Influence of filtration on olive oil quality during storage

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Abstract: The purpose of this work was to evaluate the influence of filtration on the quality of olive oil. The influence on some physicochemical and sensorial properties was also evaluated. Results showed that free fatty acids of unfiltered oils were higher than filtered olive oils, while peroxide values were low in unfiltered oils. After filtration, the oxidative stability was reduced. The decrements in phenols content were occurred by the filtration process, causing drooping in the oxidative stability for all filtered extra virgin olive oil samples. The results could help olive oil producers to improve EVOO quality and establish the optimal storage conditions.
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1. Introduction

Virgin olive oil is the oil obtained from the fruit of olive tree (*Olea europaea*) solely by mechanical or other physical means under conditions that do not lead to alteration in the oil, which have not undergone any treatment other than washing, decantation, centrifugation, or filtration **(IOC, 2016).** Extra virgin olive oil (EVOO) is unique and one of the main components of the Mediterranean diet as well it has attracted increasing interest from the scientific community, due to its widely acknowledged health benefits. These benefits have been related both to its well-balanced fatty acids composition, where oleic acid is the main component in the fatty acids and to the presence of minor biomolecules, such as phytosterols, carotenoids, tocopherols and phenols **(Fortini *et al*., 2016).**

Virgin olive oil quality depends on many factors related to olive tree cultivation and to the harvesting, storage and extraction process steps **(Di Giovacchino *et al*., 2002).** Cloudy extra-virgin olive oil (EVOO) is the fresh crude olive oil obtained exclusively by mechanical and physical processes. The extraction process includes the following main steps: collecting, washing, crushing of olives, malaxation of olive paste, decantation, centrifugation, storage, and packaging (bottling). However, European Community Regulation establishes the possibility of EVOO filtration prior to the bottling of oil. Filtration is especially important as a final step to remove suspended solids or moisture and make the olive oil more brilliant for consumer acceptance **(Lozano-Sanchez *et al*., 2012).**

Fortini *et al*. (2016) cited that crude VOO has high water content and various impurities that take the form of suspended solids, which can compromise quality. Suspended solids are usually olive fragments that remain in the oil after extraction, and consistent of proteins, sugars, phospholipids, and phenolic compounds. They cause the formation of colloidal associations that appear as micelles or flakes, and give freshly produced olive oil its typical, cloudy appearance. However, the water and suspended particulates also contain microorganisms, such as bacteria, yeasts and mold, which directly contribute to the transformation of the nutritional component in the oil. These microorganisms may contain enzymes responsible for the hydrolysis of triglycerides, namely lipase, enzymes responsible for fatty acids oxidation, peroxidase, and those responsible for the degradation of phenolic compounds, namely b-gluosidase, esterase, and polyphenol oxidase. It should be noted that water must be present for enzyme activities.

Another operation involved in olive oil stabilization is filtration. Filtration has several important benefits; in particular, it removes suspended solids and moisture and, therefore, clarifies the oil, increasing its appeal to consumers. The most widespread filtration systems in the olive oil industry are conventional filtration mechanisms, such as filter tanks and presses. In some cases, organic or inorganic filter aids (such as diatomaceous earth or cellulose fibers, cotton, or cellulose paper) are used on the surface of filtration equipment, which can enhance or enable the separation of suspended solids and water from the oil. Most of the literature on filtration has compared the quality of cloudy oil to that of filtered oil at the time of production, or during storage **(Fortini *et al*., 2016).**

Conventional filtration systems use organic or inorganic filter aids in conjunction with filtration equipment (tanks or presses) to enhance or enable suspended solids and water oil separations. Diatomaceous earth and cellulose fibers are

commonly used as filter aids, which are deposited on the surface of the filtration equipment by filtering specially prepared mixes. On occasion, non power filter aids such as cotton or cellulose paper may be used instead of diatomaceous earth and cellulose fibers in filter presses **(Lozano-Sanchez *et al*., 2012).**

During storage, oil should be kept in the dark, at temperatures lower than 25°C, in completely filled inox tanks. Within three months of production, oil should be separated from solid impurities and water by decantation or filtration and transferred into clean, dry containers. For prolonged storage, it is recommended to flash the empty space of the tank with nitrogen. Loading and unloading of the tanks must be from the bottom in order to minimize the contact of the oil with the air.

Phenolic compounds of extra virgin olive oil (EVOO) play an important role in organoleptic characteristics namely in attributes related to bitterness and pungency. Moreover, the scientific evidence is already strong enough to enable the legal use of health claims for phenolic compounds on labels of EVOO. The shelf life of EVOO, which is higher than in other vegetable oils, is mainly due to the fatty acid composition and to the presence of phenolic molecules having a catechol group, such as hydroxytyrosol and its secoiridoid derivatives **(Peres *et al*., 2016).**

EVOO is a food credited with providing multiple health benefits for humans related mainly to minor components. During this filtering operation, quantitative and qualitative changes take place, especially on these minor components, which are of great value in establishing the quality and health value of EVOO **(Lozano-Sanchez *et al*., 2012).**

Therefore, the main objective of this study was to study the effect of filtration on quality of extra virgin olive oil during storage at room temperature for 12 months.

