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The effect of different processing stages of olive fruit on the extracted olive oil polyphenol content

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RESUMEN

Efecto de las diferentes etapas del proceso de extracción en la aceituna sobre el contenido de polifenoles en el aceite de oliva.

En el presente estudio se ha investigado la distribución de la fracción fenólica de aceitunas a través de las fases de extracción del aceite de oliva mediante los sistemas clásico y por centrifugación. Se han utilizado dos variedades de aceitunas cuya procedencia es la isla de Creta. Por otra parte, se han estudiado los aceites obtenidos en las diferentes etapas con y sin sus polifenoles, conservándolos durante un mes a 64°C y evaluándoles durante este tiempo el índice de peróxidos. En los aceites de oliva extraídos mediante centrífuga se ha observado una gran reducción en el contenido de polifenoles, reducción que alcanzó el 50% comparado con el sistema clásico. Durante las pruebas en horno los aceites obtenidos mediante el sistema de centrifugación se oxidaron mas fácilmente que los obtenidos mediante el sistema clásico. La variación en el contenido de polifenoles así como los principales parámetros de calidad han sido estudiados en función de la temperatura y del tiempo.

PALABRAS-CLAVE: Aceite de oliva - Polifenoles – Sistema clásico – Sistema por centrifugación.

SUMMARY

The effect of different processing stages of olive fruit on the extracted olive oil polyphenol content.

In the present study the distribution of olive fruit polyphenolic fraction through the phases of olive oil extraction by a classical and a centrifugal system has been investigated. Olives of two Cretan origin varieties were used. Consequently, samples from different stages of oil extraction with and without their polyphenols were stored for a month under 64°C by periodical testing their peroxide value. In olive oils extracted by the centrifugal factory a large reduction of polyphenols content was noticed during their elaboration that reached to the half amount compared with that of classical type. During oven test the control sample of olive oil obtained from the separation phase of centrifugal system was oxidized easier than that of classic one. The variation of polyphenol content as well as of the main olive oil quality characteristics with the temperature and the mixing time was also studied for a period of time.

KEY-WORDS: Centrifugal system - Classical system - Olive oil - Polyphenol content.

1. INTRODUCTION

Polyphenols are one of the most significant class of natural antioxidants of olive oil present in a considerable quantity in fruits and leaves of olives. During maturation of the olive fruit or during the processing of olives, chemical and enzymic reactions take place which result in the formation of free phenols. The latter, although polar compounds, are retained in minute amounts in the oil. The phenolic substances of virgin olive oil are important markers that can be used to characterize typical oils according to the origin area (Vekiari, et al, 1985) and they also strongly affect its sensory and nutritional quality (Monteleone, 1998). The polyphenols are responsible for the excellent quality of olive oil because of their antioxidant activity and the resistance of virgin olive oil to autoxidation is mainly related to their presence (Montedoro et al, 1992 / Tsimidou et al, 1992). The biological activity on the other hand of polyphenols and the possible mechanism by which the high quality of olive oil contributes to lower mortality from coronary heart disease is discussed (Huang, 1992 / Visioli, 1998).

The oil is separated from the other phases in the paste, liquid and solid, by pressure, centrifugation and percolation. Pressure (Figure 1) is the oldest and still a widespread method in use for extracting olive oil. Olive oil extraction by direct centrifugation system is carried out according to the diagram of Figure 2. The system of extraction used (classical, centrifugal, percolation) is critical for total phenol and o-diphenol content. Oils produced by the continuous centrifugal system generally present a lower polyphenol content than oils extracted with other systems. Di Giovacchino et al (1980) claim that the difference is approximately 50%. Other researchers found another values and generally all the authors do not seem to agree but there are discrepancies in the literature concerning the effect of the type of extraction on the polyphenol content. Apparently, the many variables involved in the entire process are responsible for the difference



Figure 1 Diagram of olive oil extraction by pressure.

found in the literature. Small diversities in the machinery of olive crushing, the temperatures applied, the duration of contact with the water and the total volume of water used may cause significant changes in the total polyphenol content (Solinas, 1975, Boskou, 1996 / Vekiari, 2001).

During the last twenty years a tendency for the classic systems to be replaced by the centrifugal factories has been appeared. More recently the efforts of the researchers have been directed to maximize the volatile and antioxidant concentration in the virgin olive oil in order that oil of better quality to be obtained. Hence, a turn to traditional methods have been noticed and the old factories of stone mill-press line properly used, came back in the production of the so called ecological olive oil (Stavroulakis, 1998).

