Frying performance of olive-extracted oils

G. Márquez-Ruiz and F. Holgado

Instituto de Ciencia y Tecnología de Alimentos y Nutrición, Consejo Superior de Investigaciones Científicas (ICTAN-CSIC)

Corresponding author: gmarquez@ictan.csic.es

Submitted: 08 February 2018; Accepted: 19 April 2018

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 fenolícos, 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

ORCID ID: Márquez-Ruiz G https://orcid.org/0000-0002-8548-837X, Holgado F https://orcid.org/0000-0003-4950-5950


Copyright: ©2018 CSIC. This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International (CC BY 4.0) License.
1. INTRODUCTION

Frying is one of the most popular methods for the preparation of foods in developed countries, on a domestic as well as an 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 during 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 from 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.  

<table>
<thead>
<tr>
<th>Olive Extracted Oils</th>
<th>Extra virgin &amp; virgin</th>
<th>Refined</th>
<th>Refined olive-pomace</th>
<th>Palm</th>
<th>Soybean</th>
<th>Sunflower</th>
<th>Canola</th>
<th>Corn</th>
<th>Rice bran</th>
<th>Cottonseed</th>
<th>Peanut</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:0</td>
<td>&lt; 0.1</td>
<td>0.5–5.9</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>&lt; 0.2</td>
<td>&lt; 0.1</td>
<td>&lt; 0.5</td>
<td>0.5</td>
<td>0.4–2.0</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>16:0</td>
<td>7.5–20.0</td>
<td>32.0–59.0</td>
<td>7.0–14.0</td>
<td>3.1–10.2</td>
<td>2.5–6.0</td>
<td>6.0–19.4</td>
<td>16.4–25.5</td>
<td>16.9–31.1</td>
<td>6.0–14.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16:1</td>
<td>0.3–3.5</td>
<td>&lt; 0.6</td>
<td>&lt; 0.5</td>
<td>&lt; 0.1</td>
<td>&lt; 0.6</td>
<td>&lt; 0.5</td>
<td>&lt; 0.3</td>
<td>0.5</td>
<td>0.5–2.0</td>
<td>&lt; 0.5</td>
<td></td>
</tr>
<tr>
<td>18:0</td>
<td>0.5–3.5</td>
<td>1.5–8.0</td>
<td>1.5–5.5</td>
<td>1.2–10.0</td>
<td>0.9–2.1</td>
<td>0.5–4.0</td>
<td>2.1–3.0</td>
<td>1.0–4.2</td>
<td>2.5–6.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:1</td>
<td>56.0–83.0</td>
<td>27.0–52.2</td>
<td>19.0–30.0</td>
<td>13.9–44.8</td>
<td>50.2–66.0</td>
<td>19.4–49.8</td>
<td>37.4–43.8</td>
<td>13.1–43.8</td>
<td>46.8–62.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:2</td>
<td>3.5–20.0</td>
<td>5.0–14.0</td>
<td>44.0–62.0</td>
<td>40.3–75.2</td>
<td>18.0–30.1</td>
<td>44.3–71.9</td>
<td>31.1–34.0</td>
<td>33.0–59.2</td>
<td>25.3–34.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:3</td>
<td>&lt; 1.5</td>
<td>&lt; 1.5</td>
<td>4.0–11.0</td>
<td>&lt; 0.7</td>
<td>2.0–14.2</td>
<td>&lt; 2.0</td>
<td>&lt; 1.2</td>
<td>0.1–2.1</td>
<td>&lt; 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unsaponifiable (%)</td>
<td>0.8–1.5</td>
<td>0.4–0.8</td>
<td>1.0–2.0</td>
<td>0.2–0.5</td>
<td>0.5–1.0</td>
<td>0.5–1.0</td>
<td>0.8–1.4</td>
<td>0.8–1.4</td>
<td>3.0–5.0</td>
<td>0.6–1.5</td>
<td>0.3–0.7</td>
</tr>
<tr>
<td>β</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>18–35</td>
<td>10–15</td>
<td>-</td>
<td>0–19</td>
<td>-</td>
<td>5–16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brassicasterol (%)</td>
<td>&lt; 0.1</td>
<td>&lt; 0.2</td>
<td>-</td>
<td>&lt; 1</td>
<td>-</td>
<td>10–23</td>
<td>-</td>
<td>&lt; 1</td>
<td>&lt; 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stigmastenol (%)</td>
<td>&lt; 1</td>
<td>4</td>
<td>&lt; 4</td>
<td>11–13</td>
<td>17–19</td>
<td>7–10</td>
<td>&lt; 1</td>
<td>4–10</td>
<td>14</td>
<td>&lt; 1</td>
<td>5–13</td>
</tr>
<tr>
<td>Δ7 Avenasterol (%)</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>2–3</td>
<td>2–4</td>
<td>2–7</td>
<td>5</td>
<td>1–9</td>
<td>5</td>
<td>2–3</td>
<td>7–19</td>
</tr>
<tr>
<td>Δ5 Stigmastenol (%)</td>
<td>&lt; 1</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>1–2</td>
<td>1–3</td>
<td>9–14</td>
<td>1–3</td>
<td>&lt; 1</td>
<td>1</td>
<td>&lt; 1</td>
<td>1–5</td>
</tr>
<tr>
<td>Δ7 Avenasterol (%)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1–2</td>
<td>1–2</td>
<td>4–6</td>
<td>-</td>
<td>&lt; 1</td>
<td>-</td>
<td>1–6</td>
<td></td>
</tr>
</tbody>
</table>