2. Materials and Methods

2.1: Materials.

The EVOOs used in this study were of Coratina and Koronieki olive varieties (Season 2015) were obtained from Olivee Co. for Production & Agricultural Manufacture, 10th of Ramadan, Sharquia Governorate, Egypt. Cloudy olive oils (unfiltered oils) were filtered through a traditional filter press consisting of a series of consecutive, horizontal type. The filter press consisted of seven filters, diameter (40cm) cardboard filter plates. Filtered and unfiltered samples were stored for 12 months in Cans (the inside surface of cans polishing with Enamel) without headspace at room temperature and all samples were analyzed monthly for 12 months.

2.2: Methods

2.2.1: Some physicochemical quality parameters: Acidity (as oleic acid %), peroxide value (meq. O2 / Kg oil), refractive index (RI) (20ºC), K_{270} nm, K_{232} nm and ΔK in EVOOs were carried out, following the analytical methods described by **IOC (2016).**

2.2.2: Total phenols:

Total phenols in Extra olive oil samples were extracted three times with 10 ml of a methanol/water mixture (60: 40 V/V). The pooled extracts were washed with 10 ml of n-hexane and solvents were removed with a rotary evaporator (Buchi, Switzerland). Total phenols (TP) content of the methanolic extract of olive oil were colorimetrically determined using the Folin-Ciocalteu method **(Gamez-Meza *et al.*, 1999).**

2.2.3: Oxidative stability:

Oxidative stability in EVOOs was evaluated by the Rancimat method **(Gutierrez, 1989).** Stability was expressed as the oxidation induction time (hours), measured with the Rancimat 679 apparatus (Metrohm Co., Switzerland), using an oil sample of 5 g heated to 100°C with air flow of 20 L/h.

2.2.4: Pigment Content:

Chlorophyll and carotenoids in EVOOs were determined calorimetrically as previously described **Minguez-Mosquera *et al*. (1991).**

2.2.5: Determination of fatty acids composition: The fatty acids methyl esters in EVOOs were prepared using trans-esterification with cold methanolic solution of potassium hydroxide. The fatty acid methyl esters were identified by GC-capillary column according to the methods of **IOC (2016).**

2.2.6: Determination of phenol compounds:

Phenol compounds in EVOOs were determined by HPLC according to the method described by **Peres *et al*. (2016)**.

2.2.7: Determination of flavonoid compounds:

Flavonoid compounds in EVOOs were determined by HPLC according to the method described by **Peres *et al*. (2016).**

2.2.8: Determination of Vitamins (A,D,E & K):

Fat-soluble vitamins in EVOOs were determined according to the method described by **Chen *et al*. (2011).**

2.2.9: Sensory analysis:

Sensory analysis of extra virgin olive oil was performed according to the method described by **IOC (2016).**

3. Results and Discussion

Tables 1 and 2 show some physico-chemical parameters of unfiltered and filtered Koroneiki and Coratina cv. virgin olive oils and stored for 12 months at ambient temperature. Quality parameters of peroxide value and free fatty acid were within the

limits fixed by **IOC (2016),** regardless of cultivar of oil in the first 9 months of storage. In consideration of the acidity, all samples were labeled with the classification of "extra virgin" class.

Table 1: Some physico-chemical parameters of unfiltered and filtered Koroneiki cv. virgin olive oil

Parameters	Koroneiki cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
Acidity %(as Oleic acid)	0.32	0.32	0.36	0.38	0.50	0.31	0.32	0.34	0.35	0.41
Peroxide value (meq O_2 / kg oil)	3.17	5.45	10.29	17.17	23.55	3.19	5.95	15.43	17.64	30.23
RI at 20^0C	1.4699	1.4674	1.4669	1.4673	1.4688	1.4692	1.4672	1.4664	1.4669	1.4688
K_{232} nm	1.389	1.504	1.978	2.300	2.951	1.575	1.629	2.387	2.465	2.977
K_{270} nm	0.046	0.138	0.152	0.178	0.203	0.079	0.163	0.170	0.182	0.210
Δk	-0.0015	-0.0005	-0.005	0.001	0.001	-0.0035	-0.0025	-0.001	0.000	0.002
Oxidative stability (h)	41.76	36.51	32.19	23.00	18.09	41.32	35.59	28.14	21.42	17.27
Total phenols (mg/kg)	350.14	330.23	285.19	200.15	176.36	325.21	287.63	233.01	190.56	150.63
Chlorophylls (mg/kg)	2.70	1.65	1.35	1.11	0.97	2.28	1.47	1.27	1.01	0.90
Carotenoids (mg/kg)	1.16	1.13	1.06	0.95	0.84	1.08	0.98	0.90	0.82	0.74

