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Comparative study on volatile analysis of extra virgin olive oil by dynamic headspace and solid phase micro-extraction

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Abstract

The dynamic headspace thermal desorption (DHS-TD) apparatus using Tenax-TA and Carbotrap-300 traps, connected to a gas chromatography (GC)-ion trap-mass spectrometry (MS) equipment, as well as the solid phase micro-extraction (SPME) tool, with polydimethylsiloxane (PDMS) and polydimethylsiloxane-divinylbenzene (PDMS-DVB) fibers and connected to a GC-time of flight-MS equipment were implemented for the isolation and identification of virgin olive oil volatile compounds under various sampling conditions. Applying the DHS-TD Tenax-TA procedure separated a higher number of compounds compared to the SPME-PDMS-DVB, which on the other hand required shorter total times for the analysis. High ratio of gas flow rate/amount of oil gave better results for DHS-TD, while a high ratio of headspace/amount of oil worked better for SPME. PDMS exhibited a low sensitivity to olive oil polar volatile compounds while PDMS-DVB showed the overall best sensitivity for all classes of volatile compounds. Results indicate that SPME may find a wide application as an analytical technique for quick analysis of quality related volatile compounds of olive oil. The analyses performed on the GC-TOF-MS-system demonstrated high sensitivity and also high selectivity due to the high quality of mass spectra obtained. The SPME-GC/TOFMS technique appears to be faster and simpler than DHS-TD/GC/MS but the latter provides higher efficiency.

Keywords: Olive oil; Purge and trap; Volatile compounds; Solid phase micro-extraction; SPME; Analysis

1. Introduction

Virgin olive oil, which is obtained from fresh and mature fruit of the olive tree *Olea europeae* has a unique volatile composition contributing to its aroma and flavor (Kiritsakis, 1998; Kiritsakis & Christie, 2000). Several researchers (Aparicio & Morales, 1998; Fedeli, 1977; Flath, Forrey, & Guadagni, 1973; Kiritsakis, 1998) reported the chemical identity of a great number of volatile compounds in olive oil. Analysis of the aroma volatile compounds has been used to evaluate the degree of ripeness of the olive fruit (Aparicio & Morales, 1998). According to Kiritsakis (1998) and Salas and Sanchez (1999), methods used and conditions applied to obtain olive oil from olive fruit affect its volatile composition. The malaxation (mixing) process during olive fruit processing in an olive oil mill affects evolution of olive oil volatiles (Angerosa, d'Alessandro, Basti, & Vito, 1998).

Various attempts to quantify these compounds have been reported. Guth and Grosch (1993) and Reiners and Grosch (1998) used the stable-isotope dilution analysis. Dynamic headspace-thermal desorption combined to a GC (DHS-TD/GC) has been a very popular technique proven for its performance and widely used in a great number of studies (Ahn, Jo, & Olson, 1999; Aparicio & Morales, 1994; Morales, Aparicio, & Rios, 1994; Sucan, Fritz-Jung, & Ballan, 1998) for the isolation of the olive oil flavor volatile compounds. However, not as much

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information has been available on the optimization of this technique in terms of purging time and temperature conditions.

Introduce din the early "90s, solid phase micro-extraction (SPME) has since been used among others for the aroma analysis of various food products such as fruit (Song, Gardner, Holland, & Beaudry, 1997), alcoholic beverages (Ng, Hupe, Harnois, & Moccia, 1996), coffee (Roberts, Pollien, & Milo, 2000) and microorganism metabolites (Vergnais, Masson, Montel, Berdague, & Talon, 1998). Lately, the SPME technique has been applied for the analysis of flavors from lipid and oil containing products (Jelen, Obuchowska, Zawirska-Wojtasiak, & Wasowicz, 2000; Snyder, King, & Zhang, 1998). For a rapid and accurate aroma compound characterization of the different products, time-of-flight mass spectrometry (TOF-MS) (Song et al., 1997), isotope ratio mass spectrometry (IRMS) (Gupry, Rochut, Robins, & Gentil, 2000), and gas chromatography/olfactometry dilution analysis (Deibler, Acree, & Lavin, 1999) have been combined with the SPME. Since the SPME analysis techniques could provide quick and accurate results (Song et al., 1997) it has been used lately in the analysis of the unique volatile spectra of olive oil. A rather more thorough investigation on the optimization of the analysis and a better understanding of its benefits and liability could be of great value in order to further understand and improve the extraction process.

