

Frying performance of olive-extracted oils

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SUMMARY: In this article, the main studies on frying performance of olive-extracted oils, namely, virgin olive oils, olive oils and olive-pomace oils, are reviewed and discussed in relation to other vegetable oils. Firstly, the most relevant compositional data of olive-extracted oils and commonly used vegetable oils are reported, including modified seed oils developed for frying uses. The influence of the degree of unsaturation and of the minor compounds with protective effect during frying are discussed, with special reference to tocopherols, other phenolic compounds, phytosterols and squalene. Results on comparative behavior of olive-extracted oils and other vegetable oils reflect that all olive-extracted oils show great stability to thermal oxidation and are highly suitable for frying, due to their high content of oleic acid, low content of polyunsaturated fatty acids and occurrence of minor components with antioxidant activity or protective effects. Among olive-extracted oils, the scarce information published on used frying pomace-olive oils is noted.

KEYWORDS: *Frying; Olive oil; Olive-pomace oil; Virgin olive oil*

RESUMEN: *Comportamiento en fritura de los aceites extraídos de la aceituna.* En este artículo se revisan los principales estudios sobre el comportamiento en fritura de los aceites extraídos de la aceituna, es decir, aceites de oliva virgen, de oliva y de orujo de oliva. En primer lugar se describe su composición, así como la de los aceites vegetales más utilizados y los aceites de semillas modificadas, y se comenta la influencia en fritura del grado de insaturación y de los componentes menores del aceite, especialmente tocoferoles, otros compuestos fenólicos, fitoesteroles y escualeno. Los estudios realizados en comparación con otros aceites vegetales reflejan la gran resistencia de los aceites extraídos de la aceituna a la oxidación térmica y su aptitud para la fritura, debido a sus altos contenidos en ácido oleico, bajos niveles de ácidos grasos poliinsaturados y presencia de componentes menores con actividad antioxidante o protectora. Entre los aceites extraídos de la aceituna, el comportamiento del aceite de orujo de oliva es el menos estudiado en fritura.

PALABRAS CLAVE: *Aceite de oliva; Aceite de oliva virgen; Aceite de orujo de oliva; Fritura*

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1. INTRODUCTION

Frying is one of the most popular methods for the preparation of foods in developed countries, on a domestic as well as on industrial level. It is a complex process that involves a high number of reactions due to the action of oxygen, high temperature and the water released by the food, which lead to organoleptic changes, increase of viscosity, foaming, darkening and decrease of the smoke point. Although there are many methods to measure these changes, the only method that evaluates the total pool of non-volatile degradation compounds formed is the polar compounds determination. Hence it is an official method included in all the countries where frying oils are fully regulated and its limit is normally established at 25% polar compounds (Firestone, 2007). Determination of polymers, the main components of the polar compounds formed during frying, is also included in regulations of certain countries (Firestone, 2007).

Oil degradation during frying depends on the oil composition, namely, the degree of unsaturation, free fatty acidity and antioxidants/prooxidants contents, as well as on factors related to the process conditions, namely, the length of heating, temperature and surface-to-oil volume ratio, and on the nature and composition of the food being fried (Márquez-Ruiz *et al.*, 2010). In discontinuous frying (domestic frying, frying in restaurants and fried-outlets), temperature, length of heating and the lack of protection of the oil by the food between frying operations greatly enhance alteration. It is essential to maintain the surface-to-volume ratio since its increase enhances the contact with air oxygen and thus oxidative reactions. However, in continuous frying (industrial frying), the food is constantly present in the fryer and oil is continuously replenished to compensate for that absorbed by food. In this case, the turnover period (time required for oil used to equal the oil in the fryer) is an essential factor and should be low (< 10–12 h) to maintain oil high-quality in the long term.

The suitability of oil for frying is mostly related to its resistance to thermal oxidation, but price, availability and functional properties are also important factors for its selection. As mentioned above, the main variables associated to the oil influencing oxidation during frying are the degree of unsaturation and the content/nature of minor compounds with protective effects, and these will be discussed below with special focus on olive-extracted oils.

2. CHARACTERIZATION OF OLIVE-EXTRACTED OILS AND MOST GLOBALLY USED OILS

Table 1 lists the most relevant compositional data, including typical ranges, found for the olive-extracted oils (virgin, refined and refined olive-pomace) and

the vegetable oils more generally used worldwide (Bockisch, 1998; Gunstone, 2002; Graciani, 2006; Erickson, 2007; White, 2008; García-González *et al.*, 2013; Boskou, 2015). Extra virgin and virgin olive oils only differ in free acidity values from the chemical viewpoint and their compositions are within similar ranges, hence have been considered together in the table. Refined olive oil and refined olive-pomace oil are included but not the commercially available blends of refined olive oil with virgin olive oil and refined olive-pomace with virgin olive oil which composition in minor compounds may vary depending on the amount and composition of the virgin olive oil added. Besides main fatty acid composition, the most important minor unsaponifiable compounds, i.e., tocopherols, sterols and squalene, have been included. As can be observed, the ranges of concentrations reported are considerably broad in general, due to varietal differences, geographical location, soil type, climate, state of maturity and agricultural practices. As to production volume, palm oil, soybean oil, rapeseed/canola oil and sunflower oil are, in that order and by far, the most important oils in the world (Oil World Annual, 2017). But, apart for traditional oils, there are nowadays new types of vegetable oils obtained from genetically modified seeds and, also, many blends of oils are commercialized. These new oils and blends have the common objective of providing altered fatty acid patterns to improve unsaturation profile in nutritional terms and from the stability standpoint (Hosseini *et al.*, 2016).