Results in Tables (1 and 2) revealed that acidity values were slight influenced by filtration, although, over time which values for unfiltered oils were greater than those for filtered oils. In fact, data showed that the acidity increased in the unfiltered samples, whereas they were low in the filtered. **Fortini *et al.* (2016)** cited that lipases act in the interface between water and oil with the following mechanism: the hydrophobic part of the enzyme bounds with the oil, whereas the active site aligns with the substrate and severs the ester bounds of the triglycerides. Hence, the increment in free fatty acids is probably due to the water content of unfiltered oils, which allows lipase enzymes to hydrolyze triglycerides during the storage period. These results are in accordance with the study of **Fregapane *et al.* (2006),** where they report that filtration reduced the rate of hydrolysis of the triacylglycerol matrix and also agreed with **Bottino *et al.*, (2008).** On the other hand, **Sacchi *et al.* (2015)** reported that the acidity did not change significantly after filtration. Results revealed that acidity was increased during storage for 12 months at room temperature.

Table 2: Some physico-chemical parameters of unfiltered and filtered Coratina cv. virgin olive oil.

Parameters	Coratina cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
Acidity %(as Oleic acid)	0.24	0.28	0.30	0.36	0.41	0.19	0.26	0.27	0.30	0.39
Peroxide value (meq O_2 / kg oil)	2.98	4.79	9.96	15.62	27.25	3.23	6.98	13.81	16.79	31.97
RI at 20^0C	1.4697	1.4674	1.4665	1.4678	1.4693	1.4690	1.4674	1.4664	1.4678	1.4686
K_{232} nm	1.566	1.771	2.165	2.213	2.992	1.652	1.919	2.166	2.377	2.999
K_{270} nm	0.056	0.157	0.166	0.170	0.210	0.057	0.158	0.166	0.176	0.220
Δk	-0.003	-0.002	0.000	0.000	0.0005	-0.0005	-0.005	-0.003	-0.001	0.001
Oxidative stability (h)	44.98	36.12	29.99	21.40	18.63	40.53	35.32	27.78	19.66	16.62
Total phenols (mg/kg)	376.01	354.21	299.16	236.14	198.20	345.23	315.54	282.69	208.45	185.45
Chlorophylls (mg/kg)	2.69	1.78	1.53	1.27	1.01	2.24	1.66	1.53	1.17	0.98
Carotenoids (mg/kg)	1.20	1.16	1.08	0.97	0.87	1.10	1.03	0.93	0.84	0.80

Regarding peroxide values (PV), results revealed that a slight difference between unfiltered and filtered oils. However, during the storage period, filtered oils show higher peroxide values than unfiltered oils (Tables 1 and 2). These results agree with **Sacchi *et al.* (2015).** As described in the literature, the increase peroxide value in filtered samples could be due to the oxygen exposure during filtration **(Fregapane *et al.*, 2006).** Results revealed that PV increased during storage for 12 months at room temperature.

UV absorbance seems very useful for the collection of information about the oxidation process during storage. Regarding the K_{270} value, none of the oil samples exceeded the upper limit of 0.22 during storage for 12 months. Among the spectrophotometric indices (K_{232}, K_{270}, Δk) of unfiltered and filtered oils, A slight increase in K_{232} and K_{270} values were evidenced for filtered EVOO. Data agreed with those found by **Bottino *et al.* (2008) and Sacchi *et al.* (2015).** On the other hand, these results are not in agreement with **Stefanoudaki *et al.* (2010)** where

filtered and unfiltered oils were indistinguishable on the basis of these parameters. Also, results revealed that UV absorbance were increased during storage for 12 months at room temperature.

The refractive index (RI) is characteristic of the group which belongs the fatty corpse. It is directly related to the acidic composition of oils (free fatty acid, unsaturation degree, length of hydrocarbon chains) and to their status of oxidation. From the findings found in Tables (1 and 2), the refractive index of unfiltered oils slight higher than those in filtered oils. This difference could be explained by a different free fatty acids and different water soluble compounds which eliminate by filtration process.

