and a high amount of oleic acid and tocopherols (Gutierrez et al. 1989; Montedoro et al. 1992; Visioli and Galli 1998). Phenolic compounds are secondary plant metabolites, with a great structural diversity and a wide phylogenetic distribution (Harborne and Williams 2000). The

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Address correspondence to Rodrigo R. Catharino, Pharmacy, Department of Clinical Pathology, School of Medical Sciences, University of Campinas – UNICAMP, Campinas, SP 13083-970, Brazil. E-mail: rrc@fcm.unicamp.br

amount and composition of phenolic compounds in virgin olive oil depends on several factors such as olive cultivar, degree of maturation, and agronomic and technological aspects of production, and is also an important parameter to evaluate virgin olive oil quality since phenols largely contribute to oil flavor and taste (Gimeno et al. 2002; Guttierrez-Rosales, Rios, and Gomez-Rey 2003; Pinelli et al. 2003; van der Sluis, Dekker and van Boekel 2005). Numerous olive tree varieties that produce different triacilglycerol (TAG) and phenolic compound profiles are used for oil production in different climates and soil types around the world, with some cultivars being characteristic of a region, whereas others are widespread. The correct classification of the geographical origin and cultivar of the olive oil is, therefore, a new and challenging analytical task that should control the quality and certify the origin of oil samples with subtle changes in chemical composition (Cerretani et al. 2006). Several techniques have been tested for such a challenging analytical task such as near infrared spectrometry (Bertran et al. 2000; Gurdeniz, Ozen, and Tokatli 2010); high performance liquid chromatography-mass spectrometry (Nagy et al. 2005), nuclear magnetic resonance spectroscopy (Mannina et al. 2010; Vlahov, Del Re, and Simone, 2003), a combination between an electronic nose, an UV-Vis spectrophotometer (Casale et al. 2007), capillary electrochromatography (Lerma-García et al. 2009), and capillary electrophoresis (Carrasco-Pancorbo et al. 2009). Profiles of phenolic compounds in the oil functioning as chemotaxonomic markers seem, therefore, as an attractive alternative and have been shown to provide certification of geographical origin and cultivars as determined mainly via liquid or gas chromatography (Japon-Lujan, Ruiz-Jimenez, and De Castro 2006; Vinha et al. 2005)

For high throughput analysis, however, fast and simple but reliable characterization methods should ideally be employed. Direct infusion electrospray ionization mass spectrometry (ESI-MS) is an attractive alternative; without chemical derivatization or prior chromatographic separation and with minimal sample preparation, it has been applied for fingerprinting characterization and quality control of food samples. We have been using this strategy in our laboratory with excellent results for various samples such as spices (Moller, Catharino, and Eberlin, 2007), soybean extracts (Santos et al. 2006), fruit juices (Gollucke et al. 2009; Roesler et al. 2007, 2008), and biodiesel (Catharino et al. 2007). Direct infusion ESI-MS or APCI-MS have also been applied to characterize vegetable oils including olive oils according to TAG, free fatty acid, and/or phenolic compound profiles (Caruso et al. 2000; Goodacre et al. 2002; Oliveras-López et al. 2007; Wu, Rodgers, and Marshall 2004). We have also applied direct infusion ESI-MS to characterize vegetable oils by using a simple extraction procedure with a water:methanol (1:1) solution (Catharino et al. 2005). This extraction was shown to be beneficial particularly to characterize olive oil since the phenolic constituents (the natural chemotaxonomic markers for olive oils) were selectively extracted and, therefore, concentrated on the extracts together with the free fatty acids. We found that ESI(-)-MS provides, therefore, for the water:methanol extracts of olive oil, a very unique profile in which a characteristic set of $[M-H]^-$ ions from the free fatty acids (with typical relative abundances) was detected together with a diverse and rather intense set of similar ions from the phenolic constituents.