As shown in Table 1, all olive-extracted oils, including virgin olive oils, refined olive oils and refined olive-pomace oils, clearly stand out for their high content of oleic acid and low content of polyunsaturated fatty acids (linoleic and linolenic acids). Only palm oil shows even lower contents of polyunsaturated fatty acids. The great variability in fatty acid composition found among olive-extracted oils is not associated with categories but instead is the result of olive varietal differences and other factors (Boskou *et al.*, 2006; García-González *et al.*, 2013).

Regarding minor unsaponifiable compounds, amounts of squalene are much greater in all olive-extracted oils than in the rest of vegetable oils. And, among sterols, olive-extracted oils are primarily composed by β -sitosterol, and this only occurs also in cottonseed oil (Graciani, 2006; Boskou, 2015).

The refining process does not greatly affect the amounts and compositions of tocopherols and sterols (phytosterols) in olive-extracted oils. Thus, levels of tocopherols are similar for virgin olive oils, refined olive oils and refined olive-pomace oils. With respect to phytosterols, amounts are higher in refined olive-pomace oils than in refined olive oils because such compounds are more abundant in crude olive-pomace oil than in crude olive oil (Antonopoulos *et al.*, 2006). Also as a result of refining, the hydrocarbon fraction of phytosterols suffers certain changes, these

TABLE 1. Main compositional characteristics of olive-extracted oils and most used vegetable oils.

	Olive											
	Extra virgin & virgin	Refined	Refined olive-pomace	Palm	Soybean	Sunflower	Canola	Corn	Rice bran	Cottonseed	Peanut	
Fatty acids (%)												
14:0	< 0.1			0.5-5.9	< 0.5	< 0.5	< 0.2	< 0.1	< 0.5	0.4-2.0	< 0.1	
16:0	7.5-20.0		32.0-59.0	7.0-14.0	3.1-10.2	3.1-10.2	2.5-6.0	6.0-19.4	16.4-25.5	16.9-31.1	6.0-14.1	
16:1	0.3-3.5		< 0.6	< 0.5	< 0.1	< 0.1	< 0.6	< 0.5	< 0.3	0.5-2.0	< 0.5	
18:0	0.5-3.5		1.5-8.0	1.5-5.5	1.2-10.0	1.2-10.0	0.9-2.1	0.5-4.0	2.1-3.0	1.0-4.2	2.5-6.3	
18:1	56.0-83.0		27.0-52.2	19.0-30.0	13.9-44.8	13.9-44.8	50.2-66.0	19.4-49.8	37.4-43.8	13.1-43.8	46.8-62.0	
18:2	3.5-20.0		5.0-14.0	44.0-62.0	40.3-75.2	40.3-75.2	18.0-30.1	44.3-71.9	31.1-34.0	33.0-59.2	25.3-34.0	
18:3	< 1.5		< 1.5	4.0-11.0	< 0.7	< 0.7	2.0-14.2	< 2.0	< 1.2	0.1-2.1	< 1.0	
Unsaponifiable (%)	0.8-1.5	0.4-0.8	1.0-2.0	0.2-0.5	0.5-1.0	0.5-1.0	0.8-1.0	0.8-1.4	3.0-5.0	0.6-1.5	0.3-0.7	
Total Tocopherols (mg/kg)	110-300	150-300	185-300	350-730	720-1360	510-697	255-660	477-671	413	630-700	339-466	
α	105-152	125-160	150-160	168-330	37-110	460-630	70-190	121-168	322	322-354	77-169	
β	-	-	-	-	18-35	10-15	-	0-19	-	-	5-16	
γ	7-23	12-20	18-20	160-320	497-792	30-40	178-430	346-458	91	308-346	144-241	
δ	10-20	13-20	17-20	< 70	168-423	10-12	7-40	10-26	-	-	13-40	
Total Sterols (mg/kg)	800-2400	1000-2000	1800-3000	70-320	1300-2200	2500-4000	3500-5000	5800-10000	15000	2600-5900	900-2900	
Brassicasterol (%)		< 0.1	< 0.2	-	< 1	-	10-23	-	-	< 1	< 0.5	
Campesterol (%)	4	< 4	< 4	19-21	19-23	8-11	28-40	16-21	25	4-8	11-19	
Stigmasterol (%)	< 1	< 4	< 4	11-13	17-19	7-10	< 1	4-10	14	< 1	5-13	
β -sitosterol (%)	84	> 93	> 93	56-69	47-59	58-64	45-61	63-70	51	86-93	48-66	
Δ^5 Avenasterol (%)	10	-	-	2-3	2-4	2-7	5	1-9	5	2-3	7-19	
Δ^7 Stigmasterol (%)	< 1	< 0.5	< 0.5	1-2	1-3	9-14	1-3	< 1	1	< 1	1-5	
Δ^7 Avenasterol (%)	-	-	-	1-2	1-2	4-6	-	< 1	-	< 1	1-6	
Squalene (mg/kg)	900-12000	500-6000	500-6000	200-700	20-120	80-190	30-280	160-420	300	30-150	20-490	

Data obtained from Bockisch, 1998; Gunstone, 2002; Graciani, 2006; Erickson, 2007; White, 2008; García-González *et al.*, 2013 and Boskou, 2015.

are, a considerable amount of squalene is removed and some new hydrocarbon derivatives are formed. Still, as commented before, amounts of squalene remaining in refined olive oil and refined pomace-olive oil are very high (Nergiz and Celikkale, 2011).

