Trends in Food Science & Technology 123 (2022) 28–36

Contents lists available at ScienceDirect

Trends in Food Science & Technology

journal homepage: www.elsevier.com/locate/tifs

Cooking with extra-virgin olive oil: A mixture of food components to prevent oxidation and degradation

Julián Lozano-Castellón [a,b], José Fernando Rinaldi de Alvarenga [c], Anna Vallverdú-Queralt [a,b], Rosa M. Lamuela-Raventós [a,b,*]

[a] Department of Nutrition, Food Science and Gastronomy, XIA, Faculty of Pharmacy and Food Sciences, Institute of Nutrition and Food Safety (INSA-UB), University of Barcelona, 08028, Barcelona, Spain

[b] CIBER Physiopathology of Obesity and Nutrition (CIBEROBN), Institute of Health Carlos III, 28029, Madrid, Spain

[c] Department of Food Science and Experimental Nutrition, School of Pharmaceutical Sciences, Food Research Center (FoRC), University of São Paulo, 05508-060, São Paulo, Brazil

ARTICLE INFO

Keywords:
Healthy fat
Phenolic compounds
Carotenoids
Acrylamide
Vitamin E
Bioavailability

ABSTRACT

Background: Extra virgin olive oil (EVOO), the main fat in the Mediterranean diet, is consumed both raw and cooked. During the cooking process, its major and minor fractions are transformed, degraded, and oxidized due to exposure to heat and oxygen.

Scope and approach: This review examines the effect of cooking on EVOO, including the modification of its fatty acids and minor compounds; the interaction between EVOO and food matrices; the migration of components from the oil to food and vice versa; and how EVOO may enhance the stability and health properties of the cooked food.

Key findings and conclusions: EVOO has several advantages over other vegetable oils used in cooking. Its fatty acid profile and minor constituents keep the oil stable under high temperatures. By absorbing the oil, the cooked food is likewise protected from oxidation and enriched with EVOO health-promoting bioactive compounds. Finally, food bioactive compounds become more bioavailable upon migration to the oil.

1. Introduction

Extra-virgin olive oil (EVOO) is the main source of fat in the Mediterranean diet, considered one of the healthiest dietary patterns (Estruch et al., 2018). EVOO is the fatty fraction of olive juice extracted only by mechanical and physical processes, without any refinement (International Olive Council, 2021a). The absence of any refining techniques ensures that the minor lipophilic compounds and hydrophilic phenols, responsible for the sensory and main health properties of EVOO, are partially transferred from the olives to the oil (Lozano-Castellón, López-Yerena et al., 2020; Prata et al., 2018). Over the last 60 years, EVOO production worldwide has tripled (International Olive Council, 2021b). Currently, the country with the biggest consumption of olive oil per capita is Greece, but every year the global market for EVOO is increasing due to appreciation of its organoleptic qualities and growing awareness of its health benefits (De Gennaro et al., 2021; International Olive Council, 2021b).

EVOO is consumed raw, but is also considered one of the best oils for cooking, as its healthy properties are preserved despite heat-induced degradation and transformation (De Alzaa, Guillaume, & Ravetti, 2021; Lozano-Castellón, Vallverdú-Queralt et al., 2020). Cooking is a complex process to study, due to the diversity of food matrices, cooking techniques, and the reactions taking place, which are affected by temperature, oxygen, pH, and other factors (Sun et al., 2021). A key reaction when frying or cooking with oil is the oxidation of fatty acids (Choe & Min, 2007). EVOO has previously not been recommended for frying because it has a relatively low smoke point (≈205 °C) compared to other oils (peanut oil ≈225 °C, sunflower oil ≈255 °C, soybean oil ≈242 °C, palm oil ≈227 °C) (Ahmad Tarmizi & Ismail, 2008; De Alzaa, Guillaume, & Ravetti, 2018; Man, Liu, Jamilah, & Rahman, 1999), since it is believed that low smoke point means that fats are oxidized. However, recent studies have shown that the smoke point is not an accurate indicator of oil performance and stability (De Alzaa et al., 2018). EVOO is now described as the best oil for frying, as it is rich in monounsaturated

* Corresponding author. Department of Nutrition, Food Science and Gastronomy, XIA, Faculty of Pharmacy and Food Sciences, Institute of Nutrition and Food Safety (INSA-UB), University of Barcelona, 08028, Barcelona, Spain.

E-mail address: lamuela@ub.edu (R.M. Lamuela-Raventós).

https://doi.org/10.1016/j.tifs.2022.02.022
Received 4 November 2021; Received in revised form 5 February 2022; Accepted 14 February 2022
Available online 24 February 2022

fatty acids and poor in polyunsaturated fatty acids, and because its antioxidant compounds exert a protective effect against degradation during cooking (Cui, Hao, Liu, & Meng, 2017; Santos, Molina-Garcia, Cunha, & Casal, 2018).

The aim of this review is to summarize the state of the art of cooking with EVOO, focusing on how EVOO degrades differently from other oils due to its fatty acid profile and minor constituents. Also is examined the interaction of EVOO with food matrices, and its inhibitory effects on the formation of some undesired compounds during cooking.

2. EVOO oxidation during cooking

This section provides an overview of the oxidative effect of cooking on EVOO, with particular focus on studies investigating how oxidation is reduced by the minor compounds of the oil. The degradation of these compounds is also described in order to understand their reactivity and protective role against fatty acid oxidation. Finally, the oxidative effects of different cooking techniques on EVOO are compared.

2.1. Fatty acid oxidation

During cooking, triglycerides in oil are hydrolyzed, oxidized and polymerized (Santos, Cruz, Cunha, & Casal, 2013). Also, combinations of several mechanisms can occur, such as hydrolyzation and isomerization (Brühl, 2014). Polymerized products show only weak physiological effects due to their limited absorption. Heat induced isomerization during frying increases the content of *trans*-fatty acids to a low extend only, about 1–2g/100 g of oil, which is not significant for physiological effect (Brühl, 2014). The hydrolysis products, mainly free fatty acids, have been proposed as a marker of cooked oil (Cao et al., 2019). Fatty acid oxidation occurs through an autocatalytic free radical reaction. Radicals may be generated by different processes, including autoxidation, photooxidation or thermal oxidation, the latter being the most important in cooking. In lipid autoxidation, one hydrogen is extracted from the carbon near the allylic bond, forming a delocalized radical species with the odd electron divided between three carbons. In photooxidation, light excites sensitizers such as chlorophylls, which turn triplet oxygen into singlet oxygen; the latter then reacts with the double bond to generate a peroxide group and subsequently a radical species. In thermal oxidation, the reaction is similar to autoxidation, but as it is initiated by the application of heat it occurs at a higher rate. The radical species will react with other fatty acids or other compounds to yield cyclic or bicyclic epoxides. Cleavage of the carbon chain can generate volatile compounds responsible for rancid odors (Frankel, 2005; Issaoui, Flamini, Hajaij, Cioni, & Hammami, 2011; Katsuta, Shimizu, Yamaguchi, & Nakajima, 2008).

The off-flavor compounds formed during oxidation include ketones, hydrocarbons, alcohols, carboxylic acids and aldehydes, such as the carcinogenic acrolein (Duffy, Cauven, & Morrin, 2021; Katsuta et al., 2008). An increase in molecule unsaturation can also promote oxidation. The heating of EVOO contributes to the formation of linoleic acid, due to the interaction of peroxides with oleic acid, which generates a new unsaturation (Romano, Giordano, Vitiello, Grottaglie, & Musso, 2012). Our group's comprehensive identification of oxidized fatty acid derivatives in EVOO during cooking (Lozano-Castellón et al., 2021) showed that epoxides, peroxides and lactones were predominant, a

