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review

Specific Components of Virgin Olive Oil as Active Participants in Oxidative Processes

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Summary

The oxidative changes in the chain of unsaturated fatty acids are the main problem of preserving quality and nutritive value of vegetable oils. According to numerous researches, virgin olive oil is one of the most stable oils. It is a complex system of active substances whose role in the oxidation processes is determined by their interactions and by influence of external factors. From this system we selected the most important components – phenolic substances, tocopherols, carotenoids, chlorophylls and oleic acid, and explained their importance in the oxidative changes of olive oil.

Keywords: virgin olive oil, oxidative processes, phenolic substances, tocopherols, carotenoids, chlorophylls

Introduction

In the last ten years and more a general trend toward correct and balanced nutrition has been observed in the world. Virgin olive oil has been unavoidable and favourable object of interest for many years, particulary the 70s, when it was again »discovered« in the Mediterranean diet. The exceptionality of olive oil comes from the fact that this oil is completely produced by plant metabolism. This is not the case with most edible oils which must previously be submitted to refining processes. From the fruit of *Olea europaea* olive oil is obtained which beside triglycerides contains a few hundreds of various components of unsaponifiable part. These components, although making up only 1–2% of the composition, are the main holders of exceptional sensoric, nutritional and some therapeutic characteristics of virgin olive oil.

The main problem in maintaining the quality and nutritive value of freshly produced olive oil, as well as of all vegetable oils, are oxidative changes in the chain of unsaturated fatty acids. The consequences which are noticeable to human senses are the changes of colour, the increase of viscosity and the development of unpleasant odour and taste, known as »rancidity«. However, this is only a top of an iceberg. Much more worrying is the harmful effect that some oxidation products have on human health. For that reason, it would be interesting to explain the importance of specific components of olive oil, primarily of phenolic components, tocopherols, chlorophylls and carotenoids. They take an active part in processes of oxidation and reduction, although the substratum itself, fatty acids, plays also an important role.

Oxidative Changes of Lipids

The phenomenon of lipid oxidation takes place if three conditions are accomplished:

1. presence and accessibility of oxygen,
2. presence of unsaturated bond in fatty acid chain, and
3. presence of sensitizers (reaction catalysts).

Depending on the type of sensitiser, the alterations can follow two ways: auto-oxidation and photo-oxidation. The complex mechanism and kinetics of these reactions have been studied by Farmer, Boland and Bateman (*1,2*). The auto-oxidation starts by free-radical mechanism, by homolytic bond cleavage of unsaturated fatty acid hydrocarbon chain (RH) and the creation of alkyl radical (R•):

$$RH \rightarrow R\cdot + \cdot H \qquad /1/$$

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This reaction is usually the initiation phase. Its activation energy is over 146.5 KJ/mol (35 kcal/mol) so it is thermodynamically very hard to be carried out without help of some sensitizer: light, heat, traces of metal ions (*e.g.* Fe and Cu), peroxides or enzyme lipoxygenase. Alkyl radicals are highly reactive, they react very quickly with oxygen (activation energy, in this case, is almost zero) creating hydroperoxide radicals (ROO•) by which starts the next phase in chain reaction – propagation (*1*):

$$R\bullet + O_2 \rightarrow ROO\bullet \qquad /2/$$

A faster way that leads to the creation of hydroperoxide radicals is photo-oxidation. In this case the catalysts are photosensitizers such as chlorophyll *a* or pheophytin *a*. They absorb the energy of light and transmit it to oxygen which changes into excited state (singlet oxygen). This one is about 1500 times more reactive than normal oxygen and it reacts directly with double bonds of unsaturated fatty acids.

During propagation period hydroperoxide radicals react with other fatty acids creating hydroperoxides (ROOH) (Reaction /3/). These molecules generally have no odour or taste, but they decompose into volatile compounds responsible for off-flavour: aldehydes, hydrocarbons and alcohols. Hydroperoxides can also decompose into hydroperoxide radicals and alcoxy radicals (RO•) (Reaction /4/).