The refining process also removes polyphenols and triterpenic acids (Ruiz-Méndez *et al.*, 2013). Contents of polyphenols are high in virgin olive oils although levels vary greatly (200–800 mg/kg), as well as in crude olive-pomace oil (400–700 mg/kg), are almost absent in refined olive oils and refined olive-pomace oils and found at about 400 mg/kg in commercial olive oils and about 150 mg/kg in commercial olive-pomace oils (García *et al.*, 2003; 2006; Brenes *et al.*, 2004), but these figures may vary depending on the amounts of phenolic compounds in the initial crude oils and in the virgin olive oils added. The most abundant phenolic compounds found in olive oils are secoiridoid derivatives (the dialdehydic form of decarboxymethyl ligstroside aglycone, the dialdehydic form of the decarboxymethyl oleuropein aglycone, the aldehydic form of oleuropein aglycone and the aldehydic form of ligstroside aglycone), lignans (pinoselinol and 1-acetoxypinoselinol), together with hydroxytyrosol and tyrosol formed by hydrolysis of their corresponding secoiridoid derivatives (Mateos *et al.*, 2001).

In the case of crude olive-pomace oil, the longer the storage period of “alpeorujó” (the resulting by-product from two-phase extraction of olive oil), the higher the content of phenolic compounds in the oils extracted, reaching levels about 900 mg/kg in some oils extracted by second centrifugation. In such oils, the most relevant phenolic compounds are hydroxytyrosol, hydroxytyrosol acetate, tyrosol, catechol, 4-ethylphenol, vanillin and the lignans pinoselinol and 1-acetoxypinoselinol. However, lower amounts are present in olive-pomace oils extracted with hexane being hydroxytyrosol, its acetate and lignans the most representative (Brenes *et al.*, 2004). 4-Ethylphenol is a volatile phenol with strong, unpleasant odor which is generally formed by microorganisms. It is present in crude olive-pomace oils in about 50 mg/kg but may reach very high concentrations (about 400 mg/kg) in oils extracted by second centrifugation of “alpeorujó” stored for 8 months.

Although in very low amounts, there are some phenolic acids present in seed oils. Corn and cottonseed oils contain ferulic acid, as an ester of dihydro- β -sitosterol (about 6 mg/kg) in the former. Cottonseed oil also contains *trans-p*-cumarinic acid (present in peanut and soybean oils as well), *p*-hydroxybenzoic acid and *trans*-caffeic acid. Besides, canolol is present in canola oil. Nevertheless, it must be stressed that the phenolic content of seed oils is much lower than that in olive and olive-pomace oils (Colquhoun, 1996; Hidalgo *et al.*, 2002).

As to triterpenic acids, only average amounts of 200–500 mg/kg are found in extra virgin and virgin

olive oils while as much as 2000–10,000 mg/kg can be found in crude olive-pomace oils as a result of enrichment during storage of “alpeorujó” (Pérez-Camino and Cert, 1999; García *et al.*, 2008; Ruiz-Méndez *et al.*, 2013). Regarding the relative abundance of maslinic and oleanolic acids, it has been reported that both triterpenic acids can be extracted at high concentrations by means of centrifugation instead of solvent extraction with hexane (García *et al.*, 2008). Since most of triterpenic acids are lost during refining (García *et al.*, 2006), a new procedure of physical refining has been patented to obtain an edible oil with high concentration in triterpenic acids from olive-pomace oils obtained by centrifugation (Ruiz-Méndez *et al.*, 2008).

Also as a consequence of the storage of “alpeorujó”, crude olive-pomace oil is enriched in triterpenic alcohols (erythrodiol and uvaol), waxes and aliphatic fatty alcohols (García *et al.*, 2008). These compounds are constituents of the fruit skin therefore higher concentrations are found in olive-pomace oil, especially after solvent extraction. In fact, erythrodiol and uvaol are normally used as markers for detection of olive-pomace oil in olive oils and are limited in olive oils in 4.5% of the sterol fraction. Aliphatic fatty alcohols increase during the storage of “alpeorujó” in large ponds, reaching amounts as high as 6000 mg/kg in crude olive-pomace oils. After refining, aliphatic alcohols also result from the hydrolysis of waxes that occurs in the saponification step. Ultimately, considerably high amounts of both groups of alcohols remain in refined olive-pomace oil (about 500 mg/kg of triterpenic alcohols and 2000–2500 mg/kg of aliphatic fatty alcohols), being always higher than those in refined olive oil (García *et al.*, 2008).

