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EFFICENT AND SIMPLE DETERMINATION OF OLIVE OIL RANCIDITY

BRZO I JEDNOSTAVNO ODREĐIVANJE UŽEGLOSTI MASLINOVOG ULJA

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ABSTRACT

There are two major factors that cause cooking oils to become rancid. The first one is exposure of oil to light, starting a cascade of radical reactions leading to the breaking down of chains of unsaturated fatty acids. Thus shorter length acids are being formed, uncharacteristic of cooking oils. The presence of these acids attributes additional negative organoleptic properties which degenerate the quality of oil. The second factor is exposure to oxygen. Oxygen solubility in oil is eight times higher than in water, while the impact of this very gas is unfavourable for the storage of oil. Auto oxidation is the commonest form of deterioration– this means that in contact with oxygen from air the processes start to develop automatically, however they may be accelerated by unfavourable conditions of storing /keeping. Simultaneously higher fatty aldehydes and acids are formed, having organoloptic properties completely extraneous to oils. This paper analyses two samples of olive oil of same origin. The first sample of olive oil was kept in a dark glass bottle, at room temperature, for a year. The second sample was kept in a transparent glass bottle, exposed to light and to variable temperatures. qualitative analysis of these two samples of olive oil was conducted by gas chromatography with mass spectrometry (GC-MS). By this method it is possible to determine total qualitative content of main components as well as of components produced by degradation in only 35 minutes. Results have shown that the first sample is in initial phase of rancidity, while the second one is in an advanced stage of rancidity.

Key words: *olive oil, GC-MS, qualitative analysis, rancidity.*

REZIME

Dva su glavna uzroka pojave užeglosti jestivih ulja. Prvi uzrok je izloženost ulja svetlosti. Pri tome započinje kaskada radikalskih reakcija koje dovode do cepanja nizova nezasićenih masnih kiselina. Tako nastaju kiseline sa kraćim nizovima, koje nisu karakteristične za jestiva ulja. Prisustvo tih kiselina unosi dodatne loše organoleptičke osobine koje narušavaju kvalitet ulja. Drugi uzrok je prisustvo kiseonika. Kiseonik se osam puta lakše rastvara u uljima nego u vodi, a baš je uticaj ovog gasa nepoželjan za čuvanje ulja. Autooksidacija je najčešći oblik kvarenja – to znači da se u kontaktu sa kiseonikom iz vazduha procesi odvijaju sami od sebe, ali ih mogu ubrzati nepogodni uslovi skladištenja/čuvanja. Pri tome nastaju viši masni aldehidi i kiseline, koji imaju organoloptički karakter potpuno stran uljima. U ovom radu analizirana su dva uzorka maslinovog ulja istog porekla. Prvi uzorak maslinovog ulja je čuvan u tamnoj staklenoj boci na sobnoj temeraturi godinu dana. Drugi uzorak je čuvan u svetloj staklenoj boci izložen svetlosti i promenljivim temperaturama. Za kvalitativnu analizu ova dva uzorka maslinovog ulja primenjena je gasna hromatografija sa masenom spektrometrijom(GC-MS). Ova metoda omogućava da za 35 minuta utvrdi potpuni kvalitativni sadržaj kako osnovnih tako i komponenti nastalih degradacijom. Rezultati su pokazali da je prvi uzorak u početnom, a drugi u poodmaklom stadijumu užeglosti.

Ključne reči: *maslinovo ulje, gasna hromatografija sa masenom spektrometrijom, kvalitativna analiza, užeglost.*

INTRODUCTION

The olive tree is one of the oldest known cultivated trees in the world and olive oil has been used for various purposes since antiquity. Modern historians consider the olive tree a cultural marker and a compass to explore the development of civilizations. Through the centuries olive oil has become one of the most widely accepted and used oils in culinary applications. The olive tree possesses an amazing ability to survive in unfavorable conditions based on its strong resistance. On the other hand, it is a demanding crop if it is to produce well. Therefore, a suitable environment and proper agricultural care are necessary for the full development of the agronomic characteristics and steady production conditions. The tree is cultivated today in many countries including Spain, Italy, Greece, Turkey, Montenegro, and other (Boskou, 2009).