Data in Tables (1 and 2) show that filtration process caused a reduce in total phenols. This behavior could be related to remove the aqueous phase by filtration. These results agree with **Koidis and Boskou (2006) and Lozano-Sanchez *et al*. (2012). Fortini *et al*. (2016)** found that the total phenolic content was on the average 337mg/kg in unfiltered oil, and 313mg/kg in filtered oil. On the other side, **Sacchi *et al*. (2015)** mentioned that filtered oil had more phenol content (431.17mg/kg) than those of unfiltered oil (410.31mg/kg). Over time, total phenols were decreased during storage for 12 months. This reduction in the total phenol content of oils during storage is a result of the decomposition processes that occur in the oxidation activities. The presence of pigments not only determines the color of the product but also plays an important role in the oxidative activity of processed foodstuff, due to their antioxidant nature in the dark and pro-oxidant activity in the light **(Oueslati *et al*., 2009).**

Data in Tables (1 and 2) show that there were a slight tendency of oxidative stability to decrease after filtration. These differences were be related to the relation between water content and antioxidant capacity of phenols. **Bendini *et al*. (2007)** have demonstrated that polar-phenol compounds oriented in the water-in-oil emulsion interface are more protective against oxidation. As a consequence, the oxidative stability of virgin olive oil is lower when the water content is decreased after filtration. The results revealed that total phenols related to the corresponding oxidative stability for the filtered and unfiltered oils. The oils with the highest total phenols content have the highest oxidative stability, confirming the positive direct proportion between these parameters **(Beltran *et al*., 2000; Salvador *et al*., 2001). Velasco and Dobarganes (2002)** mentioned that filtered oils are less stable than cloudy oils containing suspended and dispersed materials. Apparently, due to its composition, these suspended materials play a stabilizing role by acting as antioxidants. Thus, filtering should be avoided to increase oil sheilf life. Over time, the results showed that filtration affects on total phenolic content especially, during storage for 12 months at room temperature.

Table 3: Fatty acids composition (%) of unfiltered and filtered Koroneiki cv. virgin olive oil.

Fatty acids	Koroneiki cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
$C_{16:0}$	14.36	13.86	12.71	14.45	14.31	14.28	13.97	13.05	14.58	14.32
$C_{16:1}$	1.34	1.29	1.14	1.35	1.32	1.44	1.28	1.17	1.35	1.32
$C_{17:0}$	0.04	0.06	0.05	0.05	0.05	0.05	0.04	0.05	0.05	0.05
$C_{17:1}$	0.14	0.16	0.08	0.08	0.07	0.08	0.08	0.07	0.07	0.07
$C_{18:0}$	2.65	2.64	2.69	2.50	2.58	2.45	2.61	2.71	2.56	2.59
$C_{18:1}$	71.20	71.96	72.93	71.63	71.73	71.39	71.94	72.59	71.66	71.67
$C_{18:2}$	8.44	8.20	8.41	8.19	8.23	8.43	8.44	8.42	8.17	8.26
$C_{18:3}$	0.89	0.84	0.87	0.84	0.80	0.93	0.88	0.88	0.83	0.81
$C_{20:0}$	0.48	0.52	0.59	0.47	0.48	0.49	0.48	0.55	0.45	0.47
$C_{20:1}$	0.32	0.32	0.35	0.30	0.29	0.32	0.28	0.34	0.28	0.30
$C_{22:0}$	0.14	0.15	0.18	0.14	0.14	0.14	ND	0.17	ND	0.14
Σ SFA*	17.67	17.23	16.22	17.61	17.56	17.41	17.10	16.53	17.64	17.57
Σ USFA**	82.33	82.77	83.78	82.39	82.44	82.59	82.90	93.47	82.36	82.43
MUSFA***	73.00	73.73	74.50	73.36	73.41	73.23	73.58	74.17	73.36	73.36
PUSFA****	9.33	9.04	9.28	9.03	9.03	9.36	9.32	9.30	9.00	9.07
$C_{18:1}$/ $C_{18:2}$	8.43	8.77	8.67	8.74	8.71	8.46	8.52	8.62	8.77	8.67
MUSFA / PUSFA	7.82	8.15	8.02	8.12	8.13	7.82	7.89	7.97	8.15	8.08

* SFA: Saturated Fatty Acids. ** USFA: Unsaturated Fatty Acids. *** MUSFA: Monounsaturated Fatty Acids. **** PUSFA: Polyunsaturated Fatty Acids

The amount and nature of pigments in olive oil were affected by filtration. Regarding chlorophylls and carotenoids contents (Tables 1 and 2), data showed that unfiltered oils had more chlorophyll and carotenoids than filtered oils and their contents of chlorophyll and carotenoids decreased over time during storage for 12 months. It can be assumed that the turbidity of these samples has a shielding effect with respect to light, decrease the light intensity in the oils, thus slowing down chlorophyll degradation. As several works pointed out, chlorophylls degradation is fast in presence of light **(Psomiadou and Tsimidou, 1998),** thus it is supposable that the reduction in light intensity reduces the chlorophylls degradation rate. The chlorophyll content in all filtered olive oils were lower than unfiltered oils, because these compounds are removed during the filtration. **Fortini *et al.* (2016)** mentioned that filtered oils may be more sensitive to the pro-oxidant action of light. This phenomenon may be correlated with the increase in peroxide values in filtered oils.