The objective of this paper was to examine preliminary the steps of the loss of polyphenol content during the elaboration of olives through two different olive oil extraction systems in two of the most popular Greek varieties and also the stability of the oil obtained during olive processing to be measured. The influence of some factors as is the temperature and the mixing time on the extracted olive oil quality has also been studied.

2. MATERIALS AND METHODS

Olive fruits of the varieties Koroneiki and Tsounati were harvested from the cultivations of Institute of Subtropical Plants and Olive in the mature firm condition. The olive oil was extracted a day after fruit collection by two factories: a classical of Theocharis and a centrifugal of Alfa-Laval. Five trials from the same olive fruits under the same conditions were done. Analyses were performed in triplicate. The polyphenol content in olive oil and olives was measured by the Spanish method (Vàzquez R. *et al*, 1973 / Vàzquez R. *et al*, 1976 respectively) by the use of 60% MeOH and absorption at 725nm.

Samples of crushed olive fruit were taken in the beginning of mixing phase, in the middle and in the end (the olive oil was extracted by a laboratory mill). Then, samples were also obtained from the phase of pressure (classical system), centrifugation (centrifugal system) and separation. The olive oil was filtered. The samples obtained from the middle of the mixing and from the separation phase and the same oils with their polyphenols taken off were stored for about one month in an oven under 64°C for their stability to be measured through the variation of their peroxide value. The polyphenols were extracted from the oils according to the method described by Gutfinger (1981). Storage test of the oils was done at 64°C. Two gr of the oil were stored in containers 3cm in diameter and of 1,5cm height. Peroxide values of the stored oils were periodically determined.

Consequently, four trials of six repetitions were done by the use of the both varieties, Koroneiki and Tsounati, in the centrifugal system under different conditions of temperature and mixing time. The objective of these experiments was the influence of these factors on the total polyphenol content, PV and coefficient extinction K_{232} and K_{270} of the extracted olive oil to be investigated. Peroxide value and the absorption of olive oil in UV were determined according to the Commission Regulations (EEE) (No2568/1991).

On the received data the ANOVA analysis was performed in order that the significance of polyphenol content variation due to the varieties and olive processing procedure to be evaluated.

3. RESULTS AND DISCUSSION

The processing of olive oil extraction by the classical and the centrifugal type is described in



Figure 2 Diagram of olive oil extraction by centrifugation.

Figures 1 and 2 respectively. In Table I the variation of polyphenol content during olive oil extraction in the two varieties, is presented. It was noticed that a large amount of olive polyphenols doesn't pass in the oil. The interaction between polysaccharides and phenolic compounds of olive pastes may be involved in the loss of phenols during processing. In fact, polysaccharides may link phenolic compounds reducing their release in the oil during crushing and mixing. So far however, the enzymatic oxidation of these compounds during oil processing, catalyzed by the endogenous polyphenoloxidase and peroxidase in the pastes during mixing also reduced phenolic concentration in virgin olive oil (Kiritsakis, 1988).

It is known that the variety is connected directly with the olive oil quality and especially with its sensory characteristics. It is a factor among the others that influence the polyphenol content (Montedoro, 1984). The variety koroneiki showed significantly higher polyphenol content in comparison with Tsounati.

As can be seen in the Table I the natural antioxidant content of virgin olive oil is significantly affected by the extraction system. In our results the polyphenol content was continually decreased from the beginning until the end of the mixing in both factories. A high decrease of this content was noticed from the beginning to the middle of the mixing phase. In the contrary, from the middle until the end of the mixing this decrease was very low in the two systems. In the classical system we can see that from the middle of the mixing phase until the separation phase we hadn't a significant decrease in the polyphenol content while in the centrifugal system it reached the half. A significant loss of polyphenol content was found to be from the end of mixing phase until the end of centrifugal phase due rather to the quantity of water added and diluted a large amount of them. Phenols present in olive paste are soluble in water and oil, depending on their partition coefficients and temperature. Addition of water to the paste alters the partition equilibrium between liquid phases and causes a reduction of phenol concentration through dilution of the aqueous phase. A coincident lower concentration of these substances occurs in the oily phase. The addition of water to olive oil removes water-soluble phenols.

In the Table II the changes of olives and olive oil average of four experiments polyphenol content with the temperature and the time mixing is presented. In

Table I

Variation of polyphenol content (in ppm of caffeic acid) during olive oil extraction. (The prices vertically followed by different letters are significantly different at P=0,05).