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \qquad /3/$$

$$2\ ROOH \rightarrow RO\bullet + ROO\bullet + H_2O \qquad /4/$$

Finally, free radicals react together giving less harmful products:

$$ROO\bullet + ROO\bullet \rightarrow ROO\text{-}OOR \qquad /5/$$

$$ROO\bullet + R\bullet \rightarrow ROOR \qquad /6/$$

$$RO\bullet + R\bullet \rightarrow ROR \qquad /7/$$

$$R\bullet + R\bullet \rightarrow R\text{-}R \qquad /8/$$

Phenolic Components of Virgin Olive Oil

Phenolic components present in virgin olive oil are generally called *polyphenols*. First analytical procedures which used thin-layer chromatography and reactions of characterisation (*3,4*) pointed to existing *phenolic acids* (caffeic, *p*-coumaric, ferulic, *p*-hydroxybenzoic, protocatechuic, vanillic) as well as *phenolic alcohols*: tyrosol (main component which makes up to 40% of total phenolic fraction) and hydroxytyrosol (product of hydrolysis of oleuropeine glycoside) (*3*).

Later on gas chromatography with capillary column (*5*) and HPLC in reverse phase with UV-detector were used which enabled separation and identification of complex molecules: elanoic acid and derivatives of oleuropeine and ligstroside aglycon (*6–9*).

For quantitative determination of total polyphenols in virgin olive oils the method with the Folin-Ciocalteu reagent is used very often. However, this reagent is not specific because other readily oxidable substances can interfere. This value, which is expressed in mg/kg of gallic or caffeic acid, gives only an approximate information and for virgin olive oil it is from 50 to 500 mg/kg, while in olive fruit these values are from 20 to 100 g/kg, expressed on dry matter. The quantity of simple phenols in oil phase depends on a number of factors such as variety of olive, ripeness, duration of fruit storage, extraction technique and storing conditions of oil.

Phenolic substances in fruit are in the form of glycosides and esters, or they are bound in complex molecules, and therefore, they are weakly or not at all dissolved in oil. During ripening as well as during crushing and kneading, the hydrolytic enzymes liberate simple phenols that are partly dissolved in oil (*10*). The distribution equilibrium coefficient is shown by equation

$$K = [\text{phenols}]_{\text{water}} \,/\, [\text{phenols}]_{\text{oil}}\,,$$

where the value of coefficient K depends only on temperature. Higher temperature in kneading phase (about 30 °C) hastens dissolution of phenolic substances in oil, but the prolongation of this phase results in a decrease of phenols quantity in oil. This is probably due to very active phenoloxidases from olive fruit. They catalyze the oxidation of polyphenols in quinones and then the formation of polymers (*11,12*). The presence of colloidal structures (proteins, pectins, polysaccharides) to which phenolic substances are bound by hydrogen bonds and Van der Waals forces also leads to their loss with olive mill waste water (*13*). Usually, oils obtained by centrifugation have lower quantity of total polyphenols and *o*-diphenols in comparison with the oil obtained by pressing or percolation (*4,14–17*). This difference is due to addition of water to the centrifugal system, which disrupts the distribution equilibrium.

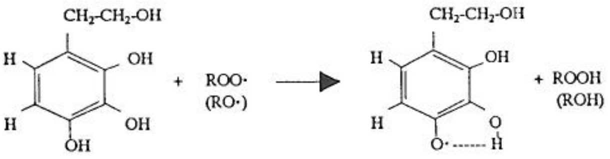
Mechanism of activity of phenolic antioxidants (PH) appears in physical quenching of free radicals which are the initiators of oxidation reactions. That is realised due to the fact that they are excellent donors of hydrogen and electrons (Reactions /9/ and /10/). Their radical intermediates – phenoxy radicals (P•) are stabilised by delocalization of unpaired electrons around aromatic ring. This fact prevents their oxidation in chain reaction /1/.