The average fatty acids (FA) composition for filtered and unfiltered olive oils from each cultivar presented in Tables (3 and 4). For all olive oil samples, the fatty acid values were in accordance with **IOC (2016).** As reported in Tables (3 and 4), fatty acids composition were not affected by the filtration process. No differences were found among samples concerning $C_{18:1}/C_{18:2}$ and MUFA/PUFA ratios. These date agree with **Lozano-Sanchez *et al.* (2012) and Sacchi *et al.* (2015).**

During storage, fatty acids in EVOO undergo oxidative degradation. Lipid oxidation occurs by the interaction of lipids with molecular oxygen by a self-catalyzed mechanism **(Bendini *et al.*, 2006).**

Table 4: Fatty acids composition (%) of unfiltered and filtered Coratina cv. virgin olive oil.

Fatty acids	Coratina cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
$C_{16:0}$	13.17	12.98	12.4	13.18	13.2	13.12	12.92	11.76	13.15	13.37
$C_{16:1}$	0.63	0.61	0.52	0.63	0.63	0.68	0.61	0.49	0.62	0.64
$C_{17:0}$	0.05	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
$C_{17:1}$	0.07	0.07	0.06	0.07	0.07	0.07	0.07	0.06	0.06	0.06
$C_{18:0}$	2.38	2.44	2.54	2.43	2.45	2.34	2.44	2.66	2.45	2.44
$C_{18:1}$	70.22	70.50	71.02	70.43	70.51	70.19	70.53	71.34	70.43	70.44
$C_{18:2}$	11.42	11.35	11.34	11.28	11.19	11.43	11.38	11.43	11.31	11.12
$C_{18:3}$	0.94	0.88	0.88	0.85	0.82	0.95	0.91	0.88	0.85	0.82
$C_{20:0}$	0.50	0.51	0.54	0.48	0.48	0.53	0.50	0.59	0.48	0.48
$C_{20:1}$	0.49	0.49	0.51	0.47	0.47	0.51	0.46	0.56	0.47	0.46
$C_{22:0}$	0.13	0.13	0.14	0.13	0.13	0.13	0.13	0.18	0.13	0.12
Σ SFA*	16.23	16.10	15.67	16.27	16.31	16.17	16.04	15.24	16.26	16.46
Σ USFA**	83.77	83.90	84.33	83.73	83.69	83.83	83.96	84.76	83.74	83.54
MUSFA***	71.41	71.67	72.11	71.60	71.68	71.45	71.67	72.45	71.58	71.60
PUSFA****	12.36	12.23	12.22	12.13	12.01	12.38	12.29	12.31	12.16	11.94
$C_{18:1}/ C_{18:2}$	6.14	6.21	6.26	6.24	6.30	6.14	6.19	6.24	6.22	6.33
MUSFA / PUSFA	5.77	5.86	5.90	5.90	5.96	5.77	5.83	5.88	5.88	5.99

* SFA: Saturated Fatty Acids. ** USFA: Unsaturated Fatty Acids. *** MUSFA: Monounsaturated Fatty Acids. **** PUSFA: Polyunsaturated Fatty Acids

The qualitative and quantitative composition of hydrophilic phenols in VOO is strongly affected by technological conditions of its production. Several technological parameters can modify the phenolic concentration of VOO. For these reasons, the identification and the quantification of individual components of VOO have great interest.

Regarding oleuropein derivatives, as presented in Tables 5 and 6, there was increase in hydroxytyrosol and a difference in the formation rate of hydroxytyrosol was observed. Accordingly, the amount of this compound was higher in unfiltered oils than in filtered oils. This difference was increased with storage time until 9 months and then fell, clearly indicating that hydrolysis of complex oleuropein derivatives is great in unfiltered oils which could be explained by the deglycosilation of oleuropein, This is hydrolysis may be due to the action of b-glucosidase, presented by water. The formation of hydroxytyrosol is due to the rupture of the ester bond in the dialdehydic form of decarboxymethyloleuropein aglycon. This is a hydrolytic reaction, favored by the presence of water **(Fortini *et al.* 2016).** Filtration process slowed down the rate of secoiridoid aglycones

hydrolysis and the disappearing rate, due to the oxidation and nonoxidative degradation of this compound **(Fregapane *et al*. 2006).**

Table 5: Some phenolic compounds (mg/kg) of unfiltered and filtered Koroneiki cv. virgin olive oil.