Recently, a series of new mass spectrometric techniques such as DESI (Takats et al. 2004) and DART (Cody, Laramee, and Durst 2005) that are able to perform

desorption and ionization of analytes directly from natural or auxiliary surfaces at ambient conditions have been developed (Venter, Nefliu, and Cooks 2008). These direct desorption/ionization methods present advantages as compared to ESI-MS analysis in terms of greater simplicity through further simplification of sample preparation and potentially much higher sample throughput. Among these ambient MS techniques, EASI (originally termed desorption sonic spray ionization, DeSSI) (Haddad, Sparrapan, and Eberlin 2006) is among the simplest, gentlest, and most easily implemented. An EASI source can be constructed and installed in a few minutes from a few simple MS laboratory parts (Figure 1) and is assisted only by compressed nitrogen (or even air). The EASI uses super-sonic spray ionization (Hirabayashi, Sakairi, and Koizumi 1995) to create very minute droplets which end up being charged due to statistical imbalance distribution of cations and anions. The dense stream of the super-sonic charged droplets causes analyte pick up from the surface and its ionization. The EASI-MS has, therefore, a further advantage as compared to ESI (and other desorption techniques based on ESI) since it uses no voltage in the process of ionization; hence, the risk of ESI-induced oxidation or ionization (instead of protonation) of the analytes is eliminated (Benassi et al. 2009). The EASI-MS has already been applied with success to fast fingerprinting

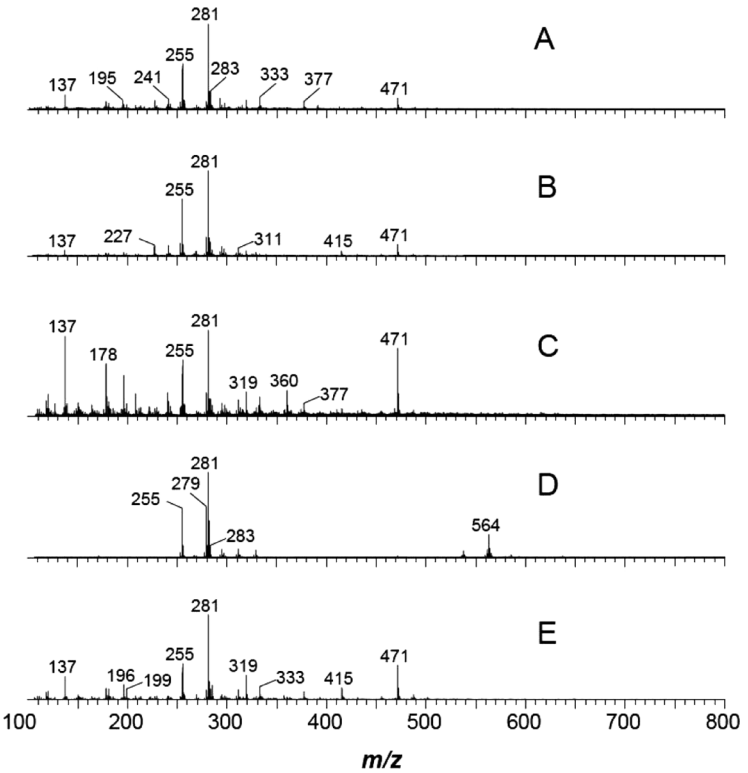

Figure 1. Typical EASI(-)-MS of dry water:methanol extracts from samples of olive oil from: A) Portugal, B) Italy, C) Spain D) Lebanon, and E) Greece. The most important ions to differentiation are of m/z 137 (tyrosol), 255 (palmitic acid), 279 (linoleic acid), 281 (oleic acid), and 283 (stearic acid).

characterization of diverse analytes in different matrixes (Abdelnur et al. 2008; Eberlin et al. 2009; Haddad, Catharino, et al. 2008; Haddad, Milagre, et al. 2008; Haddad, Sparrapan, et al. 2008; Saraiva et al. 2009). Herein, we show that EASI(-)-MS fingerprinting allowed simple, secure, and ultrafast characterization of olive oils from different geographical origins.

MATERIAL AND METHODS

Samples and Chemical Reagents

All reagents used were chromatographic grade. A total of thirty (30) samples of extra virgin olive oil with less than 0.5% acidity, 6 of each from five different geographical regions (countries of Portugal, Italy, Spain, Greece, and Lebanon) and from different lots were purchased in the market and analyzed. All samples ($n = 6$) are included in this experiment to validate the method and as such are a blind unknown from one of the five countries represented. All samples were within their shelf life validity, showed proper labels and security items, and presented no apparent damage or any sign of adulteration or forgery.