$$PH + ROO\bullet \rightarrow ROOH + P\bullet \qquad /9/$$

$$PH + RO\bullet \rightarrow ROH + P\bullet \qquad /10/$$

Not all phenolic components have the same antioxidative activity. A number of authors have investigated the antioxidative power of single phenolic components (*4,18–23*), and all agree that the most important are *o*-diphenols, especially hydroxytyrosol. According to Servili and Montedoro (*18*) its activity is 2–3 times higher than the activity of BHA and BHT. In fact, hydroxytyrosol is an *o*-diphenol whose phenoxy radical is stabilised by intermolecular hydrogen bond with another hydroxy group in *ortho*-position (*1*):

/11/



According to Papandopoulos and Boskou (*5*) antioxidative power of some phenolic substances from olive oil decreases in the following order:

hydroxytyrosol > caffeic acid >
protocatechuic acid > syringic acid >
p–hydroxybenzoic acid > tyrosol >
o–coumaric acid > vanillic acid.

The first three of them belong to a group of *o*–diphenols while tyrosol belongs to monophenols. Tyrosol is in a quantitative sense the main component of total phenolic fraction, but it shows almost no antioxidative activity.

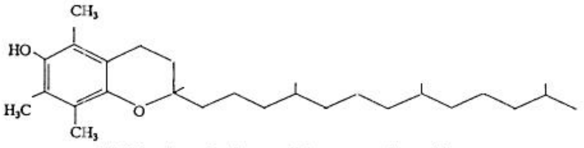
During the oil oxidation phenolic components are exposed to degradation, so they change into aldehydes, alcohols and ketones which can form dimers. Their dimers probably still keep antioxidative activity, as it was already proved for products of degradation of BHA and BHT (*1*).

As micronutrients, polyphenols are considered physiologic regulators of oxidative potential, so they are among of the most active eu-oxidants. They exhibit protective activities, particularly on liver (alleviating hepatopaty and experimental liver cirrhosis); they prevent creation of atherosclerotic plaques (*23*), probably by the inhibition of LDL oxidation (*24*). Polyphenols take a part in prevention of miocard infarct (*23*), they are credited with diuretic, hypoglycemic and antihypertensive properties (*25,26*), while oleuropein showed the effects of decreasing lipids and cholesterol in blood (*23*).

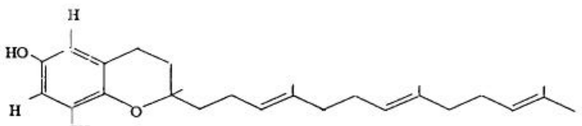
Phenolic substances are responsible for the characteristic fruity flavour and specific bitter and piquant taste whose balance and intensity are in direct relation with acceptability of olive oil. According to Vazquez Roncero (*27*) there is a good correlation between sensory characteristics and quantity of total polyphenols. The products of fatty acid oxidation (aldehydes and ketones), although in very low mass fraction (< 0,00002%), have a marked unpleasant taste and odour (*25*). It is clear that the presence of phenolic antioxidants is of a great benefit to organoleptic characteristics of olive oil.

Tocopherols

In this case we refer to monophenolic antioxidants. Eight different structures belonging to two groups are known: tocols and tocotrienols – with prefixes α-, β-, γ- or δ- depending on the number and position of methyl groups attached to chromane rings. Molecular structures of one tocol and one tocotrienol are shown in Fig. 1 (*1*).



5,7,8-trimethyl tocol (α-tocopherol)



8-methyl tocotrienol (δ-tocotrienol)

Fig. 1. Tocopherol and tocotrienol structure

Compared with other vegetable oils virgin olive oil does not contain a great fraction of total tocopherols. The richest oils are wheat germ oil, peanut oil and corn germ oil (Table 1). Tocopherol content in oil decreases with increasing degree of ripeness of olive fruits (*14,28*) and it depends on the processing. It has been observed that traditional systems (pressing) give oil richer in tocopherols (*14,15*).

Table 1. Mass fraction of tocopherols in some vegetable oils (*29*)

Oil from	w(total tocopherols)	w(α-tocopherol)
	mg/kg	mg/kg
Corn	1000	100
Soybean	900	150
Rapeseed	560	150
Sunflower	500	500
Peanut	220	110
Olive	140	110

From the nutritive point of view it is interesting to note that the major part of olive oil tocopherols (95%) is in α-form (*25*). Namely, α-tocopherol is known as vitamin E and it performs antioxidative activity *in vivo* (*30*). Considering values shown in Table 2. it can be concluded that biological activities and antioxidative properties of four main tocopherols are inversely proportional.