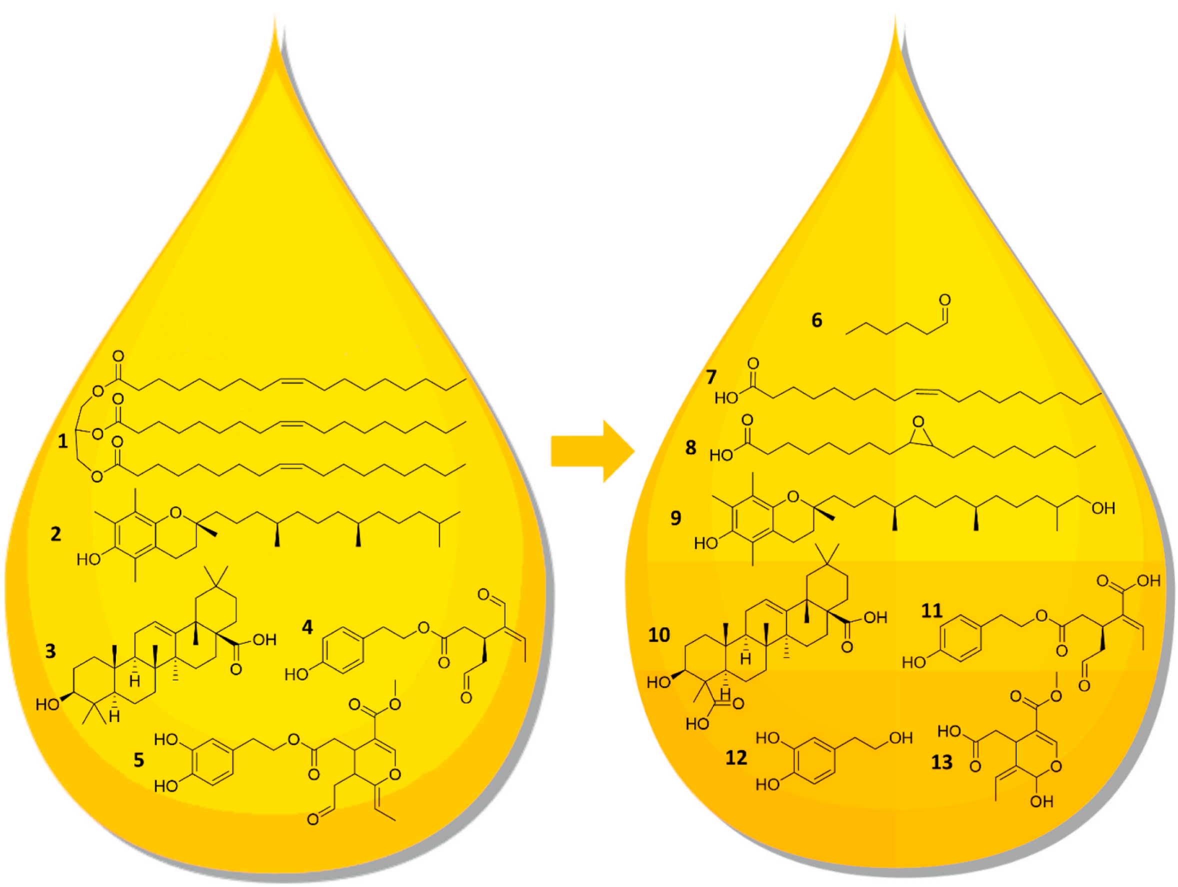

Fig. 1. Transformation of EVOO components during cooking: tryglycerydes (1: Oleic triglyceride) to fatty acids (7: oleic acid), epoxides (8: epoxide of oleic acid) and volatile compounds (6: hexanal); α-tocopherol (2) to its oxidized form (9); oleanolic acid (3) to its oxidized form (10: gypsogenic acid); oleocanthal (4) to oleocanthalic acid (11); and oleuropein aglycone (5) to hydroxytyrosol (12) and elenolic acid (13). (Transformations extracted from (Frankel, 2005; Katsuta et al., 2008; Lozano-Castellón et al., 2021; Lozano-Castellón, Vallverdú-Queralt et al., 2020)).

profile similar to that found in EVOO during storage (Capriotti et al., 2021). Sterols are also oxidized when olive oil is heated, leading to the formation of different sitosterol oxides (Zhang et al., 2005). Some of those transformations are outlined in Fig. 1.

As the degree of fatty acid unsaturation is a determining factor in oxidative radical formation (the more unsaturated the fat, the higher the oxidation rate), the high component of monounsaturated fatty acids in EVOO ensures it undergoes less oxidation during cooking compared to other vegetable oils rich in polyunsaturated fatty acids, such as sunflower oil (Casal, Malheiro, Sendas, Oliveira, & Pereira, 2010). Dordevic et al. (2020) reported that cycles of heating temperatures at 180 °C and at 220 °C affect the fatty acid profile of olive oils. The study also indicated that EVOOs can be used for culinary heating in the same way as refined olive oil, though only at a lower temperature below 180 °C and not at 220 °C. In this study, monounsaturated fatty acids changed more rapidly in refined olive oil, while polyunsaturated fatty acids changed more rapidly in EVOOs. The changes in antioxidant compounds after and before the three heating cycles also showed statistical reduction, especially among samples heated at 220 °C (in both refined and EVOOs samples). Moreover, the oxidation of other compounds is avoided, for example, less sitosterol oxides are formed in olive oil than in sunflower oil (55% reduction frying at 200 °C for 60 min) (Zhang et al., 2005). The content of oleic acid, the principle fatty acid of EVOO, has been inversely correlated with the production of toxic volatiles such as acrolein and crotonal during frying (Procida et al., 2009).

Fatty acid oxidation can be measured determining the new compounds formed, with techniques such as mass spectrometry or nuclear magnetic resonance or using chemical markers. Between those last it is peroxide value, a measure of primary oxidation products, fresh EVOO should not exceed 20 meq of peroxides/kg of EVOO (International Olive Council, 2021a). P-anisidine value is a measure of secondary degradation products, measures the amount of non-volatile aldehydes present in the oil (Ben Hammouda, Triki, Matthäus, & Bouaziz, 2018). Others markers are the spectrophotometric indices K_{232}, K_{270} and the ΔK, which are measures of diene conjugates (K_{232}) and trienes conjugates (K_{270} and ΔK) (Giuffrè, Caracciolo, Zappia, Capocasale, & Poiana, 2018), K_{270} must be less than 0.22, K_{232} less than 2.5 and ΔK less than 0.01 for fresh EVOO, according to the international olive council (International Olive Council, 2021a). Total polar compounds are oxidation products that are more polar than triglycerides, those are generated from peroxides and hydroperoxides, some of those compounds are short chain fatty acids, ketones, aldehydes and fatty alcohols (Ju et al., 2019). The maximum total polar a fat can achieve according to the regulations during frying in Spain is of 25% (Gobierno de España, 1989). During cooking those markers increase together with the oxidation of the oil (Casal et al., 2010). Interestingly, some experiments showed that peroxides value decreased at the beginning of frying followed by an increase (following a U curve) (Carrasco-Pancorbo et al., 2007; Quiles, Ramírez-Tortosa, Gomez, Huertas, & Mataix, 2002), this could be explained because fatty acid peroxides degrade to more oxidized compounds, which is seen in the increase of total polar compounds, and that the formation of new peroxides is lower than its disappearance rate (Quiles et al., 2002). This phenomena is not showed by other authors, which observed an increase of peroxide value with time and temperature of cooking (Giuffrè, Zappia, & Capocasale, 2017).

Besides fatty acids, other EVOO compounds take part in oxidation reactions, interacting directly with radicals or inhibiting or promoting their formation of this group. As mentioned above, chlorophyll can enhance photooxidation, exciting a triplet oxygen to the reactive singlet state and initiate radical reactions (Boskou, 1998). In contrast, antioxidants such as α-tocopherol and other forms of vitamin E, carotenoids and phenolic compounds will inhibit oxidation by reacting with singlet oxygen and forming triplet oxygen (Frankel, 2005). Phenolic compounds stabilize oxygen radicals by intramolecular hydrogen bonding (Sroka & Cisowski, 2003) and are able to trap reactive groups from lipids, thus avoiding the formation of toxic oxidized lipids (Zamora & Hidalgo, 2018). Vitamin E also has radical scavenger activity (Castro, Rogero, Junqueira, & Carrapeiro, 2006). As EVOO contains phenolic compounds as well as vitamin E, it is less prone to oxidation than a refined olive oil, which only has vitamin E (Casal et al., 2010). The protective effect of EVOO antioxidants is evidenced by a lower production of *trans* fatty acids, volatiles and aldehydes during frying compared to other monounsaturated oils such as peanut and canola oils (Santos, Molina-Garcia et al., 2018).

Thus, EVOO produced from olive cultivars (cv) with a higher phenolic content, such as the Spanish *Picual*, have greater oxidative stability during cooking (Abenoza, De Las Heras, Benito, Oria, & Sánchez-Gimeno, 2016). Another influential factor is the ripening index, which is calculated using the color of the pulp and the skin, oils obtained from green olives have more phenolic compounds and vitamin E (Olmo-Cunillera et al., 2021). Although unripe EVOOs have more chlorophyll, which promotes photooxidation, their higher antioxidant content confers greater resistance to oxidation compared to ripe EVOOs. Additionally, oxidation or degradation of phenolic compounds can protect other minor compounds from oxidation. Tocopherols from a phenol-rich *Picual cv* EVOO had greater stability during frying compared to those in an *Arbequina* cv EVOO (Abenoza et al., 2016). Phenolic content of EVOO is influenced by several agronomical and technological factors, apart from cultivar and ripening index, such as the growing system (organic or conventional) or the time and temperature of malaxation (López-Yerena et al., 2019; Olmo-Cunillera et al., 2021).

In summary, although fatty acids and minor compounds in EVOO are degraded by heat, EVOO is arguably the most suitable oil for cooking due to its high content of monounsaturated fatty acids, which are more resistant to oxidation than polyunsaturated fatty acids. In addition, EVOO phenolic compounds and other antioxidants protect fatty acids and vitamins from thermal degradation. While oils rich in saturated fatty acids, such as palm oil, degrade less during cooking, it does not have the minor compounds, such as polyphenols, which give EVOO its health effects.