3. EFFECT OF DEGREE OF UNSATURATION OF OLIVE-EXTRACTED OILS ON FRYING

Oils are mostly triacylglycerols (95–98%) and the unsaturated allylic bonds of their esterified fatty acids are active sites that can react with oxygen, hence susceptibility to alteration during frying increases exponentially as the number of double bonds is higher. For the reaction with air oxygen, it is required that a hydrogen is removed from the carbon adjacent to the double bond in the fatty acid esterified in triacylglycerols and the strength of hydrogen-carbon bonds depends on their position respect to the double bond, what explains the great differences of oxidation rates of oleic (18:1), linoleic (18:2) and linolenic (18:3) acids. Stable frying oils usually require low linolenic acid (<3%), increased oleic acid (>40%) and decreased linoleic acid (<50%) (Márquez-Ruiz *et al.*, 2010). The excellent frying properties of virgin olive oils are well established and are in great part due to the high-oleic acid content (Chiou and Kalogeropoulos, 2017). As already

commented, all oils derived from olives, including virgin olive oils, olive oils and olive-pomace oils, show similar fatty acid composition and variability found depends mostly on olive variety and other factors.

Hydrogenation and genetic modification are two of the processes intended to decrease the unsaturated fatty acids of frying oils. However, hydrogenation gives rise to undesirable *trans* fatty acids which occurrence in foods now requires its inclusion on the labels in many countries. Besides, hydrogenation produces metallic flavor and does not improve the quality of oils with low linolenic acid (Choe and Min, 2007).

Recently, a plethora of modified seed oils and oil mixtures have been proposed to achieve the desired balance of fatty acids, including high-oleic, high-palmitic and low-linoleic modified seed oils and mixtures of two, three and even four oils (canola, palm olein, corn oil and others) in different proportions (Gunstone, 2002; Hosseini *et al.*, 2016). Some of these mixtures are labelled as “special oils intended for frying” and often contain the antifoaming additive dimethylpolysiloxane (DMPS).

Figure 1 includes, for comparative purposes, average values of fatty acids (FA) expressed as saturated FA, oleic acid (18:1), linoleic acid (18:2) and linolenic acid (18:3) in olive-extracted oils and in the main modified seed oils and oil blends commercialized or recently developed for frying uses (Gunstone, 2002; Graciani, 2006; Hosseini *et al.*, 2016).

The oils coming from modified sunflower and canola (low-erucic rapeseed) seeds are widely commercialized in Europe and the United States. Among modified seed oils, high-oleic sunflower (HOSO) and high-oleic canola oils (HOCO) achieve very similar, high-oleic acid content to that of olive-extracted oils, although show slightly higher values of linolenic acid. However, other modified canola oils such as LLnCO (low-linolenic canola oil) and HOLLnCO (high-oleic low-linolenic canola oil) contain more linoleic acid (Hosseini *et al.*, 2016). With lower costs than high-oleic sunflower oil and about 65% oleic acid, medium-oleic sunflower oil (MOSO) was commercialized in the United States with great success in 1998 (Gunstone, 2002). Medium-oleic canola oil (MOCO) shows similar fatty acid composition. More recently, high-oleic high-palmitic sunflower oil (HOHPSO), also with about 65% oleic acid, but with increased levels of palmitic acid (25%) and only 2% linoleic acid, has shown excellent frying performance (Marmesat *et al.*, 2005, 2008).

With respect to oil blends, although there are many others proposed (Hosseini *et al.*, 2016), Figure 1 includes those most common. Mixtures generally contain palm olein, which is the liquid fraction obtained by fractionation of palm oil and has been largely used in industrial deep-frying because of its adequate fatty acid profile, i.e., 39–45% oleic acid, 10–13% linoleic acid and linolenic acid lower than 1%. In fact, palm olein is often used in binary