Recommended daily intake, which is enough to prevent the occurrence of symptoms of insufficiency in healthy adults is 15 I.U. (1 mg of α-tocopherol is equivalent to 1.49 I.U.) (*31*). However, the optimal quantity depends on fatty acids composition in diet. The complete information about oil nutritive value is obtained from the ratio of mass fractions α-tocopherol mg/kg ·100 : polyunsaturated fatty acids g/kg ·100, which should be above 0.8 (*30*) and which is 1.3 in the case of virgin olive oil (*32*).

Table 2. Biological and antioxidative activity of tocopherols (*29*)

	Biological activity	Antioxidative activity
α-tocopherol	100	100
β- tocopherol	33	110
γ- tocopherol	1	160
δ- tocopherol	1	170

In the organism, vitamin E is transported by lymph in the form attached to β-lipoproteins, while the main part is built into double phospholipid bilayer of cell membrane. Thanks to the very quick reaction of α-tocopherol with free radicals, polyunsaturated fatty acids in biological membranes are protected from radical attack. Hydroperoxide radicals affinity towards α-tocopherol is about 1000 times higher than it is towards polyunsaturated fatty acids in phospholipid bilayer (*33*). Tocopherol radicals that proceed from these cases can be recuperated by reductive cytoplasmatic systems such as ascorbic acid and glutathione (*34*). They can also transfer into stable tocopheryl quinones and dimers of α-tocopherol which still show antioxidative properties (*1*).

Tocopherol reactivity towards singlet oxygen can be compared to biological activity – proportion of relative quenching singlet oxygen velocity is α- : γ- : δ- = 100 : 69 : 38. This process of quenching is almost completely physical so one molecule of α-tocopherol can deactivate about 120 molecules of singlet oxygen before being destroyed (*25*).

All these characteristics give α-tocopherol an important role in the prevention of conditions caused by free radicals, such as cardiovascular and neurodegenerative diseases, chronic inflammations, and some forms of cancer (*34–37*), particularly of colon cancer (*23*).

Liposoluble Pigments

The olive oil colour originates from liposoluble pigments: chlorophylls and carotenoids. However, they are not included among the factors of quality in EU Regulation (*38*) and Trade Standards IOOC (*39*). The official method for organoleptic evaluation of virgin olive oil prescribes the use of dark glasses to avoid the observation of colour.

However, the role of chlorophylls and carotenoids in the occurrence of oil oxidation is very important. The data about their activity are contradictory, depending on the presence of lights and oxygen in researched system.

The mass fraction of β-carotene and other carotenoids in virgin olive oil ranges from 0.5 to 15.0 mg/kg. It depends on the variety of olive, ripeness grade of fruit, storage of fruit, as well as on the method of oil extraction (*40–42*). It has been noticed that the quantity of carotenoids in the olive fruit decreases during ripening as well as during the storage of fruits before oil extraction (*43*).

The amount of total carotenoids in olive oil can be determined by measuring the absorbance at 470 nm. Around this wavelength is the region where there is no interference of pheophytin and where there still exists the absorption of ionone ring in a carotenoid molecule. By chromatographic methods (TLC and HPLC) with previous separation from lipid part, eight different carotenoids were separated and identified in virgin olive oil. They are: auroxanthin, luteoxanthin, violaxanthin, neochrome, neoxanthin, and the major components: β-carotene and lutein (*44*).

In biological systems, that is in conditions of low partial pressure of oxygen, carotenoids behave as exceptionally active physical quenchers of singlet oxygen. One molecule of β-carotene is capable of capturing from 250 to 1000 molecules of singlet oxygen at a rate of $1.3 \cdot 10^{10}$ M^{-1} s^{-1}. This rate is a function of the number of conjugated double bonds in the polyunsaturated chain. Only carotenoids with ten and more conjugated double bonds can accept the energy from singlet oxygen (*25*). β-carotene is capable of accepting energy even from an excited sensitizer (particularly chlorophyll) which confirms its characteristic as exceptionally powerful inhibitor of photo-oxidation. It has been observed that degradation of carotenoids in olive oil exposed to light starts as late as after 14 days and the total degradation of β-carotene occurs after three months (*45*).