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 Celikkan, 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 oils and refined pomace-oil products 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 (pinoresinol and 1-acetoxy pinoresinol), 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 “alpeorujo” (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 pinoresinol and 1-acetoxy pinoresinol. 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 “alpeorujo” 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-cumaric 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 “alpeorujo” (Pérez-Camino and Cert, 1999; García et al., 2008; Ruiz-Méndez et al., 2013). Regarding the relative abundance of maslinic and oleaionic 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 “alpeorujo”, 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 “alpeorujo” 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 aliphic 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 linolenic 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](https://example.com/figure1.png)

**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 oil 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 variable-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 hydroxyanyclic acid derivatives), phenylethyl alcohols (tyrosol and hydroxytyrosol), flavonoids (apigenin, luteolin), lignans (pinoresinol and 1-acetoxyiioresinol) 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-acetoxyiioresinol (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, Δ7-stigmasterol, 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, 1983).

At first, antioxidant activity was exclusively attributed to the presence of an ethylidene side chain, as occurs in Δ5-avenasterol, Δ7-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 stera-
diene played a prominent role in limiting polymers
formation in frying oils was obtained by comparing
the effect of sitosterol and sitostanol. The ineffi-
ciency 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 stabil-
ity of phytosterols during frying depends on the oil
degree of unsaturation, similarly as it was found
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 differ-
ces between olive-extracted oils and other vegeta-
ble 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 con-
taining 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 regen-
erated 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 res-
aurants 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 dur-
ing 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 elimi-
nated or drastically reduced during the refining pro-
cess 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 (phyto-
sterols) 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 commer-
cial 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 unsatura-
tion degree and antioxidant action of polyphenols
and other minor compounds in virgin olive oils sur-
passes largely that of tocopherols, otherwise much
more abundant in seed oils (Valdés and García, 2006;
Aki et al., 2015; Kalogianni et al., 2017; Molina-
Garcia 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 ripen-
ing degree (Olivo-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 satu-
rated because of its high content (36–39%) of pal-
mitic 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 polyphe-
nols 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 com-
pared 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 signifi-
cantly 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. Chantzos 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.

ACKNOWLEDGMENTS

The authors thank the Spanish Ministry of Economy, Industry and Competitiveness (Project SAFEFRYING AGL2015-64234-R) and ORIVA (Interprofesional del Aceite de Orujo de Oliva) for financial support.

REFERENCES

during the domestic deep-frying and pan-frying of potatoes.


addition to edible oils: dependence on the main variables of the frying process. 
Food. Chem. 221, 123–129. https://doi.org/10.1016/j.foodchem.2016.10.051
Nahrung 38, 135–140. https://doi.org/10.1022/food.19901035025
Manzi P, Panfili G, Esti M, Pizzoferrato L. 1992. Simple and hydrolyzable phenolic compounds in virgin olive oil.1. Their extraction, separation, and quantitative and semi-quantitative evaluation by HPLC. 
J. Am. Oil. Chem. Soc. 73, 421–425. https://doi.org/10.1021/jf9300031
Márquez-Ruiz MV, Dobarganes MC, Sánchez-Moral P. 2008. Aceite de orujo de oliva comestible concentrado en ácidos tripterpenicos, procedimiento de refinacion fisica utilizado...