2.2. Minor compound oxidation

The loss of phenolic compounds from EVOO during cooking (Carrasco-Pancorbo et al., 2007) affects the sensory and beneficial health attributes of the oil (Lozano-Castellón, López-Yerena et al., 2020; Prata et al., 2018). They include phenolic acids, lignans and flavones, but above all secoiridoids, which are produced via the secologanin pathway, and not the shikimate pathway like the majority of phenolic compounds (Jensen, 2002). Secoiridoids, which are responsible for the distinct properties of EVOO (Lozano-Castellón, López-Yerena et al., 2020), are ligstroside and oleuropein derivatives, which differ structurally only in one alcohol group: the former has a simple phenol and the latter an *ortho*-diphenol. The oleuropein derivatives (its aglycone, oleacein and hydroxytyrosol) are more susceptible to oxidation during cooking (Carrasco-Pancorbo et al., 2007; Lozano-Castellón, Vallverdú-Queralt et al., 2020), cooking at 180 °C for 30 min hydroxytyrosol concentration diminishes 60% while tyrosol concentration just diminishes 20% (Carrasco-Pancorbo et al., 2007). This happens because the *ortho*-diphenol quickly turns into *ortho*-quinone through a radical reaction, the intermediate radical form being stabilized by the hydroxyl group in the *ortho* position (Vallverdú-Queralt, Regueiro, Rinaldi de Alvarenga, Torrado, & Lamuela-Raventos, 2014). This greater instability is reflected in the higher activation energy observed for oleacein compared to oleocanthal, a ligstroside derivative with a simple phenolic group (Attya, Benabdelkamel, Perri, Russo, & Sindona, 2010). In the degradation of oleuropein and ligstroside aglycones, cleavage of the ester bond releases elenolic acid and hydroxytyrosol (Fig. 1) or tyrosol, respectively (Lozano-Castellón, Vallverdú-Queralt et al., 2020), the latter pair of derivatives having antioxidant properties and bioactivity (Sacchi et al., 2002). If the cooking process is moderate, i.e., 120 °C for 60 min and the initial phenolic content is high (>800 mg/kg), the EVOO still retains more than 5 mg of tyrosol and hydroxytyrosol derivatives per 20 g, the level required for the European health claim regarding its protective effects on blood lipids (European Commission, 2012; Lozano-Castellón, Vallverdú-Queralt et al., 2020). The degradation of oleocanthal and oleacein during cooking occurs not only by a radical reaction on the phenol, but also through the oxidation of the aldehyde group in the enolic part of the molecule to oleocanthalic and oleaceinic acids (Fig. 1) (Angelis, Antoniadi, Stathopoulos, Halabalaki, & Skaltsounis, 2018), considered as markers of EVOO degradation (Tsolakou et al., 2018). In contrast, lignans are relatively stable under heating (Lozano-Castellón, Vallverdú-Queralt et al., 2020). Besides oxidation, phenolic compounds can also be lost by leaching into water during cooking, and their content is drastically reduced by boiling, up to a 90% of reduction is observed when cooking potatoes in a water/oil medium (Ramírez-Anaya et al., 2019).

During cooking, tocopherols form dimers and trimers, which retain antioxidant capacity. The predominant and most labile tocopherol in EVOO is α-tocopherol (Boskou, 1998). The vitamin E content of EVOO is reduced by frying, but after a certain time, its degradation stops and further cooking has no more effect, then time seems to not have an effect in vitamin E degradation (Quiles et al., 2002). As with fatty acids, the presence of phenolic compounds in the oil helps to protect vitamin E from oxidation, its degradation constant is reduced more than a half when an olive leave extract is added to sunflower oil before frying potatoes at 180 °C (Jiménez, García, Bustamante, Barriga, & Robert, 2017).

Some measures can assess the protection against oxidation that phenolic compounds and vitamin E, together with other antioxidant compounds, confer to the oil. Some of these measures are DPPH assay, ABTS assay, total phenolic content, between others (Giuffrè et al., 2018). As during cooking the antioxidant compounds are degraded, the antioxidant capacity is also diminished (Giuffrè et al., 2018).

Squalene, a triterpene, is quite stable during cooking; about 80% remained in the oil after eight processes of deep-frying or pan-frying potatoes (Kalogeropoulos & Andrikopoulos, 2004). Volatile compounds degraded during cooking as well (Giuffrè et al., 2020). As those compounds are volatile, during heating can be volatilized and lost (Katsuta et al., 2008). However, as those compounds are formed through the fatty acid oxidation, some volatile compounds that are more stable and less volatile increase its concentration during cooking, such as 2-undecenal (Giuffrè et al., 2020).

In brief, by undergoing oxidation during cooking, the minor constituents of EVOO, such as phenolic compounds, prevent the oxidation of fatty acids and other compounds, thus helping to maintain the stability of the oil.

2.3. Effect of the cooking technique

EVOO is used with a variety of cooking techniques, ranging from traditional, as pan-frying, to more innovative, as low-pressure cooking, each one differing in factors such as temperature, duration, the form of heat application (e.g., conduction or irradiation), and oxygen availability. Therefore, each cooking method has a different degradative effect on EVOO. For instance, pan-frying degrades EVOO more than deep-frying because of greater oxygen availability, which results in an increase in epoxides, a 33% more are formed after 8 frying cycles of potatoes at 170 °C (Kalogeropoulos, Salta, Chiou, & Andrikopoulos, 2007). Polymeric acylglycerols and the anisidine value increase during a pan frying as well, compared to a deep frying process, polymeric acylglycerols increase 3 times and anisidine value is almost doubled when comparing pan frying at 180 °C with deep frying at 190 °C (Zribi et al., 2014). Moreover, if the oil is heated discontinuously, as occurs in a restaurant with intermittent service, the frying process will increasingly favor the formation of diverse toxic products (Le Gresley, Ampem, Grootveld, Percival, & Naughton, 2019).

Our group recently compared the effects of different types of cooking on EVOO using an untargeted lipidomic and metabolomic approach. When submitted to three innovative cooking techniques (slow-cooker, vacuum pot and low-temperature cooking), the EVOO was less degraded than with three traditional methods (oven, deep-frying and pan-frying/sautéing). The lipidomic and phenolic profiles associated with pan-frying differed clearly with respect to the other two conventional techniques. The newer methods that apply a low temperature (70–85 °C), such as slow cooking, or an oxygen-free environment, such as the vacuum pot, minimized the oxidation process in EVOO (Lozano-Castellón et al., 2021). It was demonstrated that fatty acids are more degraded by temperature, regardless of oxygen availability, whereas phenolic compounds are affected by both factors. This phenomenon was apparent in the hierarchical cluster analysis, which showed a distinct lipidic profile associated with cooking at 170 °C or above in comparison with lower temperatures. In contrast, cooking at a moderate temperature (i.e., 120 °C) in a sauteing process, in which oxygen availability was high, presented similar phenolic profile than cooking at high temperature. In the vacuum pot, however, EVOO exposed to 140 °C had a phenolic profile more similar to that of raw oil than EVOO submitted to a higher temperature (Lozano-Castellón et al., 2021). Among the different controllable parameters for each cooking technique, temperature has a marked effect on the phenolic compound content, 120 vs 170 °C, whereas cooking duration does not, 30 vs 60 min, (in a domestic context) (Lozano-Castellón, Vallverdú-Queralt et al., 2020).

Microwave cooking is detrimental for the composition of EVOO, as it increases free acidity, K_{270} and acrolein, and decreases the phenolic content to a greater extent than pan-frying (Kishimoto, 2019). When boiling with EVOO, the phenolic compounds of EVOO migrate to the boiling water and degrade (Silva, Garcia, & Paiva-Martins, 2010), a degradation that accelerates in the presence of vegetables, due to their metal content, in the presence of vegetable the reduction is about 85% while without vegetables this reduction is about 50% (Silva et al., 2010). Goulas and collaborators (2015) studied the effect of different cooking techniques on EVOO phenolic compounds and reported that microwaving for 5 min had no effect on EVOO antioxidant capacity. Frying reduced the total phenolic compounds to a greater extent than boiling and baking, frying 1 h at 180 °C reduced a 70% the total phenolic content, while boiling for 1 the reduction was about a 50% and baking at 180 °C for 90 min achieved about 10% of reduction (Goulas, Orphanides, Pelava, & Gekas, 2015).

Thus, the impact of cooking on the health benefits of EVOO varies with the technique used, and fatty acid and minor compound degradation can be avoided by using more innovative methods, such as vacuum pot cooking.

3. Interaction between EVOO and food

As well as a raw salad dressing, EVOO is used as a heat vehicle to process other foods. EVOO can be degraded by cooking, as explained in the previous section, but it also reacts with the cooked food to produce new compounds and enriches it with different constituents. Moreover, some compounds of the food matrix such as carotenoids and phenols, are released into the oil, where they are more bioavailable. This section reviews the interactions between EVOO and different foods during cooking, focusing on compound exchange between matrices, and how EVOO phenolic compounds can protect food components from degradation. Special attention is given to carotenoids, due to the role played by oil in enhancing their bioavailability and consequently their health benefits.