However, in the conditions of atmospheric concentration of oxygen, by auto-oxidation of carotenoids their radicals appear and final product of their degradation is a mixture of compounds with epoxy, hydroxyl and carbonyl groups. This explains the prooxidative proprieties of carotenoids in the simple model-systems of triglycerides when they are exposed to light and heat (*46–48*). Addition of other antioxidants, for example γ-tocopherol, even in very small quantities (*e.g.* 10 mg/kg, mass ratio 1 : 2 with regard to lutein) inhibits the prooxidative activity of lutein and also shows sinergic antioxidative effect (*47*). Since the ratio of α-tocopherol and total carotenoids in virgin olive oil is approximately 20 : 1, it can be expected that the risk of prooxidative activity of carotenoids is minimal.

On the other hand, antioxidant activity of β-carotene in physiological conditions of oxygen concentration explains its anticarcinogenic (*49,50*), provitaminic and antiulcer properties (*43*). Epidemiological studies have proved its protective role in cardiovascular illnesses. One of the supposed mechanisms by which β-carotene and vitamin A act against atherosclerosis is protection of endothelial integrity (*36,37*).

The quantity of total chlorophylls in virgin olive oil is in the range from 5 to 35 mg/kg (*40,42,43*). Similarly to other components discussed here, their quantity and composition depend on variety, ripeness grade of fruits, duration of fruit storage, extraction method and conditions of oil storage. The three-phase centrifugation system gives oils with higher quantities of chlorophyll pigments in comparision with the to two-phase system; the lowest quantities of chlorophyll are found in oils obtained by traditional systems (pressing) (*16,35,51*).

The quantity of total chlorophylls in oils can be determined by measuring the absorbance at 670 nm. Four components of this group of pigments were separated and identified by chromatographic techniques: chlorophyll *a*, chlorophyll *b*, pheophytin *a* and pheophytin *b* (*44*). Chlorophyll *a* prevails in unripe fruits (about 45% of total chlorophylls). During ripening it loses one atom of magnesium and changes into pheophytin *a*. In completely ripe fruits, pheophytin *a* prevalents and constitutes about 40% of total chlorophylls. The same type of change is observed during fruit storage after harvesting and during milling of olive fruits. It is supposed that these changes are the consequence of acid-catalysed reaction (pH value of milled fruits is about 5) and of lipoxygenase activity. This enzyme probably indirectly affects the degradation of chlorophylls by inducing the creation of fatty acids hydroperoxides in damaged cells of over-ripe or milled fruits (*41,44*).

Chlorophylls and their derivatives are well-known as photosensitizers. Even 6 mg/kg of chlorophylls in olive oil exposed to the fluorescent light, brings about fast oxidation. Prooxidative activity of chlorophyll is linked to its ability to transfer light energy to the triplet oxygen that changes into excited state. This activity is in direct function of concentration, but it also depends on the type of molecule: the strongest effect has pheophytin *b* and the weakest has chlorophyll *a*: (pheophytin *b* > pheophytin *a* > chlorophyll *b* > chlorophyll *a*) (*25*).

In darkness, the changes of concentration and composition of chlorophylls in virgin olive oil are very slow and they take months. The main characteristic of these changes is the loss of magnesium atom from the molecule, which enables the transformation of chlorophylls into pheophytins. Moreover, the antioxidative behaviour of chlorophylls in darkness is also observed. They probably act by quenching the free radicals in a way similar to α-tocopherol (*45*).

Fatty Acids of Virgin Olive Oil

The main characteristic of fatty acid composition of virgin olive oil is high fraction of oleic acid that comes up to 80%. It is considered to be one of the most easily digestible fatty acids, having the melting point above body temperature that enables the maximum hydrolysis velocity to pancreatic lipase.