Factories	Phases	Total polyphenol (ppm)		
		Tsounati	Koroneiki	
Classical (Theocharis)	Crushing (olives)	1350	1730	
	Beginning mixing (olive oil)	284a	260a	
	Middle of mixing (olive oil)	236b	230b	
	End of mixing (olive oil)	226b	225b	
	Pressing (olive oil)	236b	240b	
	Centrifugal separation (olive oil)	250b	230b	
	Crushing (olives)	1370	1750	
Centrifugal	Beginning mixing (olive oil)	290a	270a	
(Alfa – Laval)	Middle of mixing (olive oil)	270b	220b	
	End of mixing (olive oil)	262b	180b	
	Centrifugation (olive oil)	164c	115c	
	Centrifugal separation (olive oil)	168c	125c	

Table II

Changes of olives and olive oil polyphenol content with temperature and time mixing (The prices horizontally followed by different letters are significantly different at P=0,05)

	Temperature						
		20	°C	30°C			
		T ime heating					
	Trials	0`	30`	0,	30`		
	1	1564 a	1528,8b	1638,2c	1641,1d		
Olives	2	1599a	1570,9b	1624c	1599d		
	3	837,5a	784b	886c	832d		
	4	907,5a	848,5b	875c	859d		
	1	109,1a	60,6b	183,2c	89,1d		
Oliveoil	2	78,3a	58,6b	88,1c	67d		
	3	99,8a	56,8b	105,2c	72,9d		
	4	93,3a	81,5b	105,2c	93,2d		

the Table III the variation of the rest main quality characteristics of olive oil is seemed. It is obvious that the peroxide number as also the K232 and K270 of the obtained oil measured in triplicate (Table III)

increase with the temperature and with the prolongation of mixing phase, maybe because of the more time touch of the paste with atmospheric air and of the higher temperature that, as it is known are factors helpful of the oxidation phenomenon.

Concerning the effect of different time mixing the decrease of polyphenol content with the time increase (Table II) as well in the paste as in the olive oil, could be attributed to the action of atmospheric O₂ and of phenoloxydase, enzymes that catalyses the oxidation of phenols into quinones. In the contrary, a higher temperature leads to an increase of the values of polyphenol content. This increase in total polyphenols with the temperature (Table II) could be explained by the dilution of olive oil polyphenolic substances (that are released by enzymatic reactions in olive elaboration phases before the centrifuging of juice from the total polyphenols less or undiluted in olive oil. In the contrary, a higher temperature (from 20°C to 30°C) during the elaboration helps the dilution of polyphenols of paste and then gives an enrichment of olive oil polyphenols resulting the increase of them. These results are in agreement with those reported by Solinas (1978).

In the oven test a better protection against oxidation in the samples with their polyphenols than in them without polyphenols was found. In Figure 3 the protective activity of olive oil extracted from the olives during the mixing phase of two factories with

Table III Changes of the main quality characteristics of olive oil in varieties "Koroneiki" and "Tsounati" with temperature and mixing time. (The prices vertically followed by the different letters are significantly different at P=0,05)

Variety	Temperature	Time	Acidity	PV	K232	K270
			(%)	(meqO ₂ /Kg)		
Kananalhi		0	0.4	7.0	4.04	0.45
Koroneiki		0	0,4a	7,9a	1,04a	0,15a
	20°C	30`	0,6b	10,0b	1,13b	0,20b
		0`	0,4a	8,2c	0,98a	0,18a
	30°C	30`	0,3c	12,2d	1,16b	0,99c
Tsounati		0`	0,3a	7,2a	0,71a	0,04a
	20°C	30`	0,3a	8,8b	0,85b	0,06a
		0`	0,4b	10,4c	1,09c	0,21b
	30°C	30`	0,3b	11,6d	1,30d	0,28c



Figure 3 Evolution of Peroxide Value (PV) of olive oils with different polyphenol content stored in oven under 64°C

and without polyphenols is presented. The samples numbered by 5-8 in the Figure 3 were obtained by the centrifugal system while them numbered by 1-4 in the same Figure from the classical one. As can be seen the induction time is significantly lower in olive oils extracted with a centrifugation system. The oil extracted from the classical system in the middle of mixing phase and also that of separation phase seem to be protected against heating better than the respective sample of the centrifugal system. This fact could be attributed to the higher polyphenol content of this sample (Gutfinger, 1981 / Gutiérrez, 1977).