Experimental Procedures

A Q-TOF mass spectrometer (Micromass, Manchester, UK) was used to acquire the EASI-MS data in the negative-ion mode using methanol doped with an 0.1% of aqueous ammonium hydroxide (100 μL per 10 mL) for spraying at a flow rate of 20 uL min^{-1} and a nebulizing gas backpressure of c.a. 30 bar. The EASI(-)-MS was obtained from the air-dried extracts obtained using 0.3 mL of the oil and 1 mL of the water:methanol (1:1) solution. A few droplets of the extract was placed on a sample spot in a glass surface and allowed to dry. EASI-MS/MS of selected ions were acquired by low energy (ca 15–30 eV) collision-induced dissociation (CID) with argon. The mass spectra were acquired over a 50–2000 m/z range.

Statistical Data Treatment

The EASI-MS data were extracted using the MassLynx 3.5 software (Waters, Manchester, UK). The spectra were accumulated for 30 s, centered, and aligned to generate a matrix containing the 50 most intense variables. Principal Component Analysis (PCA) was performed using Unscrambler v. 8.0 (CAMO Process A/S, Oslo, Norway) software.

RESULTS AND DISCUSSION

Figure 1 presents a typical negative EASI-MS spectrum for the dry extracts of each of the five samples from different geographical origins. Note the characteristic and reproducible (Figure 1) profiles of fatty acids as well as phenolic compounds (Table 1) detected as their respective $[M–H]^-$ ions, and the great abundance and

Table 1. Components identified by EASI(-)-MS in the dry water:methanol extracts of olive oil samples from different geographical regions

Component	Origin[a]					[M-H]$^-$ (m/z)	CID Fragments (m/z)
	Pt	It	Sp	Lb	Gr		
Tyrosol	√	√	√	nd	√	137	119
2-(4-hydroxyphenyl) ethyl acetate	√	nd	√	nd	√	195	137, 153, 123
Lauric acid	√	nd	√	nd	√	199	nd
Miristic acid	nd	√	√	nd	nd	227	nd
Elenolic acid	√	√	√	nd	nd	241	nd
Palmitic	√	√	√	√	√	255	nd
Linoleic	√	√	√	√	√	279	nd
Oleic	√	√	√	√	√	281	nd
Stearic	√	√	√	√	√	283	nd
Arachidic	√	√	√	nd	√	311	nd
Decarboxylated-oleuropein aglycon	√	nd	√	nd	√	319	199, 111, 153
Ligstroside aglycon	nd	nd	√	nd	nd	360	291, 101, 259
Oleuropein aglycon	√	nd	√	nd	√	377	275, 307, 333, 301
1-acetoxypinoresinol	nd	√	nd	nd	√	415	nd
α-tocopheryl acetate	√	√	√	nd	√	471	nd
Oleurin glycoside	nd	nd	nd	√	nd	539	nd
Unknown	nd	nd	nd	√	nd	564	nd

[a]Pt: Portugal, It: Italy, Sp: Spain, Lb: Lebanon, and Gr: Greece. √ = detected; nd = not detected.

diversity of these chemotaxonomic markers, owing to the selective extraction and concentration of the dry extracts and efficient desorption and ionization by EASI. These profiles seem to provide a straightforward indication of the geographical origin of the oil.

Table 1 lists the olive oil components which were identified based on previous studies (Lerma-García et al. 2008) and by comparison with the chemical composition indicated by the high-resolution and high accuracy mass measurements provided by the QTOF-MS analysis. Most of these anions showed high resistance towards dissociation, but a few ions dissociated properly and Table 1 also list their main CID fragments.

Figure 2 shows the PCA (Martin, Morris, and Zhang, 1996) plot of the negative EASI-MS data. Principal component analysis (PCA) reveals the relationships between samples without peak-choice bias and without neglecting a significant amount of the information in the spectra. Herein, was used the PCA to treat the ESI(-)-MS data so as to statistically evaluate the performance of this method in differentiating olive oils. Figure 2 shows the PC1 vs. PC2 scores plot. Note that the 30 samples investigated are clearly placed in five well-resolved groups, and that the grouping matches their known geographical origins. The PCA describes the underlying orthogonal variables in the set of multivariate data as a set of principal components (PC), being a linear additive model in which each PC accounts for a portion of the total variance of the data, resynthesizing the data as a function of two or three PCs. Plotting our data in the space provided by these PCs (scores plot) permits