Olive oil is a staple food for the people of the countries surrounding Mediterranean Sea, but its use is now expanding to other parts of the world due to its unique flavor, high content of healthy monounsaturated fatty acids, and presence of biologically important minor constituents. In 2004 the US Food and Administration (FDA) announced the availability of a qualified health claim for reduced risk of coronary heart disease (CHD) on monounsaturated fat from olive oil.

Separation and quantification of compounds from the complex matrices of olives and oils have been achieved mainly by well-recognized chromatographic methods. The excellent resolving power and detection capabilities of GC, especially when it is combined with mass spectrometry (GC-MS), has established this technique as a valuable analytical tool. Gas chromatography was used mainly by Angerosa (2006) and Visioli et al. (2002).

Taking into consideration the large body of evidence indicating the beneficial role of olive oil in cancer prevention, we have to keep in mind its unique characteristics, namely, the presence of the ω-9 monounsaturated fatty acid, oleic acid, in high quantities (56–84%), (Arsenijević, 2005). Indeed, many epidemiological studies revealed that intake of oleic acid is protective against several carcinomas (Bartsch et al., 1999; Wahle et al., 2004). Indeed, oleic acid restrained cancer cell growth (breast, colon, lungs) (Llor et al., 2003; Menendez et al., 2005).

Olive oil has a remarkable oxidative stability. If stored properly, it can retain its characteristics for 18 months or more.

This resistance to the development of rancidity, combined with a variety of flavors and distinct features, offers the opportunity for many culinary applications, many of which demand no or very mild processing (addition to salads, marinades, sauces, dressings, dips).

This paper analyses two samples of olive oil of same origin. The first sample of olive oil was kept in a dark glass bottle, at room temperature, for a year. The second sample was kept in a transparent glass bottle, exposed to light and to variable temperatures. Qualitative analysis of these two samples of olive oil was conducted by gas chromatography with mass spectrometry (GC-MS) (Cazes, 2009).

MATERIAL AND METHOD

Two samples of olive (domestic production - Montenegro) oil of same origin were analysed. The first sample of olive oil was kept in a dark glass bottle, at room temperature, for a year. The second sample was kept in a transparent glass bottle, exposed to light and to variable temperatures. From the oily was taken an amount of 10 μL, reconstituted to 400 μL of methanol and additionally added 100 μL of transesterification reagent: TMSH (Trimethylsulfonium hydroxide, 0.2M in methanol, Macherey-Nagel). With such a transesterification reaction fatty acids from acilglycerol esterify to methyl-esters. All the testing was conducted on a gas-chromatography system. The GC–MS analyses were performed on Agilent Technologies 7890 instrument coupled with MSD 5975 equipment (Agilent Technologies, Palo Alto, CA, USA) operating in EI mode at 70 eV. An DP-5 MS column (30 m 0.25 mm 25 μm) was used. The temperature programme was: 50-130°C at 30°C/ min and 130–300°C at 10°C/ min. Injector temperature was 250°C. The flow rate of the carrier gas (helium) was 0.8 mL/min. A split ratio of 1:50 was used for the injection of 1 μl of the solutions.

RESULTS AND DISCUSSION

This analysis can be considered as time efficient since classical preparation of the sample was not necessary. Actually, the oil sample was mixed with a derivatization agent in vial placed in an autosampler. Such a procedure reduced the sample preparation process only to the reaction of transesterification in a gas chromatograph injector. The second important factor is the briefness of chromatographic analysis duration. Figure 1 shows a chromatogram of 30 minutes duration. The same result may be achieved by changing of the temperature program, so that chromatographing lasts for 10 minutes, without any loss of existing peaks. In this way the processes of sample preparation and sample analysis will last ten miniutes all together. Such an approach is highly suitable for the performance of analysis of a larger number of samples, i.e. for quality control.