4. CONCLUSIONS

The SD line gave average polyphenol content that were significantly different between two varieties and showed strong reduction from the initial step to the middle of mixing in the two systems as well also a significant difference between them at P=0,05.

Comparison of the oxidative stability of the oils during storage before and after the polyphenol extraction showed that removal of the polyphenols increased markedly the oxidation showed that removal of the polyphenols increased markedly the oxidation rate of the oils.

Further, a detailed analysis of the olive oil polyphenol fraction obtained from different extraction stages could be interesting.

REFERENCES

- Boskou, D. (1996). In: OLIVE OIL: Chemistry and Technology. Thes/niki, 161p. Commission Regulations of EE. (1991). No 2568.
- Di Giovacchino, L., Fedeli, E., Di Gregorio, P., Solinas, M. and Kiritsakis, A.K. (1980). Quality characteristics of olive oil and factors that influence on them. Proceedings of 3th International Congress for Biological Value of olive oil, 545-638.
- Gutfinger, T. (1981). Polyphenols in Olive Oils. Journal of American Oil Chemist's Society, 966-968.
- Gutiérrez Gonzalez-Quijano, R., Janer Del Valle, C., Janer Del Valle, M.L., Gutierrez Rosales, F. and Vasquez Roncero, A. (1977). Relationship between polyphenol contents and the quality and stability of virgin olive oil. *Grasas y Aceites*, 28, 101-106.
 Huang, M.T.and Ferraro, T. (1992). In Chi-Tang Ho, Chang Y.
- Huang, M.T.and Ferraro, T. (1992). In Chi-Tang Ho, Chang Y. Lee, Mou -Tuan Huang (Editors), Phenolic Compounds in Food and their Effects on Health I: Analysis, Occurrence and Chemistry, ACS Symp., II, No 506.
- Kiritsakis A. (1988). Olive oil, Thes/niki. 307 p.
- Montedoro, G. and Garofolo, G. (1984). Quality characteristics of virgin olive oils. Influence of some variables: variety, enviroment, extraction, packaging of the final product. *Rivista Italiana delle Sostanze Grasse*, **61**, 157-162.
- Montedoro, G., Servili, M., Baldioli, M. and Miniati, E. (1992). Simple and Hydrolyzable phenolic compounds in virgin olive oil. 1. Their extraction, separation, and quantitative and semiquantitative evaluation by HPLC. *Journal of Agriculture and Food Chemistry*, **40**, 1571-1576.
- Monteleone, E., Caporale, G., Carlucci, A.and Pagliarini, E. (1998). Optimisation of extra virgin olive oil quality. *Journal of the Science of Food and Agriculture*, **77** (1), 31-37.
- Stavroulakis, G. and Petrakis, C. (1998). Production and quality of ecological olive oil. 18th Scientific Meeting of Greek Company of the Vegetable Science (in press).
- Solinas, M., Di Giovachino, L and Mascolo, A. (1978). I polifenoli delle olive e dell'olio d'oliva. Nota III: Influenza della temperatura e della durata della gramolatura sul contenuto in polifenoli degli oli. *La Rivista Italiana delle Sostanze Grasse*. LV, 19-23.
- Tsimidou, M., Papadopoulos, G. and Boskou, D. (1992). Phenolic compounds and stability of olive. *Food Chemistry*, **45**, 141-146.
- Vázquez Roncero, A., Janer Del Valle, C. and Janer Del Valle, M.L. (1973). Determinacion de los polifenoles totales del aceite de oliva. *Grasas y Aceites*. **24**, 350-357.
- Vázquez Roncero, A., Janer Del Valle, C. and Janer Del Valle, M.L. (1976). Phenolic compounds in olive fruits. Polyphenols in olive oils. *Grasas y Aceites.* **27**, 185-190.
- Vekiari, S.A., Parouti, C., Blekas, G. and Boskou, D. (1985). Polyphenols in Greek olive oils, Proceedings of A' Panhellenic Congress of Food, Thes/niki, 249-254.
- Vekiari, S.A. (2001). Olive oil polyphenols and their significance in its quality. Chemica Chronica, General Edition, **63** (2), 45-48.
- Visioli, F. and Galli, C. (1998). The effect of minor constituents of olive oil on cardiovascular disease: new findings. *Nutrition Reviews*, **56** (5-1), 142-147.

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