In triglycerides of olive oil, oleic acid appears in the position 2 on glycerol in very high percentage (98–99%). This biochemical law also contributes to good digestibility, since 2-monoolein that is produced by pancreatic lipase, makes digestive micelle more stable (*52*).

Besides this, oleic acid is a powerful cholecystokinetic and it inhibits the creation of gallstone (*23,53*). Highly unsaturated lipids in diet can reduce total and LDL cholesterol in blood. A result of this is prevention of cardiovascular diseases. Oleic acid is preferable in this case because it does not reduce the level of »good« HDL cholesterol (*54*).

The quantity of other unsaturated fatty acids (linoleic and linolenic) is low. The ratio polyunsaturated : monounsaturated : saturated is about 0.5 : 5 : 1 in olive oil and about 5 : 2 : 1 in seed oils, while the optimal ratio in a balanced diet is 1 : 2 : 1 (*32*). Nevertheless, this gives olive oil an advantage in stronger potential resistance to oxidation. Its stability is also evident when one takes into consideration the oxidation rate that is 10 times higher for linoleic acid (18:2), and 20 times higher for arachidonic acid (20:4) than for oleic acid (18:1) (*30*).

Fatty acid peroxides are considered responsible for degradation of vitamins and for toxic effects observed in experimental animals: retarded growth, increase of kidney and liver volume, irritation of gastroenteric mucous membrane and inhibition of lipid absorption (*52*).

Fatty acids, albeit insignificantly, affect also the sensory properties. It was observed that good sensory quality can be expected when the fraction of oleic acid is over 73%, of linoleic acid above 10% and when the ratio oleic acid : linoleic acid is not above 7 (*52*).

Conclusions

Virgin olive oil is a complex system of active substances whose role in the oxidation processes is determined by their mutual interactions and by the influence of external factors: light, heat and oxygen concentration.

Thanks to the particular proportion among polyunsaturated, monounsaturated and saturated fatty acids (0.5:5:1), olive oil has the advantage over most vegetable oils.

Phenolic components can be considered as unique protection arm of virgin olive oil. They act by physical quenching of free radicals almost without influence of any external factors. In this way they inhibit the appearance of rancid off-flavour and they are responsible for the pleasant organoleptic properties.

The quantity of the other important group of antioxidants – tocopherols is relatively small if compared with other vegetable oils. The main form is α-tocopherol that has the weakest antioxidative but the highest biological activity. It can be supposed that polyphenols protect the vitaminic proprieties of α-tocopherol during the storage of oil by physical quenching of free radicals.

The role of carotenoids in oxidative processes is not entirely explained. Despite the high power of singlet oxygen quenching in biological environment, carotenoids in simple model system and in conditions of higher partial pressure of oxygen manifest prooxidative properties. Due to the favourable ratio between carotenoids and α-tocopherol in virgin olive oils, these properties are revealed during the storage of oil, especially if air admission is reduced by suitable packaging.

Chlorophylls, which give virgin olive oil its recognisable green colour, are photosensitizers. In presence of light they act as prooxidants, whereas in the darkness they manifest antioxidative properties. Also in this case, the process of oxidation can be controlled by choosing the suitable packaging.

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Specifični sastojci prirodnog maslinovog ulja u ulozi aktivnih sudionika u procesima oksidacije

Sažetak

Oksidacijske promjene na lancu nezasićenih masnih kiselina glavni su problem očuvanja kakvoće i prehrambene vrijednosti biljnih ulja. Prema brojnim istraživanjima, prirodno maslinovo ulje pokazalo se u tom smislu jednim od najstabilnijih ulja. Radi se o složenom sustavu aktivnih tvari čija je uloga u procesima oksidacije određena njihovim međudjelovanjem, te utjecajem vanjskih čimbenika. Iz tog su sustava, kao najvažniji, izdvojeni fenolni sastojci, tokoferoli, karotenoidi, klorofili i oleinska kiselina te je obrazložena njihova važnost pri oksidacijskim promjenama maslinovog ulja.