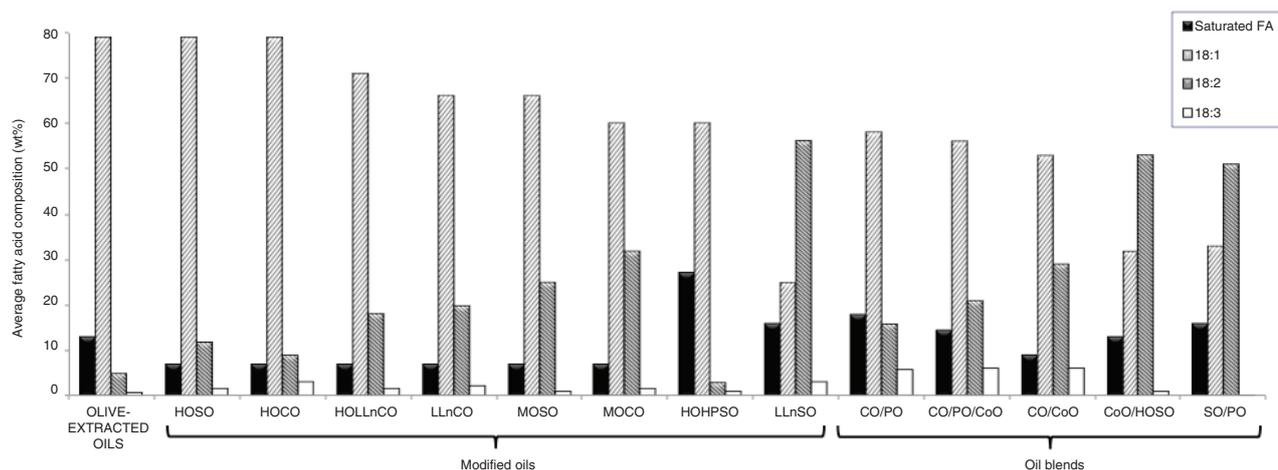


FIGURE 1. Average fatty acid composition expressed as saturated fatty acids (FA), oleic acid (18:1), linoleic acid (18:2) and linolenic acid (18:3) in olive-extracted oils, modified seed oils and oils blends.

Abbreviations: HOSO, high-oleic sunflower oil; HOCO, high-oleic canola oil; HOLLnCO, high-oleic low-linolenic canola oil; LLnCO, low-linolenic canola oil; MOSO, medium-oleic sunflower oil; MOCO, medium-oleic canola oil; HOHPSO, high-oleic high-palmitic sunflower oil; LLnSO, low-linolenic sunflower oil; CO/PO, canola oil/palm olein mixture; CO/PO/CoO, canola oil/palm olein/corn oil mixture; CO/CoO, canola oil/corn oil mixture; CoO/HOSO, corn oil/high-oleic sunflower oil mixture; SO/PO, sunflower oil/palm olein mixture.

Data obtained from Gunstone, 2002; Graciani, 2006 and Hosseini *et al.*, 2016

blends with canola oil or sunflower oil and also in trinary blends (see mixtures canola oil/palm olein (CO/PO), canola oil/palm olein/corn oil (CO/PO/CoO) and sunflower oil/palm olein (SO/PO) in Figure 1). It is also worthy to note that some blends contain linoleic acid as major fatty acid (over 50%), as corn oil/high-oleic sunflower oil (CoO/HOSO) and sunflower oil/palm olein (SO/PO), and still are commercialized as “special oils for frying”.

The frying performance and stability depends on the overall composition of oil, including the unsaturation degree and the contribution of minor compounds with antioxidant action present in the unsaponifiable fraction. Therefore, the studies of interest on the effect of unsaturation degree evaluate the performance of oils from modified seeds with changed fatty acid composition as compared to that of their homologous, conventional oils therefore maintaining similar unsaponifiable fractions (Dobarganes *et al.*, 1993; Normand *et al.*, 2001; Guinda *et al.*, 2003; Marmesat *et al.*, 2008; Warner and Fehr, 2008). Results have commonly shown that the oil performs better as the degree of unsaturation is lower. Also, removal of tocopherols and other minor compounds stressed the great influence of the fatty acid composition (Lampi and Kamal Eldin, 1998; Barrera-Arellano *et al.*, 2002; Steel *et al.*, 2005, 2006).

4. EFFECT OF MINOR COMPOUNDS PRESENT IN OLIVE-EXTRACTED OILS ON FRYING

Many naturally occurring minor compounds in olive-extracted oils show antioxidant activity, and their capacity to protect oils under frying conditions has been discussed in recent reviews (Márquez-Ruiz *et al.*, 2014; Aladedunye, 2014). Among them, four groups of compounds are of special relevance; namely, tocopherols, polyphenols, phytosterols and squalene.

4.1. Tocopherols

Tocopherols and tocotrienols constitute a family of natural, structurally related compounds which are also called globally vitamin E. Tocopherols are the main natural antioxidants occurring in edible oils and are also used as additives in frying oils to improve their oxidative stability. They constitute the lipophilic antioxidant group and mainly act as chain breakers by donating a hydrogen radical to the alkylperoxyl radicals formed during the propagation step of lipid oxidation, forming subsequently a stable radical. The tocopherol content of virgin olive oils is highly variety-dependent and usual values reported range between 100 and 300 mg/kg (Velasco *et al.*, 2002). Once refined, tocopherols are partly lost hence amounts about 200 mg/kg are

normally found in refined olive oil and refined olive-pomace oil.

The loss of tocopherol at frying conditions is, in general, faster as the degree of oil unsaturation is lower (Yuki and Ishikawa, 1976; Jorge *et al.*, 1996a, 1996b). However, the opposite is found at storage temperatures and even at about 100°C, as in the accelerated tests used to evaluate oxidative stability (Yuki and Ishikawa, 1976; Martín-Polvillo *et al.*, 2004; Márquez-Ruiz *et al.*, 2008). These studies demonstrate that a mechanism dependent on temperature is involved in their action and an important practical consequence from this fact is that oxidative stability values obtained in Rancimat, normally at 100–120°C, are not indicative of the stability during frying. However, a method using the Rancimat apparatus that allows estimating the comparative stability of oils in frying has been proposed (Barrera-Arellano *et al.*, 1997; Márquez-Ruiz *et al.*, 2014). Briefly, conditions established are temperature set at 180°C, no air bubbling, oil samples in tubes at a surface-to-oil volume ratio close to that in domestic frying and analysis of polar compounds or polymers after 10–15 hours.