Phenolic compounds	Koroneiki cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
Gallic acid	1.04	0.850	0.411	0.392	0.275	0.702	0.533	0.335	0.243	0.211
Pyrogallol	4.019	3.736	2.354	2.104	1.98	5.492	4.365	2.220	1.975	1.756
3-hydroxytyrosol	2.52	2.742	3.214	3.840	2.320	2.02	2.541	2.957	3.654	2.145
Protocatchouic	0.210	0.542	1.133	2.156	2.354	0.304	0.616	1.029	2.142	2.231
Catechin	0.576	0.610	0.554	0.322	0.245	0.494	2.286	0.552	0.352	0.274
Chlorogenic	0.732	0.760	0.865	0.549	0.325	0.443	0.731	0.489	0.378	0241
Catechol	0.930	0.798	0.531	0.314	0.210	0.662	0.518	0.253	0.142	0.095
Epi-Catechin	2.138	1.325	0.716	0.423	0.132	1.252	0.782	0.547	0.321	0.100
P-OH- Benzoic	3.791	2.578	1.254	0.127	0.00	5.472	3.580	1.548	0.371	0.00
Caffeic acid	0.127	0.037	0.051	0.032	0.022	0.127	0.103	0.057	0.034	0.025
Vanillic acid	0.978	0.756	0.202	0.200	0.158	2.381	0.422	0.391	0.314	0.275
P-Coumaric	0.423	0.289	0.164	0.098	0.059	0.891	0.647	0.357	0.138	0.064
Ferulic acid	0.490	0.360	0.245	0.155	0.108	0.636	0.472	0.316	0.130	0.115
Iso-Ferulic	0.613	0.199	0.092	0.053	0.045	1.534	0.408	0.117	0.097	0.084
Oleuropien	10.231	7.568	6.324	5.474	5.054	8.397	7.094	5.614	5.127	4.560
Ellagic	2.087	1.425	0.778	0.637	0.415	1.069	0.984	0.592	0.356	0.145
Coumarin	0.542	0.405	0.205	0.122	0.023	0.834	0.624	0.315	0.198	0.042
Salicylic	2.476	1.395	0.624	0.432	0.251	1.047	0.908	0.571	0.367	0.210
Cinnamic	0.286	0.313	0.163	0.152	0.110	0.338	0.378	0.137	0.143	0.106

Table 6: Some phenolic compounds (mg/kg) of unfiltered and filtered Coratina cv. virgin olive oil.

Phenolic compounds	Coratina cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
Gallic acid	0.333	0.158	0.124	0.110	0.103	0.313	0.277	0.142	0.098	0.051
Pyrogallol	12.368	9.662	5.253	3.561	1.739	9.660	5.848	2.275	1.987	1.125
3-hydroxytyrosol	3.24	3.451	3.425	3.941	2.524	2.96	3.211	3.284	3.784	2.235
Protocatchouic	0.404	0.821	0.918	1.145	1.234	0.323	0.775	0.856	0.987	1.123
Catechin	1.333	1.508	0.034	0.243	0.142	0.643	3.258	0.043	0.287	0.146
Chlorogenic	0.171	0.312	0.265	0.168	0.019	0.953	0.785	0.422	0.214	0.123
Catechol	0.713	0.547	0.365	0.140	0.033	0.987	0.776	0.541	0.367	0.168
Epi-Catechin	12.163	8.354	5.059	3.475	1.263	5.437	2.231	1.644	1.125	0.986
P-OH- Benzoic	1.597	0.854	0.488	0.033	0.000	3.025	1.472	0.956	0.224	0.000
Caffeic acid	0.571	0.254	0.052	0.025	0.005	0.261	0.073	0.065	0.047	0.024
Vanillic acid	0.513	0.614	0.205	0.142	0.016	0.609	0.704	0.209	0.152	0.043
P-Coumaric	0.244	0.208	0.112	0.052	0.012	0.697	0.542	0.246	0.145	0.139
Ferulic acid	0.343	0.234	0.175	0.122	0.007	1.102	0.458	0.263	0.176	0.140
Iso-Ferulic	0.251	0.172	0.160	0.098	0.004	0.367	0.197	0.180	0.110	0.082
Oleuropien	12.698	12.456	10.257	8.236	7.354	11.647	9.546	7.396	6.996	6.551
Ellagic	2.866	1.256	0.626	0.278	0.186	2.361	1.025	0.754	0.110	0.094
Coumarin	0.549	0.327	0.307	0.030	0.002	0.652	0.320	0.301	0.095	0.002
Salicylic	2.625	1.532	0.630	0.290	0.061	2.392	1.894	0.937	0.512	0.347
Cinnamic	0.241	0.442	0.148	0.046	0.007	0.325	0.668	0.178	0.114	0.088

Considering these results, it can be surmised that the oxidative stability of olive oil recorded low value after filtration, where water content is decreased, which occurred loss in phenolic compounds and reduction in their antioxidant activities. The decrease of antioxidant activity can be explained by the polar paradox, phenolic compounds, being polar molecules, have the highest activity in a water-in-oil emulsion. However after filtration the water content reduced. As consequence, the antioxidant capacity of these compounds diminished, probably due to their particular orientation around small droplets of water **(Gomez-Caravaca *et al*., 2007).**