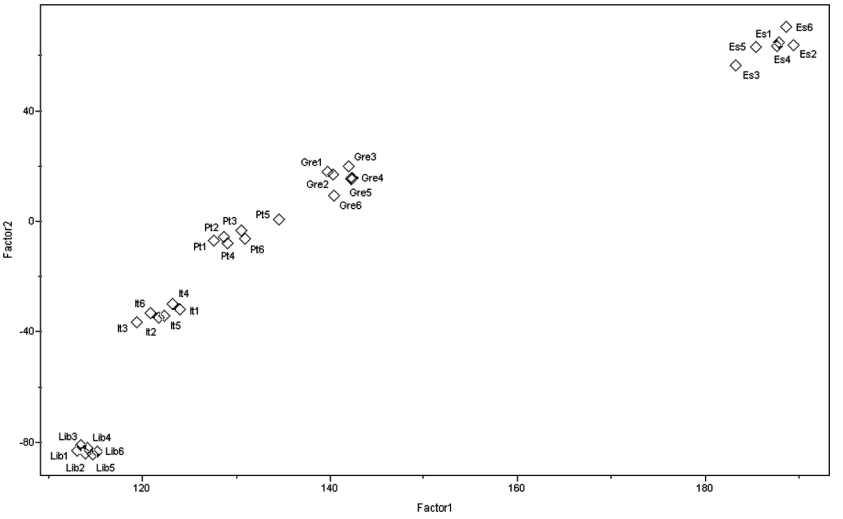

Figure 2. PCA plot just confirm what observed in visual inspection with 100% confidence interval of the EASI(-)-MS data of the five different types of olive oils analyzed from: Pt: Portugal, It: Italy, Es: Spain, Lib: Lebanon, and Gre: Greece.

the rapid discrimination of these samples and a clear visualization of their similarities and differences. The PCA analysis confirms therefore the negative EASI-MS certification of origin, which is also clearly suggested by visual inspection of the sets of chemotaxonomic markers identified in the fingerprints of the dry extracts. Note that samples from Spain and Lebanon display the most statically distinct set of markers, as Figure 1 also indicates by their richest (Spain) and simplest (Lebanon) EASI(-)-MS profiles.

Although each sample of olive oil presented a set of characteristic phenolic ions, the set of four ions of m/z 255, 279, 281, and 283 corresponding to free fatty acids (Table 1) were, as expected, common to all samples. As shown before (Catharino et al. 2005) their relative ratios and the predominance of the ion of m/z 281 (oleic acid) characterizes most of these samples (except those from Lebanon, see the following section) as pure olive oil samples. Other patent features of the negative EASI-MS of Figure 1 are the greatest relative abundance of phenols identified in the EASI-MS fingerprints of the samples from Spain, and the very low abundance of such compounds in the ones from Lebanon.

Two other distinctive features of the samples from Lebanon are the unique ion of m/z 564 (still unidentified but we suspect that it may be related to a phenol glycoside) and the highest ratio (7:10) for linoleic (m/z 279) and oleic acid (m/z 281). This ratio seems to indicate the admixture of a more unsaturated oil such as soybean oil to olive oil (Catharino et al. 2005)

CONCLUSION

Negative EASI-MS of the air dried water:methanol extracts is found to provide fingerprinting data with characteristic profiles of chemotaxonomic markers of olive

oils (mainly free fatty acids and phenols) that is able to discriminate samples from different geographical regions. The results for the 30 proof-of-principle samples investigated herein from 5 different geographical regions (countries) indicates that the method is reliable and reproducible, and may offer a fast and simple technique for quality control and certification of the geographical origin of olive oils. As judged by recent results from direct infusion ESI-MS with the untreated oil (Lerma-García et al. 2008), EASI(-)-MS of the water:methanol extracts might also be able to discriminate samples from different genetic varieties with even more subtle differences in chemotaxomic marker composition, and this ability is currently being evaluated in our laboratory. We envisage that, particularly for the challenging task of geographical origin certification, reference materials provided by major producers could be used as standards to calibrate extraction methods and MS acquisition parameters so as to perform the most reliable as possible comparisons of the characteristic negative EASI-MS fingerprints. These carefully obtained negative EASI-MS could then serve as "chemical seals" of authenticity for the oils.

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