3.1. Exchange between food and EVOO

An exchange occurs between food and oil matrices during cooking (Kalogeropoulos, Chiou, Mylona, Ioannou, & Andrikopoulos, 2007; Rinaldi de Alvarenga et al., 2019), in which the food, on absorbing the oil, becomes enriched with its components, such as phenols, while the oil also extracts bioactive compounds from food. This interchange of compounds depends on the cooking technique and temperature, which modify the physico-chemical characteristics of the system. In some processes, polar compounds, such as EVOO phenols, are lost by leakage into water (Ramírez-Anaya et al., 2019). However, phenol migration can be advantageous; for example, EVOO phenolic compounds enhanced the stability of canned tuna after they migrated to the brine during the thermal processing (Sacchi et al., 2002). Kalogeropoulos, Salta, et al. (2007) found that finfish was enriched with fatty acids, squalene, phytosterols and polyphenols when fried with virgin olive oil. An exchange of phenolic compounds between EVOO and fried Mediterranean vegetables was also observed (Kalogeropoulos, Mylona, et al., 2007). EVOO phytosterols were reported in French fries (Salta, Kalogeropoulos, Karavanou, & Andrikopoulos, 2008) and fried potatoes were enriched with vitamin E, phytosterols, polyphenols, squalene, triterpenes, and carotenoids, depending on the oil used (Chiou, Kalogeropoulos, Boskou, & Salta, 2012). Interestingly, after migration from the oil, polyphenols seemed to gain stability in the food matrix, where their concentrations were higher (Chiou et al., 2012).

In a study by Ramírez-Anaya, Samaniego-Sánchez, Castañeda-Saucedo, Villalón-Mir, and de la Serrana (2015), cooked vegetables were found to be enriched with EVOO phenols, even those processed in a water/oil mixture. Similarly, during the preparation of a tomato sofrito, EVOO phenolic compounds migrated both to the water and the insoluble fraction (Rinaldi de Alvarenga et al., 2019). This enrichment process and the matrix breakdown during cooking enhances the antioxidant and anti-inflammatory properties of vegetables (Valderas-Martinez et al., 2016; Vallverdú-Queralt, de Alvarenga, Estruch, & Lamuela-Raventos, 2013). Santos, Molina-Garcia, Cunha, and Casal (2018) found that potatoes cooked in a convection oven or microwave grill, both low-fat techniques that minimize oil oxidation, were less enriched with EVOO components, such as β-carotene, than deep-fried potatoes. Thus, if the aim is to enrich food, it should be cooked with plenty of oil in a deep-frying or sautéing process.

When plant cell walls are broken during the cooking process, phenolic compounds are released to the oil, where they become more bioavailable (Tulipani et al., 2012). The use of higher amounts of EVOO to prepare tomato sauce increased the extraction of phenolic compounds from the tomato and the phenolic content of the final product, for example when using a 10% of EVOO for the preparation of the sauce the concentration of chlorogenic acid was 4 mg/kg while it was 2.5 mg/kg when using 5% of EVOO in the recipe (Vallverdú-Queralt et al., 2014). Similarly, the phenolic compounds of tomato, garlic and onion were released to the EVOO during a sofrito home-cooking process, particularly the more lipophilic compounds, such as naringenin (Rinaldi de Alvarenga et al., 2019). After their release, some phenolic compounds then undergo a transformation, for example, into 3,4-dihydroxyphenylglycone, which has anti-inflammatory and anti-platelet properties (Rinaldi de Alvarenga et al., 2020).

Additionally, EVOO phenolic compounds can complex with food macromolecules, changing its absorption and its plasma kinetics profile (Zhang et al., 2014). In the case of proteins, non-covalents interactions predominate between those and phenolic compounds, diminishing its absorption and health effect. On the other hand, carbohydrates and fats interaction with phenolic compounds increase its absorption (Zhang et al., 2014). However, few studies have been carried out to assess the effect of the interaction between EVOO phenolic compounds and food macronutrients on its absorption and health effects. EVOO phenols create interactions with fatty acids, the resulting complex still present antiproliferative effects in CRC1 and CRC5 colorectal cancer cell lines, as well as angiotensin 1-converting enzyme inhibitory activity (Alu'datt et al., 2014).

Despite not being studied effect on bioavailability of EVOO phenolic compounds with a protein or starch rich food, it has been studied the effect on sensory profile of tomato puree, potato pure and bean paste added with an increasing content of EVOO wastewater mill phenolic extract. Bean paste suppressed pungency and partially suppressed astringency, thus indicating an interaction between bean protein and the phenolic compounds. This interaction could impact on the bioavailability and the kinetics in blood of the EVOO phenolic compounds. Food polyphenols react with macromolecules using EVOO as a reactant medium (De Toffoli et al., 2019).

In summary, during cooking with EVOO there is an exchange of compounds between the oil and the food, increasing food stability and bioactive compounds bioavailability. In addition, new compounds are formed due to the reaction between food and EVOO components. However, further research is needed on the new compounds formed during cooking with EVOO and the reaction products that arise from the interaction between its minor components and cooked food. More data are also required about how different food matrices affect EVOO and vice versa.

3.2. EVOO diminishes food oxidation

EVOO antioxidants that protect the oil from thermal oxidation can have the same effect on the cooked food. Canned tuna, being rich in polyunsaturated fatty acids, is highly prone to oxidation, but this is inhibited if EVOO is used in the canning process (Medina, Satué-Gracia, German, & Frankel, 1999). Similarly, cod was significantly protected from lipid oxidation when fried in EVOO, an effect not observed in salmon, which as a fattier fish absorbs less oil (Ansorena, Guembe, Mendizábal, & Astiasarán, 2010). The absorption of EVOO antioxidants can be used as a strategy to increase the shelf-life of food products (Difonzo et al., 2018), including bakery snacks. The addition of EVOO rich in phenolic compounds to dough resulted in less lipid oxidation, this is observed in the induction period (of the RapidOxy test) of the snacks which is 80 min against 40 min of the snacks prepared with the EVOO poor in phenolic compounds (Difonzo et al., 2018). Also in dough, the degradation of heat-sensitive phycocyanin, a bioactive pigment from spirulina, was prevented by the addition of EVOO (Niccolai et al., 2021). In domestic cooking, the oxidation of broccoli and chicken nuggets was lower when they were fried in EVOO compared to canola and grapeseed oil, EVOO was also less oxidized than the other oils (De Alzaa et al., 2021). The antioxidants of vegetables were preserved when roasted in EVOO, which synergistically helped to preserve EVOO antioxidants (Brkić Bubola, Klisović, Lukić, & Novoselić, 2020). On the other hand, EVOO used to fry an egg was not substantially modified from an EVOO heated for the same time, showing a similar fluorescence spectrum (Saleem et al., 2017), probably because eggs contain an insignificant amount of compounds that can affect EVOO oxidation.

Compound transfer between EVOO and food can also inhibit the formation of undesired compounds, such as acrylamide, or other Maillard reaction intermediates. The addition of virgin olive oil (VOO) to a Maillard reaction model system inhibited the formation of mutagenic heterocyclic amines (HAs); the effect was higher when using recently produced oil, which contained a higher amount of phenolic compounds, than a one-year-old oil (Monti et al., 2001). In further experiments, a similar effect was observed when using a phenolic extract from VOO, demonstrating that these constituents were responsible for this inhibition (Monti et al., 2001). VOO also prevented the formation of HAs in roasted meat; it was combined with different proportions of a green tea extract and the samples with more VOO produced fewer HAs (Awney, 2011). However, Ekiz and Oz (2019) found that the formation of HAs in fried meatballs was similar when using EVOO or other edible oils. These discrepant results could be due to different behavior of EVOO in roasting compared to frying, or because the VOO and EVOO differed in composition.

Apart from HAs, during frying acrylamide formation is a concerning issue, which it is estimated to be over the recommendation limit in the household preparations (>500 μg/kg) (Mesias, Delgado-Andrade, Holgado, & Morales, 2018). Acrylamide is formed through Maillard reaction, but also through the oxidation and nitrogenation of acrolein, a lipid oxidation product (Weisshaar, 2004). Depending on the oil, different content of acrylamides is formed, corn oil seems to facilitate its formation, in comparison to sunflower, olive and hazelnut oils (Başaran & Turk, 2021). The acrylamide content is related to the color of the resulting French fries (Mesias et al., 2018).

Napolitano, Morales, Sacchi, and Fogliano (2008) studied the inhibitory effect of VOO phenolic compounds on acrylamide formation during potato frying. Although potatoes fried with different oils had the same color, acrylamide formation was faster in the oil with the lowest phenolic content. Moreover, the VOO with the highest concentration of *ortho*-diphenolic compounds efficiently inhibited acrylamide formation in crisps in mild to moderate frying conditions. This inhibitory effect is supported by different works using EVOO by-products as a phenolic compounds source. The addition of fresh leaves to sunflower oil achieved a reduction of 75% in the formation of acrylamide while frying potatoes at 190 °C (Ismial, Ali, Askar, & Samy, 2013). An olive mil wastewater phenolic extract diminished acrylamide, acrolein and hexanal formation when added to refined olive oil in a potato frying process at 180 °C (Sordini et al., 2019).