From the results in Tables 5 and 6, the concentration of some phenolic compounds were increased after filtration. These increments may be related to the fact that filtration reduce the water content even though the loss of phenolic compounds was not proportional. In fact, it was assumed that the majority of phenolic compounds located around water droplets remain in olive oil **(Gomez-Caravaca *et al*., 2007).**

Oleuropein has been found at concentration of 12.6 mg/kg in unfiltered Coratina cv. olive oil higher than that of filtered oil (11.6 mg/kg). These findings were not agreement with **Fortini *et al*. (2016)** who, found that oleuropein and its derivatives, and derivatives of ligstroside were decreased in unfiltered oils. Usually, oleuropein was not detected or detected in trace in olive oils, few works reported that it had the highest of concentration about 10 mg/kg in the olive oil **(De Fernandez *et al*., 2014, Del Monaco *et al*., 2015, Fortini *et al*. 2016).** Oleuropein trend was decreased during storage. **Morellò *et al*. (2004)** found that phenolic compound content decreases significantly during storage.

Among the numerous phenols present in plants, the class of flavonoids is one of the most studied for their biological and pharmacological properties, comprising more than 6000 different compounds. These compounds have a complex structure with several functional groups. Four representative flavonoids were selected from the class of flavanones (hesperetin), isoflavones (genistein), and flavones (apigenin and luteolin) **(Ferreira and Pinho, 2012).**

Luteolin is one of the most common flavones. It is thought to play an important role in the human body as an antioxidant, a free radical scavenger, an agent in the prevention of inflammation, a promoter of carbohydrate metabolism, and an immune system modulator. These characteristics of luteolin are also believed to play an important part in the prevention of cancer. Multiple research experiments describe luteolin as a biochemical agent that can dramatically reduce inflammation and the symptoms of septic shock **(Xu *et al*., 2009).**

In the case of Luteolin, results in Tables (7 and 8) revealed that filtered oils had more content of luteolin than those in unfiltered oils. The flavones luteolin and apigenin were less polar compounds **(Boskou *et al*., 2006).** Although, luteolin used as antioxidant also its antioxidant activity was strong when combined with phospholipids. **Xu *et al*., (2009)** revealed that luteolin combined with phospholipids might result in an improvement of the lipophilic properties of luteolin. **Koidis and Boskou, (2006)** found that the filtration significantly reduces the phospholipids content in olive oils. These observations agree with oxidative stability of unfiltered oils which were higher than filtered oils. Luteolin contents were decreased during storage for 12 months at room temperature. Also, results revealed that Naringin contents were higher value in unfiltered oils than filtered oils. This may be due to the solubility of Naringin in water which had a bitter taste **(Pulley, 1936).**

Table 7: Some flavonoids compounds (mg/kg) of unfiltered and filtered Koroneiki cv. virgin olive oil.

Flavonoids compounds	Koroneiki cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
Luteolin	0.357	0.257	0.181	0.174	0.104	0.641	0.363	0.229	0.186	0.089
Naringin	0.696	0.486	0.269	0.180	0.125	0.300	0.236	0.113	0.055	0.000
Rutin	0.365	0.242	0.102	0.075	0.023	0.517	0.312	0.114	0.086	0.037
Hespirdin	0.655	0.417	0.250	0.130	0.108	0.962	0.625	0.464	0.164	0.124
Quecetrin	0.607	0.154	0.139	0.108	0.085	0.581	0.163	0.087	0.034	0.011
Quercetin	0.261	0.170	0.038	0.024	0.018	0.259	0.134	0.052	0.042	0.023
Naringenin	0.161	0.136	0.108	0.086	0.049	0.150	0.121	0.065	0.045	0.028
Apigenin	0.554	0.364	0.195	0.150	0.049	0.558	0.387	0.203	0.167	0.086

Table 8: Some flavonoids compounds (mg/kg) of unfiltered and filtered Coratina cv. virgin olive oil.

Flavonoids compounds	Coratina cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
Luteolin	0.263	0.221	0.159	0.076	0.009	0.428	0.251	0.210	0.145	0.086
Naringin	0.346	0.278	0.169	0.056	0.016	0.283	0.195	0.107	0.035	0.000
Rutin	0.187	0.123	0.086	0.031	0.005	0.195	0.143	0.121	0.098	0.009
Hesperidin	0.699	0.462	0.256	0.124	0.046	0.823	0.697	0.412	0.210	0.103
Quecetrin	0.472	0.296	0.250	0.198	0.175	0.315	0.225	0.213	0.185	0.123
Quercetin	0.412	0.347	0.201	0.154	0.021	0.671	0.465	0.227	0.174	0.086
Naringenin	0.406	0.340	0.234	0.167	0.033	0.356	0.254	0.147	0.098	0.010
Apigenin	0.523	0.310	0.183	0.126	0.008	0.547	0.325	0.230	0.166	0.012

Data in Tables (7 and 8) showed that rutin content was higher in filtered oils than those in unfiltered oils. The water solubility of rutin is low (0.125 g/L) **(Pedriali and Fernandes, 2008).** Also, the same trend found for hespirdin and apigenin.