Another interesting conclusion on tocopherols efficacy in frying obtained in experiments using different oils is that tocopherols are exhausted in monounsaturated oils at lower oil degradations (Barrera-Arellano *et al.*, 2002; Verleyen *et al.*, 2002). When monounsaturated oils only have tocopherols as antioxidants, as occurs in most vegetable oils except for olive-extracted oils, and become unprotected at polar compounds levels much lower than the limit established in official regulations, the resulting fried products maintain good quality but may be more susceptible to oxidation during commercialization and storage (Márquez-Ruiz *et al.*, 1999). This is an important aspect often ignored, which would be advantageous for olive-extracted oils in terms of frying since they contain additional minor compounds with protective effects such as polyphenols, phytosterols and squalene.

With respect to the relative stability of the different forms of tocopherol at frying temperature, there is general agreement that δ -tocopherol is more stable than α -tocopherol, whereas β - and γ -tocopherols degrade at an intermediate rate (Barrera Arellano *et al.*, 2002; Warner and Moser, 2009). As a result, new sunflower lines have been developed to increase levels of γ -tocopherol as the major natural antioxidant instead of the α -tocopherol characteristic of the standard sunflower oil (Velasco *et al.*, 2004). In particular, a modified sunflower seed oil with increased levels of oleic acid and palmitic acid, and enhanced proportion of γ -tocopherol (>95% of the total tocopherols) has been found highly stable at frying temperatures (Marmesat *et al.*, 2008).

4.2. Phenolic compounds/Polyphenols

Phenolic compounds (others than tocopherols) and polyphenols act as primary antioxidants by similar mechanism of action to that of tocopherols and constitute the hydrophilic antioxidant group. They are present in significant amounts only in virgin oils since they are practically lost during refining. The pool of phenolic compounds in virgin olive oils is composed by several classes, namely; phenolic acids (hydroxybenzoic and hydroxycinnamic acid derivatives), phenylethyl alcohols (tyrosol and hydroxytyrosol), flavonoids (apigenin, luteolin), lignans (pinoresinol and 1-acetoxypinoresinol) and secoiridoids (Bendini *et al.*, 2007). Total phenolic compounds in virgin olive oils are highly variable, ranging from 100 to 800 mg/kg (Visioli *et al.*, 1998; Kalogeropoulos and Tsimidou 2014; Boskou, 2015). Mean values of 500 mg/kg (Montedoro *et al.*, 1992), or levels between 50 and 200 mg/kg (Boskou *et al.*, 2006) have been reported. Such phenolic compounds are partly responsible for the improved frying stability reported for olive oils and their blends with conventional oils such as sunflower and canola oils (Casal *et al.*, 2010; Abdel-Razek *et al.*, 2011).

As already commented, amounts of phenolic compounds are higher in crude olive-pomace oils obtained by second centrifugation than in those extracted with hexane, being hydroxytyrosol, hydroxytyrosol acetate and pinoresinol found in similarly higher amounts than catechol, tyrosol and 1-acetoxypinoresinol (Brenes *et al.*, 2004). The complete refining process of crude olive oil and crude olive-pomace oil removes most polyphenols and therefore those present in commercial olive oil and olive-pomace oil come mostly from the virgin olive oil present in the blends (García *et al.*, 2003, 2006).

There are a large number of interesting studies focused on the relative or synergic effect of polyphenols and tocopherols. Analyses of the losses of tocopherols and polyphenols during frying have reported the highest rate of degradation for hydroxytyrosol and its derivatives, similar or intermediate rates for α -tocopherol and lowest degradation rates for tyrosol, its derivatives and lignans (Andrikopoulos *et al.*, 2002; Brenes *et al.*, 2002; Gómez-Alonso *et al.*, 2003; Nissiotis and Tasioula-Margari, 2003; Allouche *et al.*, 2007; Daskalaki *et al.*, 2009). As commented before, since α -tocopherol undergoes the fastest degradation among the tocopherol homologues, it is considered the least active tocopherol in frying. However, hydroxytyrosol and its derivatives, the most efficient antioxidants in olive oils, are lost even more rapidly than α -tocopherol during frying. Hence, the protection conferred by phenolic compounds in olive oils can be otherwise attributable to those with less antioxidant activity but

more stable at frying temperatures, namely, lignans and tyrosol and its derivatives.

Extracts obtained from olive oils or their by-products are often added to oils then commercialized as special oils (Kochhar, 2000; 2001; Gertz, 2004; Esposto *et al.*, 2015). Apart from the positive effect in frying, the interest on phenolic compounds is focused on promoting the intake of such health-promoting compounds through consumption of fried foods (Farag *et al.*, 2007; Chiou *et al.*, 2009; Jiménez *et al.*, 2017).