Thus, the protection against thermal oxidation afforded by antioxidant compounds transferred from EVOO can be harnessed in industrial food processing, for example, in baked snacks or canned tuna. The ability of these minor compounds to inhibit the formation of carcinogenic products during cooking is another reason why EVOO has beneficial application in a variety of food products and is the most suitable oil for domestic frying. Using EVOO for frying it could be achieved similar brown product but with less acrylamide and acrolein (Napolitano et al., 2008; Sordini et al., 2019).

3.3. Enhanced bioaccessibility of carotenoids from food matrices

Carotenoids are fat-soluble pigments found in plants, fungi, and photosynthetic microorganisms. They are responsible for photosynthetic light harvesting, and confer photoprotection and antioxidant activity. Carotenoid content in food of plant origin is affected by variables such as genetics, the maturation stage, and agronomic and environmental factors, whereas the release of carotenoids from the food matrix depends on how they are stored in the plant tissue, their physicochemical characteristics, and the processing techniques (Dias et al., 2021). Carotenoids stored in chromoplasts in lipid-dissolved and liquid-crystalline form are liberated more easily than those stored in crystal form, and are thus more bioaccessible and bioavailable (Schweiggert et al., 2014). A way of enhancing carotenoid bioavailability is to apply food processing techniques that destroy cell walls, such as reducing the size of food pieces by mechanical operations (González-Casado, Martín-Belloso, Elez-Martínez, & Soliva-Fortuny, 2018) or involve thermal treatment (Colle, Lemmens, Knockaert, Van Loey, & Hendrickx, 2016). However, cell wall disruption alone does not significantly enhance carotenoid bioaccessibility (Lemmens et al., 2014), and high temperatures can favor their oxidation and degradation (Colle et al., 2016). An alternative strategy is to add a lipid matrix during processing, which facilitates the solubilization of carotenoids and prevents their oxidation. The phenolic compounds and other chain-breaking antioxidants in EVOO can act synergistically to remove free radicals. Furthermore, phenolic compounds from the food matrix, such as quercetin and naringenin, that migrate to the oil phase during the cooking process promote a more stable environment for carotenoids, even favoring their isomerization (Rinaldi de Alvarenga et al., 2019). The carotenoids found in EVOO include lutein, which does not have pro-vitamin A activity but improves the bioaccessibility of carotenoids from other food being cooked.

Olive oil plays a fundamental role in the solubilization of carotenoids, and can overcome the barriers of the food matrix. Carotenes, such as lycopene and β-carotene, are usually found in tightly packed crystalloid aggregates, especially *E*-lycopene, whose planar structure facilitates strong intermolecular interactions with other *E*-lycopenes (Chacón-Ordóñez, Carle, & Schweiggert, 2019). The resulting resistance to solubilization can be overcome by the presence of an oil matrix and the application of heat. Carotenes are more dependent on lipids for absorption than the less lipophilic xanthophylls (Chacón-Ordóñez et al., 2019), whose oxygen content increases polarity and favors solubilization in aqueous systems; this also facilitates their migration to and stability in olive oil drops (Chacón-Ordóñez et al., 2019).

The addition of a lipid matrix also contributes to the isomerization of carotenoids during processing (Honda, 2021, pp. 173–220). Carotenoids contain multiple conjugated double bonds that can generate a variety of geometric isomers (*E/Z*, *trans/cis*). Due to their physicochemical properties, the *Z*-isomers are less crystalline and more soluble, but also less stable than *E*-isomers (Honda et al., 2018). Most carotenoids in plants and food have an *E*-configuration (Khoo, Prasad, Kong, Jiang, & Ismail, 2011), whereas many of those found in the human plasma, especially lycopene and astaxanthin, have a *Z*-configuration, which may indicate that this isoform is more bioavailable (Arranz et al., 2015). Studies show that the Z-isomer of lycopene has a higher plasmatic and tissue concentration than *E*-lycopene (Arranz et al., 2015) and exerts stronger antioxidant, antilipidemic and anti-inflammatory effects (Arranz et al., 2015; Valderas-Martinez et al., 2016). This pattern does not apply to all carotenoids; for example, β-carotene *Z*-isomers are reported to have less bioavailability and provitamin A activity (Nagao & Olson, 1994).

Due to its lipid profile, EVOO improves carotenoid bioaccessibility to a greater extent than other oils, probably due to the acyl chain length and degree of unsaturation in its fatty acids (Lemmens et al., 2014). The hydrolysis of long-chain triglycerides in digestion results in swollen micelles that facilitate carotenoid absorption, whereas medium-chain triglycerides, as found in coconut oil, lead to smaller micelles. The importance of the degree of unsaturation in fatty acids for carotene bioaccessibility has still not been clarified. Some studies indicate that oils rich in polyunsaturated fats, such as fish oil, are less bioaccessible than monounsaturated fats, such as oleic acid, the monounsaturated long-chain fatty acid characteristic of EVOO. However, the impact on carotenoid bioaccessibility also depends on the lipid load, and differences between oils can be minimized by processing (Lemmens et al., 2014).

In summary, due to its unique polar fraction, EVOO provides a stable environment for carotenoids that migrate from food, preventing oxidation and favoring the isomerization process, which is crucial for absorption. Furthermore, the fatty acid profile of EVOO facilitates the formation of stable mixed micelles in the digestion process, which is important for the absorption of less polar compounds.

4. Conclusions

EVOO, rich in monounsaturated fatty acids, phenolic compounds, and other antioxidants, undergoes less degradation during cooking than other edible oils. Fatty acid oxidation is further inhibited by phenolic trapping of reactive groups, which impedes the formation of toxic oxidized lipid products. However, those antioxidant compounds also degrade during cooking, some more readily than others according to their chemical structure; this is the case of *ortho-*/diphenols, whereas lignans are less prone to oxidation. The degradation of EVOO varies with the cooking technique, and the use of innovative methods, such as vacuum pot cooking, can reduce the formation of oxidation products, while otherwise obtaining similar results to traditional techniques. Additionally, during cooking, some compounds migrate from EVOO to food and vice versa, producing different phenomena. Once enriched with EVOO antioxidants, food is less prone to oxidation, and the formation of undesirable products is diminished. Finally, beneficial food compounds may be preserved by transfer to EVOO and their bioaccessibility is improved.

Funding

This research was funded by CICYT [AGL2016- 75329-R]; Ministry of Science and Innovation [PID2020-114022RB-I00], funded by [AEI/10.13039/501100011033]; CIBEROBN from the Instituto de Salud Carlos III, ISCIII from the Ministerio de Ciencia, Innovación y Universidades (AEI/FEDER, UE), and Generalitat de Catalunya [2017SGR 196]. Julián Lozano-Castellón thanks the Ministry of Science Innovation and Universities for the FPI contract [BES-2017-080017]. Anna Vallverdú-Queralt thanks the Ministry of Science Innovation and Universities for the Ramon y Cajal contract [RYC-2016-19355]. José Fernando Rinaldi de Alvarenga thanks for the grant to Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) [2019/11324-8] [2013/07914-8].

Acknowledgements

The authors wish to thank Carlos Guimerà for Fig. 1 (https://carloswk.wordpress.com/).

References

Abenoza, M., De Las Heras, P., Benito, M., Oria, R., & Sánchez-Gimeno, A. C. (2016). Changes in the physicochemical and nutritional parameters of picual and arbequina olive oils during frying. *Journal of Food Processing and Preservation, 40*(3), 353–361. https://doi.org/10.1111/jfpp.12612

Ahmad Tarmizi, A. H., & Ismail, R. (2008). Comparison of the frying stability of standard palm olein and special quality palm olein. *Journal of the American Oil Chemists' Society, 85*(3), 245–251. https://doi.org/10.1007/s11746-007-1184-8

Alu'datt, M. H., Rababah, T., Ereifej, K., Gammoh, S., Alhamad, M. N., Mhaidat, N., et al. (2014). Investigation of natural lipid–phenolic interactions on biological properties of virgin olive oil. *Journal of Agricultural and Food Chemistry, 62*(49), 11967–11975. https://doi.org/10.1021/jf504557k

Angelis, A., Antoniadi, L., Stathopoulos, P., Halabalaki, M., & Skaltsounis, L. A. (2018). Oleocanthalic and oleaceinic acids: New compounds from extra virgin olive oil (EVOO). *Phytochemistry Letters, 26*(June), 190–194. https://doi.org/10.1016/j.phytol.2018.06.020

Ansorena, D., Guembe, A., Mendizábal, T., & Astiasarán, I. (2010). Effect of fish and oil nature on frying process and nutritional product quality. *Journal of Food Science, 75*(2), H62–H67. https://doi.org/10.1111/j.1750-3841.2009.01472.x

Arranz, S., Martínez-Huélamo, M., Vallverdu-Queralt, A., Valderas-Martinez, P., Illán, M., Sacanella, E., et al. (2015). Influence of olive oil on carotenoid absorption from tomato juice and effects on postprandial lipemia. *Food Chemistry, 168*, 203–210. https://doi.org/10.1016/j.foodchem.2014.07.053