Fat-soluble vitamins have important roles in several functions of the human body, such as vision (vitamin A), calcium absorption (vitamin D), antioxidative protection in cell membranes (vitamin E), and blood coagulation (vitamin K). These vitamins are substances often found associated in food and pharmaceutical **(Chen *et al*., 2011).** Results in Tables 9 and 10 revealed that vitamins A and D were not detected in olive oils. Also, results revealed that filtered oils had more vitamins (E and K) than those in unfiltered oils. According to storage time, data showed that the vitamins content were decreased with the increasing storage time. This reduction may be related to oxidation and hydrolysis as the result of storage process.

Table 9: Fat-soluble vitamins content (mg/kg) of unfiltered and filtered Koroneiki cv. virgin olive oil.

Vitamins	Koroneiki cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
A	ND*	ND	ND	ND	ND	ND	ND	ND	ND	ND
E	125.54	102.78	95.47	80.47	70.58	135.65	107.32	100.47	88.47	74.23
D	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
K	0.71	0.59	0.42	0.25	0.12	0.76	0.61	0.48	0.28	0.14

***ND: Not detected.**

Table 10: Fat-soluble vitamins content (mg/kg) of unfiltered and filtered Coratina cv. virgin olive oil.

Vitamins	Coratina cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
A	ND*	ND	ND	ND	ND	ND	ND	ND	ND	ND
E	122.45	104.36	96.65	85.54	75.62	140.33	110.10	103.23	90.56	80.23
D	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
K	0.52	0.35	0.22	0.15	0.08	0.57	0.39	0.25	0.17	0.10

***ND: Not detected.**

All olive oil samples were free of defects excepts for stored samples for 9 months. The sensory evaluation revealed that filtered oils remained fruity longer time than unfiltered oils (Tables 11 and 12). The sensory results agreed with **Fortini *et al*., (2016)** who, concluded that filtration enhances this sensory attribute. As the fruity attribute is closely linked to E-2-hexenal (the most abundant volatile compound) and Z-3- hexenal molecules which related to the lipoxygenase (LOX) pathway. On the other hand, the alcohols E-2-exenol and hexenal, and the ester E-2-hexenyl acetate were more abundant in unfiltered oils. This phenomenon could be explained by the inhibition of enzyme activity of alcohol dehydrogenase and alcohol acetyl transferase due to the removal of water during filtration, which, over time, preserves C6

aldehydes known to be responsible for the "green" aroma **(Fortini *et al*., 2016).**

Table 11: Sensory analysis of unfiltered and filtered Koroneiki cv. virgin olive oil.

Sensory attributes	Koroneiki cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
Defects	0.0	0.0	0.0	0.0	1.5 rancid	0.0	0.0	0.0	0.0	2.0 rancid
Fruity	5.5	5.0	4.0	3.0	2.0	6.0	5.5	4.5	3.5	2.0
Bitter	3.75	3.5	3	2	1.5	3.65	3.5	3.5	2.5	1.0
Pungent	4.5	4.5	3.5	2.5	1.5	4.0	4.0	3.5	2.5	1.0

Table 12: Sensory analysis of unfiltered and filtered Coratina cv. virgin olive oil.

Sensory attributes	Coratina cv.									
	Unfiltered olive oil					Filtered olive oil				
	Storage time (months)									
	Zero	3	6	9	12	Zero	3	6	9	12
Defects	0.0	0.0	0.0	0.0	1.0 rancid	0.0	0.0	0.00	0.00	1.5 rancid
Fruity	6.0	6.0	4.5	4.0	2.5	6.5	6.5	5.00	4.5	2.0
Bitter	4.25	4.00	3.0	2.5	1.5	4.00	4.00	3.5	3	1.0
Pungent	5.25	5.0	4.5	3.5	2.0	5.10	5.00	4.00	4	1.5

Tables 11 and 12 showed the results of panel test for the bitter and pungent attributes: The intensity of the bitter and pungent were higher in unfiltered oils than filtered oils, which in agreement with the content of oleuropein, its derivatives and naringin (Tables 5, 6, 7 and 8). Also, from the above Tables (11 and 12), it can be showed the results of the panel test for the rancid defect, which was higher in filtered oils than unfiltered oils.

4. Conclusions

This study can be concluded that the oxidation stability decreased after filtration due to elimination of water. This may be due to the decrease of concentration of total phenol content (high antioxidant activity), particularly hydroxytyrosol.

Therefore, it can be recommended that the filtration step should not be done in olive oil extraction steps for keeping the olive oil quality and its oxidative stability. So, packing of extra virgin olive oil must be done from storage tanks after aging step without filtration.

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