4.3. Phytosterols

Phytosterols are the major constituents of the unsaponifiable fraction of edible oils. In olive-extracted oils, total phytosterols are higher in refined oils than in crude oils, and among refined olive oils, olive-pomace oils show the highest level, over 1800 mg/kg. In all olive oils, β -sitosterol is by far the most abundant phytosterol (>93%), followed by campesterol, Δ^7 -stigmastenol, stigmasterol and brassicasterol (Table 1). Whereas phytosterols offer no protection under the low and moderate temperatures of commercialization and storage conditions, they have been reported to improve the frying stability of oils (Sims *et al.*, 1972; Gordon and Magos, 1983; Singh, 2013).

At first, antioxidant activity was exclusively attributed to the presence of an ethylidene side chain, as occurs in Δ^5 -avenasterol, Δ^7 -avenasterol, fucosterol, vernosterol and citrostadienol. Such phytosterols were considered antipolymerization agents even though they seemed to act as antioxidants considering their mechanism of action, i.e., formation of allyl radicals in a primary carbon atom followed by isomerization to a relatively stable tertiary radical (Gordon and Magos, 1983).

Later, inconsistent results were reported. Lampi and coworkers (1999) did not find any polymerization inhibition in high-oleic sunflower oil triacylglycerols added with 0.1% of fucosterol and neither did Wrinkler and Warner (2008) adding 0.05% fucosterol to oils. In contrast, a slight protective effect was found for sterols with 2 and 3 double bonds containing or not the ethylidene side chain. Other studies on phytosterols devoid of the ethylidene group, such as β -sitosterol, suggest that alternative mechanisms may account for the protective effects of phytosterols under frying conditions (Kochhar and Gertz, 2004; Wrinkler and Warner, 2008).

In an interesting study, Singh (2013) examined the effect of β -sitosterol at 1, 2 and 5% in model triacylglycerols and various oils during frying. Results clearly demonstrated that the presence of enhanced levels of β -sitosterol significantly decreased polymer formation in all samples. Acid-catalyzed conversion of sterols into steradienes at frying temperatures was suggested as a possible mechanism. Evidence of

the fact that the conjugated diene system of steradiene played a prominent role in limiting polymers formation in frying oils was obtained by comparing the effect of sitosterol and sitostanol. The inefficiency of sitostanol was attributed to the absence of a double bond in the C5 position and hence inability to generate a conjugated diene system.

It is also interesting to comment that the stability of phytosterols during frying depends on the oil degree of unsaturation, similarly as it was found for tocopherols. Thus, the loss of phytosterols was higher in high-oleic sunflower oil than in soybean oil, even though oil degradation was significantly higher for the latter (Wrinkler and Warner, 2008).

4.4. Squalene

Squalene is a highly unsaturated triterpene hydrocarbon widely distributed in vegetable oils, with olive-extracted oils containing the highest amounts, up to 40% of the unsaponifiable fraction (Table 1). In fact, one of the most important differences between olive-extracted oils and other vegetable oils is the amount of squalene. Its concentration in olive-extracted oils varies between 0.22 and 0.7%, whereas the range is as low as 0.002–0.03% in other edible vegetable oils (Graciani, 2006).

Nergiz and Celikkale (2011) evaluated the effect of the oil refining steps on the squalene content and found that, for a certain virgin olive oil containing 491 mg/100g, considerable levels remained after refining (290 mg/100g). While the antioxidant activity of squalene under food storage conditions remains controversial, it is generally agreed that squalene inhibits thermoxidative degradation of oils under frying conditions (Gertz *et al.*, 2000; Sims *et al.*, 1972; Malecka, 1991, 1994). Apparently, this is due to the combined mode of action of α -tocopherol and squalene as chain-breaking antioxidants. It has been suggested that α -tocopherol could be regenerated from the tocopheroxyl radical by squalene (Manzi *et al.*, 1998).

In an interesting study, squalene has been reported to be rather stable during frying. Specifically, its retention in seed oils and fats used for frying in restaurants remained over 50% even after 30 h of frying while a high recovery (84–96%) was observed during the domestic deep-frying of potatoes in virgin olive oils (Kalogeropoulos and Andrikopoulos, 2004).

5. FRYING PERFORMANCE OF OLIVE-EXTRACTED OILS

Virgin olive oil is highly resistant to alteration during frying mainly due to two reasons; firstly, its fatty acid composition is characterized by a high mono-unsaturated-to-polyunsaturated fatty acid ratio and secondly, it contains a pool of minor compounds with powerful antioxidant activity, among which

phenolic compounds stand out (Boskou, 2011; Chiou and Kalogeropoulos, 2017). It shows however lower smoke point as compared to refined oils.

As commented before, polyphenols are eliminated or drastically reduced during the refining process of all crude olive oils, thus are practically absent in refined olive oil and refined olive-pomace oil. However, other minor components which increase oil stability remain (squalene) or even increase (phytosterols) after refining. Once the refined olive oil and the refined olive-pomace oils are mixed with small amounts of virgin olive oils to obtain the commercial olive oil and olive-pomace oil, contribution of phenolic compounds slightly increases. Ultimately, both blends may show, even within the same class, very different composition of minor antioxidant compounds but maintain the fatty acid criteria for stable, healthful frying oils, i.e., low contribution of saturated and polyunsaturated fatty acids, very low contribution of linoleic acid and practically absence of *trans* fatty acids.