Attya, M., Benabdelkamel, H., Perri, E., Russo, A., & Sindona, G. (2010). Effects of conventional heating on the stability of major olive oil phenolic compounds by tandem mass spectrometry and isotope dilution assay. *Molecules, 15*(12), 8734–8746. https://doi.org/10.3390/molecules15128734

Awney, H. (2011). The effect of green tea and olive oil on the mutagenic activity of heterocyclic amines extracted from common food consumed in Saudi Arabia. *International Journal of Food Sciences & Nutrition, 62*(3), 295–302. https://doi.org/10.3109/09637486.2010.529070

Başaran, B., & Turk, H. (2021). The influence of consecutive use of different oil types and frying oil in French fries on the acrylamide level. *Journal of Food Composition and Analysis, 104*, 104177. https://doi.org/10.1016/j.jfca.2021.104177

Ben Hammouda, I., Triki, M., Matthäus, B., & Bouaziz, M. (2018). A comparative study on formation of polar components, fatty acids and sterols during frying of refined olive pomace oil pure and its blend coconut oil. *Journal of Agricultural and Food Chemistry, 66*(13), 3514–3523. https://doi.org/10.1021/acs.jafc.7b05163

Boskou, D. (1998). Frying temperatures and minor constituents of oils and fats. *Grasas Y Aceites, 49*(3–4), 326–330. https://doi.org/10.3989/gya.1998.v49.i3-4.734

Brkić Bubola, K., Klisović, D., Lukić, I., & Novoselić, A. (2020). Vegetable species significantly affects the phenolic composition and oxidative stability of extra virgin olive oil used for roasting. *LWT, 129*(May), 109628. https://doi.org/10.1016/j.lwt.2020.109628

Brühl, L. (2014). Fatty acid alterations in oils and fats during heating and frying. *European Journal of Lipid Science and Technology, 116*(6), 707–715. https://doi.org/10.1002/ejlt.201300273

Cao, G., Ding, C., Ruan, D., Chen, Z., Wu, H., Hong, Y., et al. (2019). Gas chromatography-mass spectrometry based profiling reveals six monoglycerides as markers of used cooking oil. *Food Control, 96*(October 2018), 494–498. https://doi.org/10.1016/j.foodcont.2018.10.013

Capriotti, A. L., Cerrato, A., Aita, S. E., Montone, C. M., Piovesana, S., Laganà, A., et al. (2021). Degradation of the polar lipid and fatty acid molecular species in extra virgin olive oil during storage based on shotgun lipidomics. *Journal of Chromatography A, 1639*, 461881. https://doi.org/10.1016/j.chroma.2021.461881

Carrasco-Pancorbo, A., Cerretani, L., Bendini, A., Segura-Carretero, A., Lercker, G., & Fernández-Gutiérrez, A. (2007). Evaluation of the influence of thermal oxidation on the phenolic composition and on the antioxidant activity of extra-virgin olive oils. *Journal of Agricultural and Food Chemistry, 55*(12), 4771–4780. https://doi.org/10.1021/jf070186m

Casal, S., Malheiro, R., Sendas, A., Oliveira, B. P. P., & Pereira, J. A. (2010). Olive oil stability under deep-frying conditions. *Food and Chemical Toxicology, 48*(10), 2972–2979. https://doi.org/10.1016/j.fct.2010.07.036

Castro, I. A., Rogero, M. M., Junqueira, R. M., & Carrapeiro, M. M. (2006). Free radical scavenger and antioxidant capacity correlation of α-tocopherol and Trolox measured by three in vitro methodologies. *International Journal of Food Sciences & Nutrition, 57*(1–2), 75–82. https://doi.org/10.1080/09637480600656199

Chacón-Ordóñez, T., Carle, R., & Schweiggert, R. (2019). Bioaccessibility of carotenoids from plant and animal foods. *Journal of the Science of Food and Agriculture, 99*(7), 3220–3239. https://doi.org/10.1002/jsfa.9525

Chiou, A., Kalogeropoulos, N., Boskou, G., & Salta, F. N. (2012). Migration of health promoting microconstituents from frying vegetable oils to French fries. *Food Chemistry, 133*(4), 1255–1263. https://doi.org/10.1016/j.foodchem.2011.08.068

Choe, E., & Min, D. B. (2007). Chemistry of deep-fat frying oils. *Journal of Food Science, 72*(5), R77–R86. https://doi.org/10.1111/j.1750-3841.2007.00352.x

Colle, I. J. P., Lemmens, L., Knockaert, G., Van Loey, A., & Hendrickx, M. (2016). Carotene degradation and isomerization during thermal processing: A review on the kinetic aspects. *Critical Reviews in Food Science and Nutrition, 56*(11), 1844–1855. https://doi.org/10.1080/10408398.2013.790779

Cui, Y., Hao, P., Liu, B., & Meng, X. (2017). Effect of traditional Chinese cooking methods on fatty acid profiles of vegetable oils. *Food Chemistry, 233*, 77–84. https://doi.org/10.1016/j.foodchem.2017.04.084

De Alzaa, F., Guillaume, C., & Ravetti, L. (2018). Evaluation of chemical and physical changes in different commercial oils during heating. *Acta Scientific Nutritional Health, 2*(6), 2–11. Retrieved from https://actascientific.com/ASNH/pdf/ASNH-02-0083.pdf.

De Alzaa, F., Guillaume, C., & Ravetti, L. (2021). Evaluation of chemical and nutritional changes in chips, chicken nuggets, and broccoli after deep-frying with extra virgin olive oil, canola, and grapeseed oils. *Journal of Food Quality, 2021*, 1–14. https://doi.org/10.1155/2021/7319013, 2021.

De Gennaro, B. C., Roselli, L., Bimbo, F., Carlucci, D., Cavallo, C., Cicia, G., et al. (2021). Do Italian consumers value health claims on extra-virgin olive oil? *Journal of Functional Foods, 81*(April), 104461. https://doi.org/10.1016/j.jff.2021.104461

De Toffoli, A., Monteleone, E., Bucalossi, G., Veneziani, G., Fia, G., Servili, M., et al. (2019). Sensory and chemical profile of a phenolic extract from olive mill waste waters in plant-base food with varied macro-composition. *Food Research International, 119*, 236–243. https://doi.org/10.1016/j.foodres.2019.02.005

Dias, M. G., Borge, G. I. A., Kljak, K., Mandić, A. I., Mapelli-Brahm, P., Olmedilla-Alonso, B., et al. (2021). European database of carotenoid levels in foods. Factors affecting carotenoid content. *Foods, 10*(5), 912. https://doi.org/10.3390/foods10050912

Difonzo, G., Pasqualone, A., Silletti, R., Cosmai, L., Summo, C., Paradiso, V. M., et al. (2018). Use of olive leaf extract to reduce lipid oxidation of baked snacks. *Food Research International, 108*(January), 48–56. https://doi.org/10.1016/j.foodres.2018.03.034

Dordevic, D., Kushkevych, I., Jancikova, S., Zeljkovic, S. C., Zdarsky, M., & Hodulova, L. (2020). Modeling the effect of heat treatment on fatty acid composition in home-made olive oil preparations. *Open Life Sciences, 15*(1), 606–618. https://doi.org/10.1515/biol-2020-0064

Duffy, E., Cauven, E., & Morrin, A. (2021). Colorimetric sensing of volatile organic compounds produced from heated cooking oils. *ACS Omega, 6*(11), 7394–7401. https://doi.org/10.1021/acsomega.0c05667

Ekiz, E., & Oz, F. (2019). The effects of different frying oils on the formation of heterocyclic aromatic amines in meatballs and the changes in fatty acid compositions of meatballs and frying oils. *Journal of the Science of Food and Agriculture, 99*(4), 1509–1518. https://doi.org/10.1002/jsfa.9325

de España, G. (1989). *Orden de 26 de enero de 1989 por la que se aprueba la norma de calidad para los aceites y grasas calentados*. Madrid: Boletin Oficial del Estado. Retrieved from https://www.boe.es/buscar/doc.php?id=BOE-A-1989-2265.

Estruch, R., Ros, E., Salas-Salvadó, J., Covas, M.-I., Corella, D., Arós, F., et al. (2018). Primary prevention of cardiovascular disease with a mediterranean diet supplemented with extra-virgin olive oil or nuts. *New England Journal of Medicine, 378*(25), e34. https://doi.org/10.1056/NEJMoa1800389

European Commission. (2012). Regulation EC No. 432/2012: Establishing a list of permitted health claims made on foods, other than those referring to the reduction of disease risk and to children's development and health. *Official Journal of the European Union L, 136*, 1–40.

Frankel, E. N. (2005). *Lipid oxidation* (2nd ed.). Woodhead Publishing Limited.