Fig. 1 shows two chromatograms of two samples of olive oils, (domestic production- Montenegro), from 4 to 30 minutes. Duration of analysis was 30 minutes, merely in order to enable clear identification of the peaks. In Table 1 retention time of components from Fig. 1 are presented. Components of olive oil samples 1 and 2 are not the same. The first sample contains elements of relatively fresh oil, while the sample 2 in addition to the components present in sample 1, also contains the components of rancid oil. This is particularly visible in the chromatogram (Fig. 1), in time intervals of 6 to 12 minutes and from 21.47 to 23 minutes. The listed components (Table 1) include the products of photo-oxidative degradation enhanced by temperature effects.

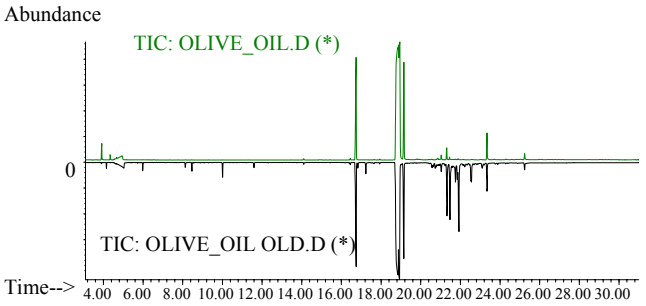

Fig.1. Combined chromatogram of samples

Table1. Retention time (R_t) of components

R_t	Component	Sample 1	Sample 2
3.91	3-methoxy-1,2-Propanediol	+*	+
4.16	Methyl ester Hexanoic acid	-	+
4.95	Glycerin	+	+
5.99	Methyl ester octanoic acid	-	+
8.13	2,4-Decadienal	-	+
10.01	Methyl ester Nonanoic acid, 9-oxo	-	+
11.59	Nonanedioic acid, dimethyl ester	-	+
14.10	Methyl ester tetradecanoic acid	+	+
15.43	Methyl ester pentadecanoic acid	-	+
16.39	Methyl ester 7-Hexadecenoic acid	-	+
16.45	Methyl ester 9-Hexadecenoic acid	+	+
16.74	Methyl ester Hexadecanoic acid	+	+
17.93	Methyl ester Heptadecanoic acid	+	+
18.89	Methyl ester 8,11-Octadecadienoic acid	+	+
18.94	Methyl ester 9-Octadecenoic acid	+	+
19.15	Methyl ester Octadecanoic acid	+	+
19.81	9,12-Octadecadienoic acid	+	+
20.55	Bicyclo[10.1.0]tridec-1-ene	+	+
21.04	Methyl ester 11-Eicosenoic acid	+	+
21.31	Methyl ester Eicosanoic acid	+	-
21.47	Unidentified hydrocarbon	-	+
21.74	Unidentified aldehyde or epoxide	-	+
21.91	Unidentified aldehyde or epoxide	-	+
22.53	Unidentified aldehyde or epoxide	-	+
23.09	Unidentified hydrocarbon	-	+
23.34	Methyl ester Docosanoic acid	+	+
24.29	Methyl ester Tricosanoic acid	+	+
25.24	Methyl ester Tetracosanoic acid	+	+

*Symbols + and – represent the presence, and/or absence of certain components

CONCLUSION

It has been successfully shown that a GC-MS analysis of brief duration can identify products of olive oil disintegration, caused by photo-oxidative degradations enhanced by temperature effects. Results are pointing to two conclusions:

The brief duration of analysis and reliability of data interpretation enables the analysis of 6 samples for 60 minutes.

Quantification of these results enables us to monitor the process of change of the quality of original olive oil.

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