This work was designed to optimize the operation conditions, and evaluate the efficiency of the dynamic headspace thermal desorption and solid phase micro-extraction analytical techniques, in the analysis of volatile compounds of olive oil. A suggestion of application guidelines towards a more efficient utilization of these techniques was also attempted.

2. Materials and methods

One-liter glass bottled commercial, cold-processed Spanish extra virgin olive oil (Aceites del Sur S.A., Spain), was purchased from a local market in East Lansing, MI. Chemical analytical evaluation of oil was not run, trusting the labeling information.

For the dynamic headspace thermal desorption the Carbotrap-300 and Tenax-TA traps of 11.5 cm × 6 mm dimensions (Supelco, Bellefonte, PA) were used, after preconditioning for 8 h at 350 °C and purging for 30 min with nitrogen gas, prior to use. Stripping of volatile compounds from olive oil, placed in 250 ml GWB with a fritted dispersion glass tube, was performed by the dynamic headspace trapping and desorption technique. Dry nitrogen gas was bubbled into the bottles containing either 80, 160 or 240 g oil. The applied gas flow rates were either 100 or 200 ml/min, while the stripping times were 10, 20, 40, 80, or 100 min. During the stripping process GWB remained in a water bath at 37 °C while the fitted glass traps at the outlet of the bottles were maintained at 23 °C. The stripping temperature of 37 °C was chosen to avoid thermal volatiles alterations, although more compounds would be possible stripped if oil samples were exposed to temperatures up to 50 °C (Reiners & Grosch, 1998). A Dymatherm 1000 (Dynatherm Analytical Instruments Inc., Kelton, PA) apparatus was used as another means for stripping oil volatiles in traps for further analysis with the DHS-TD technique. Helium gas was used as a stripping gas. Oil samples of 1, 3 and 6 g were placed in the 9 ml glass-stripping receptacle. Samples were preheated for 5 min at 37 °C and purged for 15 or 30 min applying 100 or 200 ml/min flow rate. Dry helium flowed through the traps for 1 min at 25 ml/min to remove any possible moisture. All analysis were performed at least in triplicate.

The desorption of the compounds stripped from the oil placed in both GWB and Dynatherm apparatus and retained by the traps, was performed by a Dynatherm desorption unit Model 890. The desorption unit was connected to a gas chromatography by a transfer line. Helium at 7 ml/min and 750 kPa was flowing to desorb the molecules from the trap and convey them into the chromatographic column. During desorption traps were kept at 300 °C for 8 min. All the transfer lines and the valves were maintained at 230 °C to avoid condensation of volatiles. Before using the traps again, they were cleaned by heating them for 30 min at 320 °C while purged with helium.

The chromatographic analysis for the DHS-TD technique implemented a Hewlett Packard 5890 Series II GC (Hewlett Packard, Philadelphia, PA) with a 30 m × 0.32 mm ID × 0.25 μm film thickness, fused silica SPB-5, capillary column from Supelco (Bellefonte, PA). A FID detector was used for quantifying the volatile compounds separated by both GWB and Dynatherm apparatus. Integration of chromatography peaks was performed using a Hewlett Packard HP 3395 integrator, (Hewlett Packard, Philadelphia, PA). For avoiding saturation of the GC detector by the volatile compounds, the amount of the oil and the purging time, were balanced. During striping of 160 and 240 g of oil at 200 ml/min gas flow rate for a long stripping time (80–100 min), two events were commonly occurring. The one was related to the sampling column overload which could be concluded by the end tailing of the peaks in the relevant chromatograms. The second event was the saturation of the FID detector recorded through the signal failure during the analysis. Both events may be indicative of the fact that the trapping material could collect enough volatile compounds, therefore, a poor chromatographic separation would be accomplished. Conditions used for the analysis were: initial temperature, 35 °C for 1 min, increased to 80 °C at a rate of 3 °C/min, held for 1 min,