Giuffrè, A. M., Capocasale, M., Macrì, R., Caracciolo, M., Zappia, C., & Poiana, M. (2020). Volatile profiles of extra virgin olive oil, olive pomace oil, soybean oil and palm oil in different heating conditions. *LWT, 117*, 108631. https://doi.org/10.1016/j.lwt.2019.108631

Giuffrè, A. M., Caracciolo, M., Zappia, C., Capocasale, M., & Poiana, M. (2018). Effect of heating on chemical parameters of extra virgin olive oil, pomace olive oil, soybean oil and palm oil. *Italian Journal of Food Science, 30*(4), 715–739. https://doi.org/10.14674/IJFS-1269

Giuffrè, A. M., Zappia, C., & Capocasale, M. (2017). Effects of high temperatures and duration of heating on olive oil properties for food use and biodiesel production. *Journal of the American Oil Chemists' Society, 94*(6), 819–830. https://doi.org/10.1007/s11746-017-2988-9

González-Casado, S., Martín-Belloso, O., Elez-Martínez, P., & Soliva-Fortuny, R. (2018). In vitro bioaccessibility of colored carotenoids in tomato derivatives as affected by ripeness stage and the addition of different types of oil. *Journal of Food Science, 83*(5), 1404–1411. https://doi.org/10.1111/1750-3841.14140

Goulas, V., Orphanides, A., Pelava, E., & Gekas, V. (2015). Impact of thermal processing methods on polyphenols and antioxidant activity of olive oil polar fraction. *Journal* *of Food Processing and Preservation, 39*(6), 1919–1924. https://doi.org/10.1111/jfpp.12430

Honda, M. (2021). *Carotenoid isomers: A systematic review of the analysis, biological activity, physicochemical property, and methods for isomerization*. https://doi.org/10.1016/B978-0-12-819485-0.00002-5

Honda, M., Kodama, T., Kageyama, H., Hibino, T., Diono, W., Kanda, H., et al. (2018). Enhanced solubility and reduced crystallinity of carotenoids, β-carotene and astaxanthin, by Z -isomerization. *European Journal of Lipid Science and Technology*. , Article 1800191. https://doi.org/10.1002/ejlt.201800191

International Olive Council. (2021a). *Trade standard applying to olive oils and olive pomace oils*. Madrid. Retrieved from https://www.internationaloliveoil.org/wp-content/uploads/2021/07/COI-T15-NC3-REV-16-2021-_ENG.pdf.

International Olive Council. (2021b). *World's olive oil production has tripled*. https://www.internationaloliveoil.org/worlds-olive-oil-production-has-tripled/?lang=it. (Accessed 23 July 2021).

Ismial, S. A.-M. A., Ali, R. F. M., Askar, M., & Samy, W. M. (2013). Impact of pre-treatments on the acrylamide formation and organoleptic evolution of fried potato chips. *American Journal of Biochemistry and Biotechnology, 9*(2), 90–101. https://doi.org/10.3844/ajbbsp.2013.90.101

Issaoui, M., Flamini, G., Hajaij, M. E., Cioni, P. L., & Hammami, M. (2011). Oxidative evolution of virgin and flavored olive oils under thermo-oxidation processes. *Journal of the American Oil Chemists' Society, 88*(9), 1339–1350. https://doi.org/10.1007/s11746-011-1800-5

Jensen, S. (2002). Chemotaxonomy of the Oleaceae: Iridoids as taxonomic markers. *Phytochemistry, 60*(3), 213–231. https://doi.org/10.1016/S0031-9422(02)00102-4

Jiménez, P., García, P., Bustamante, A., Barriga, A., & Robert, P. (2017). Thermal stability of oils added with avocado (Persea americana cv. Hass) or olive (Olea europaea cv. Arbequina) leaf extracts during the French potatoes frying. *Food Chemistry, 221*, 123–129. https://doi.org/10.1016/j.foodchem.2016.10.051

Ju, J., Zheng, Z., Xu, Y., Cao, P., Li, J., Li, Q., et al. (2019). Influence of total polar compounds on lipid metabolism, oxidative stress and cytotoxicity in HepG2 cells. *Lipids in Health and Disease, 18*(1), 37. https://doi.org/10.1186/s12944-019-0980-0

Kalogeropoulos, N., & Andrikopoulos, N. K. (2004). Squalene in oils and fats from domestic and commercial fryings of potatoes. *International Journal of Food Sciences & Nutrition, 55*(2), 125–129. https://doi.org/10.1080/09637480410001666531

Kalogeropoulos, N., Chiou, A., Mylona, A., Ioannou, M. S., & Andrikopoulos, N. K. (2007). Recovery and distribution of natural antioxidants (α-tocopherol, polyphenols and terpenic acids) after pan-frying of Mediterranean finfish in virgin olive oil. *Food Chemistry, 100*(2), 509–517. https://doi.org/10.1016/j.foodchem.2005.09.072

Kalogeropoulos, N., Mylona, A., Chiou, A., Ioannou, M. S., & Andrikopoulos, N. K. (2007). Retention and distribution of natural antioxidants (α-tocopherol, polyphenols and terpenic acids) after shallow frying of vegetables in virgin olive oil. *LWT - Food Science and Technology, 40*(6), 1008–1017. https://doi.org/10.1016/j.lwt.2006.07.003

Kalogeropoulos, N., Salta, F. N., Chiou, A., & Andrikopoulos, N. K. (2007). Formation and distribution of oxidized fatty acids during deep- and pan-frying of potatoes. *European Journal of Lipid Science and Technology, 109*(11), 1111–1123. https://doi.org/10.1002/ejlt.200700007

Katsuta, I., Shimizu, M., Yamaguchi, T., & Nakajima, Y. (2008). Emission of volatile aldehydes from dag-rich and tag-rich oils with different degrees of unsaturation during deep-frying. *Journal of the American Oil Chemists' Society, 85*(6), 513–519. https://doi.org/10.1007/s11746-008-1236-8

Khoo, H.-E., Prasad, K. N., Kong, K.-W., Jiang, Y., & Ismail, A. (2011). Carotenoids and their isomers: Color pigments in fruits and vegetables. *Molecules, 16*(2), 1710–1738. https://doi.org/10.3390/molecules16021710

Kishimoto, N. (2019). Microwave heating induces oxidative degradation of extra virgin olive oil. *Food Science and Technology Research, 25*(1), 75–79. https://doi.org/10.3136/fstr.25.75

Le Gresley, A., Ampem, G., Grootveld, M., Percival, B. C., & Naughton, D. P. (2019). Characterisation of peroxidation products arising from culinary oils exposed to continuous and discontinuous thermal degradation processes. *Food & Function, 10*(12), 7952–7966. https://doi.org/10.1039/C9FO02065A

Lemmens, L., Colle, I., Van Buggenhout, S., Palmero, P., Van Loey, A., & Hendrickx, M. (2014). Carotenoid bioaccessibility in fruit- and vegetable-based food products as affected by product (micro)structural characteristics and the presence of lipids: A review. *Trends in Food Science & Technology, 38*(2), 125–135. https://doi.org/10.1016/j.tifs.2014.05.005

López-Yerena, A., Lozano-Castellón, J., Olmo-Cunillera, A., Tresserra-Rimbau, A., Quifer-Rada, P., Jiménez, B., et al. (2019). Effects of organic and conventional growing systems on the phenolic profile of extra-virgin olive oil. *Molecules, 24*(10), 1986. https://doi.org/10.3390/molecules24101986

Lozano-Castellón, J., López-Yerena, A., Rinaldi de Alvarenga, J. F., Romero del Castillo-Alba, J., Vallverdú-Queralt, A., Escribano-Ferrer, E., et al. (2020). Health-promoting properties of oleocanthal and oleacein: Two secoiridoids from extra-virgin olive oil. *Critical Reviews in Food Science and Nutrition, 60*(15), 2532–2548. https://doi.org/10.1080/10408398.2019.1650715

Lozano-Castellón, J., Rocchetti, G., Vallverdú-Queralt, A., Illán, M., Torrado-Prat, X., Lamuela-Raventós, R. M., et al. (2021). New vacuum cooking techniques with extra-virgin olive oil show a better phytochemical profile than traditional cooking methods: A foodomics study. *Food Chemistry, 362*, 130194. https://doi.org/10.1016/j.foodchem.2021.130194

Lozano-Castellón, J., Vallverdú-Queralt, A., Rinaldi de Alvarenga, J. F., Illán, M., Torrado-Prat, X., & Lamuela-Raventós, R. M. (2020). Domestic sautéing with evoo: Change in the phenolic profile. *Antioxidants, 9*(1), 77. https://doi.org/10.3390/antiox9010077

Man, Y. B. C., Liu, J. L., Jamilah, B., & Rahman, R. A. (1999). Quality changes of refined-bleached-deodorized (rbd) palm olein, soybean oil and their blends during deep-fat frying. *Journal of Food Lipids, 6*(3), 181–193. https://doi.org/10.1111/j.1745-4522.1999.tb00142.x

Medina, I., Satué-Gracia, M. T., German, J. B., & Frankel, E. N. (1999). Comparison of natural polyphenol antioxidants from extra virgin olive oil with synthetic antioxidants in tuna lipids during thermal oxidation. *Journal of Agricultural and Food Chemistry, 47*(12), 4873–4879. https://doi.org/10.1021/jf990188+