When virgin olive oils have been compared to sunflower oils and soybean oils, frying behaviour has always been, as expected, much better for the former. This is because the protective effect of low unsaturation degree and antioxidant action of polyphenols and other minor compounds in virgin olive oils surpasses largely that of tocopherols, otherwise much more abundant in seed oils (Valdés and García, 2006; Akil *et al.*, 2015; Kalogianni *et al.*, 2017; Molina-García *et al.*, 2017; Santos *et al.*, 2018). Virgin olive oils have also shown better results than high-oleic sunflower oils, even though they both contain high levels of oleic acid (Romero *et al.*, 1999; Sánchez-Gimeno *et al.*, 2009). However, frying behaviour of virgin olive oils depends considerably on the olive variety (Abenoza *et al.*, 2016) and on the olive ripening degree (Olivero-David *et al.*, 2014; 2017).

Refined olive oils are also more stable than refined unsaturated seed oils, for example, soybean oil, sunflower oil and corn oil (Zribi *et al.*, 2014; Santos *et al.*, 2017) and even slightly more stable than palm olein, this latter being much more saturated because of its high content (36–39%) of palmitic acid (Tabee *et al.*, 2009; Romano *et al.*, 2012). In the study by Zibri *et al.*, (2014), this finding was in part attributed to the higher amounts of polyphenols remaining after refining in the case of refined olive oil (85 mg/kg) as compared to refined seed oils (15–10 mg/kg). However, in the study which compared refined olive oil with palm olein the almost 3-times higher content of sterols in the former was suggested to be the main responsible for the significantly better frying performance of refined olive oil (Tabee *et al.*, 2009).

However, the most interesting comparison was made between the commercially available olive oils and high-oleic sunflower oils (Dobarganes *et al.*, 1993; Barrera-Arellano *et al.*, 2002). Original oils

showed much better results for olive oil but once stripped of antioxidants, both oils behaved similarly. This demonstrates that differences in palmitic and linoleic acids between the oils did not have an influence on frying stability. When antioxidant-stripped oils were added with 500 mg/kg tocopherols, approximately the content in the original high-oleic sunflower oil, stability of olive oils was similar to that of high-oleic sunflower oil and much lower than in the initial oil. Taking into account that initial olive oils had only 200 mg/kg tocopherols, these results demonstrated the considerable protective effect of antioxidants other than tocopherols present in olive oils.

As to the comparative behaviour of commercially available virgin olive oil and olive oil in frying, Casal *et al.*, (2010) found similar results for extra virgin olive oil, virgin olive oil and olive oil in domestic frying, not attributable to the variable amounts of tocopherols and phenols. Therefore, from the stability point of view, virgin olive oils do not seem to provide additional protection than the commercially available olive oil. In other words, higher concentrations of minor compounds with protective action in virgin olive oils as compared to those in olive oil appear not to enhance frying stability. Suffice to say, however, that variations between all these classes of olive oils in minor compounds not only with antioxidant action but also with prooxidant activity can give rise to different comparative frying behaviour.

Regarding olive-pomace oil, studies published on frying are very limited. Chantzios *et al.*, (2007) included olive-pomace oil in a study directed to propose an alternative approach for monitoring oils at different temperatures through radical scavenging assays. Unfortunately, only peroxide values and *p*-anisidine values, exclusively recommended to monitor oxidation at room and moderate temperatures, were provided as measurements of oil alteration. Results seemed to indicate that olive-pomace oil and extra virgin olive oil showed similar and better stability at frying temperatures as compared to the rest of oils.

The study carried out by Tekin *et al.*, (2009) compared hazelnut, olive-pomace, grapeseed and sunflower oils during frying and found satisfactory performance of hazelnut and olive-pomace oils, even though content of oleic acid was higher and total unsaturation degree lower in hazelnut oil. As to minor compounds, even when tocopherols were lacking in olive-pomace oil and present at 250–500 mg/kg in hazelnut oil, the presence of other minor compounds not described in the compositional data could have been accounted for the good performance of olive-pomace oil. In another work, the same research group (Bulut and Yilmaz, 2010) reported that formation of polar compounds during frying was higher in sunflower oil samples than in refined olive-pomace oil samples. Contents of minor

compounds which can have influence on oil frying performance were not analyzed either, but results obtained were those expected from the comparatively higher degree of unsaturation of sunflower oil.

6. CONCLUSIONS

All olive-extracted oils, including virgin olive oils, commercialized olive oils (blends of refined olive oil and small amount of virgin olive oil) and commercialized olive-pomace oils (blends of refined olive-pomace oil and small amount of virgin olive oils), stand out for their high content of oleic acid and low content of polyunsaturated fatty acids (linoleic and linolenic acids), thereby their great stability to thermal oxidation and suitability for frying. Besides, olive-extracted oils possess naturally occurring minor components with antioxidant activity or protective effects under frying conditions, such as phenolic compounds, phytosterols and squalene. Studies carried out on different classes of olive-extracted oils have shown their excellent frying behaviour but among these, olive-pomace oils have been scarcely studied so far. Some discrepancies shown in the literature regarding comparative behaviour of olive-pomace oil with other vegetable oils is due to the variable relative contents and synergic action of protective compounds often not reported.

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