Mesias, M., Delgado-Andrade, C., Holgado, F., & Morales, F. J. (2018). Acrylamide content in French fries prepared in households: A pilot study in Spanish homes. *Food Chemistry, 260*, 44–52. https://doi.org/10.1016/j.foodchem.2018.03.140

Monti, S. M., Ritieni, A., Sacchi, R., Skog, K., Borgen, E., & Fogliano, V. (2001). Characterization of phenolic compounds in virgin olive oil and their effect on the formation of carcinogenic/mutagenic heterocyclic amines in a model system. *Journal of Agricultural and Food Chemistry, 49*(8), 3969–3975. https://doi.org/10.1021/jf010240d

Nagao, A., & Olson, J. A. (1994). Enzymatic formation of 9- cis , 13- cis , and all-trans retinals from isomers of β-carotene. *The FASEB Journal, 8*(12), 968–973. https://doi.org/10.1096/fasebj.8.12.8088462

Napolitano, A., Morales, F., Sacchi, R., & Fogliano, V. (2008). Relationship between virgin olive oil phenolic compounds and acrylamide formation in fried crisps. *Journal of Agricultural and Food Chemistry, 56*(6), 2034–2040. https://doi.org/10.1021/jf0730082

Niccolai, A., Venturi, M., Galli, V., Pini, N., Rodolfi, L., Biondi, N., et al. (2021). Vegetable oils protect phycocyanin from thermal degradation during cooking of spirulina-based "crostini. *Lwt, 138*(June 2020). https://doi.org/10.1016/j.lwt.2020.110776

Olmo-Cunillera, A., Lozano-Castellón, J., Pérez, M., Miliarakis, E., Tresserra-Rimbau, A., Ninot, A., et al. (2021). Optimizing the malaxation conditions to produce an arbequina evoo with high content of bioactive compounds. *Antioxidants, 10*(11), 1819. https://doi.org/10.3390/antiox10111819

Prata, R., Pereira, J. A., Rodrigues, N., Dias, L. G., Veloso, A. C. A., Casal, S., et al. (2018). Olive oil total phenolic contents and sensory sensations trends during oven and microwave heating processes and their discrimination using an electronic tongue. *Journal of Food Quality*, 1–10. https://doi.org/10.1155/2018/7826428, 2018.

Procida, G., Cichelli, A., Compagnone, D., Maggio, R. M., Cerretani, L., & Del Carlo, M. (2009). Influence of chemical composition of olive oil on the development of volatile compounds during frying. *European Food Research and Technology, 230*(2), 217–229. https://doi.org/10.1007/s00217-009-1160-7

Quiles, J. L., Ramírez-Tortosa, M. C., Gomez, J. A., Huertas, J. R., & Mataix, J. (2002). Role of vitamin E and phenolic compounds in the antioxidant capacity, measured by ESR, of virgin olive, olive and sunflower oils after frying. *Food Chemistry, 76*(4), 461–468. https://doi.org/10.1016/S0308-8146(01)00307-7

Ramírez-Anaya, J. D. P., Castañeda-Saucedo, M. C., Olalla-Herrera, M., Villalón-Mir, M., de la Serrana, H. L., & Samaniego-Sánchez, C. (2019). Changes in the antioxidant properties of extra virgin olive oil after cooking typical mediterranean vegetables. *Antioxidants, 8*(8), 246. https://doi.org/10.3390/antiox8080246

Ramírez-Anaya, J. del P., Samaniego-Sánchez, C., Castañeda-Saucedo, M. C., Villalón-Mir, M., & de la Serrana, H. L.-G. (2015). Phenols and the antioxidant capacity of Mediterranean vegetables prepared with extra virgin olive oil using different domestic cooking techniques. *Food Chemistry, 188*, 430–438. https://doi.org/10.1016/j.foodchem.2015.04.124

Rinaldi de Alvarenga, J. F., Quifer-Rada, P., Francetto Juliano, F., Hurtado-Barroso, S., Illan, M., Torrado-Prat, X., et al. (2019). Using extra virgin olive oil to cook vegetables enhances polyphenol and carotenoid extractability: A study applying the sofrito technique. *Molecules, 24*(8), 1555. https://doi.org/10.3390/molecules24081555

Rinaldi de Alvarenga, J. F., Quifer-Rada, P., Hurtado-Barroso, S., Illan, M., Torrado-Prat, X., & Lamuela-Raventós, R. M. (2020). Cuisinomics: MS-based untargeted approach reveals chemical modulation by a recipe during home cooking. *Food Research International, 138*, 109787. https://doi.org/10.1016/j.foodres.2020.109787. July.

Romano, R., Giordano, A., Vitiello, S., Grottaglie, L. Le, & Musso, S. S. (2012). Comparison of the frying performance of olive oil and palm superolein. *Journal of Food Science, 77*(5), C519–C531. https://doi.org/10.1111/j.1750-3841.2012.02663.x

Sacchi, R., Paduano, A., Fiore, F., Della Medaglia, D., Ambrosino, M. L., & Medina, I. (2002). Partition behavior of virgin olive oil phenolic compounds in oil−brine mixtures during thermal processing for fish canning. *Journal of Agricultural and Food Chemistry, 50*(10), 2830–2835. https://doi.org/10.1021/jf011526l

Saleem, M., Ahmad, N., Ali, H., Bilal, M., Khan, S., Ullah, R., et al. (2017). Investigating temperature effects on extra virgin olive oil using fluorescence spectroscopy. *Laser Physics, 27*(12), 125602. https://doi.org/10.1088/1555-6611/aa8cd7

Salta, F. N., Kalogeropoulos, N., Karavanou, N., & Andrikopoulos, N. K. (2008). Distribution and retention of phytosterols in frying oils and fried potatoes during repeated deep and pan frying. *European Food Research and Technology, 227*(2), 391–400. https://doi.org/10.1007/s00217-007-0733-6

Santos, C. S. P., Cruz, R., Cunha, S. C., & Casal, S. (2013). Effect of cooking on olive oil quality attributes. *Food Research International, 54*(2), 2016–2024. https://doi.org/10.1016/j.foodres.2013.04.014

Santos, C. S. P., Cunha, S. C., & Casal, S. (2018). Domestic low-fat "frying" alternatives: Impact on potatoes composition. *Food Science & Nutrition, 6*(6), 1519–1526. https://doi.org/10.1002/fsn3.683

Santos, C. S. P., Molina-Garcia, L., Cunha, S. C., & Casal, S. (June 2017). Fried potatoes: Impact of prolonged frying in monounsaturated oils. *Food Chemistry, 243*, 192–201. https://doi.org/10.1016/j.foodchem.2017.09.117, 2018.

Schweiggert, R. M., Kopec, R. E., Villalobos-Gutierrez, M. G., Högel, J., Quesada, S., Esquivel, P., et al. (2014). Carotenoids are more bioavailable from papaya than from tomato and carrot in humans: A randomised cross-over study. *British Journal of Nutrition, 111*(3), 490–498. https://doi.org/10.1017/S0007114513002596

Silva, L., Garcia, B., & Paiva-Martins, F. (2010). Oxidative stability of olive oil and its polyphenolic compounds after boiling vegetable process. *LWT - Food Science and Technology, 43*(9), 1336–1344. https://doi.org/10.1016/j.lwt.2010.05.013

Sordini, B., Veneziani, G., Servili, M., Esposto, S., Selvaggini, R., Lorefice, A., et al. (2019). A quanti-qualitative study of a phenolic extract as a natural antioxidant in the frying processes. *Food Chemistry, 279*(June 2018), 426–434. https://doi.org/10.1016/j.foodchem.2018.12.029

Sroka, Z., & Cisowski, W. (2003). Hydrogen peroxide scavenging, antioxidant and anti-radical activity of some phenolic acids. *Food and Chemical Toxicology, 41*(6), 753–758. https://doi.org/10.1016/S0278-6915(02)00329-0

Sun, J., Wang, Y., Pang, X., Tian, S., Hu, Q., Li, X., et al. (2021). The effect of processing and cooking on glucoraphanin and sulforaphane in brassica vegetables. *Food Chemistry, 360*, 130007. https://doi.org/10.1016/j.foodchem.2021.130007

Tsolakou, A., Diamantakos, P., Kalaboki, I., Mena-Bravo, A., Priego-Capote, F., Abdallah, I. M., et al. (2018). Oleocanthalic acid, a chemical marker of olive oil aging and exposure to a high storage temperature with potential neuroprotective activity. *Journal of Agricultural and Food Chemistry, 66*(28), 7337–7346. https://doi.org/10.1021/acs.jafc.8b00561

Tulipani, S., Martinez Huelamo, M., Rotches Ribalta, M., Estruch, R., Ferrer, E. E., Andres-Lacueva, C., et al. (2012). Oil matrix effects on plasma exposure and urinary excretion of phenolic compounds from tomato sauces: Evidence from a human pilot study. *Food Chemistry, 130*(3), 581–590. https://doi.org/10.1016/j.foodchem.2011.07.078

Valderas-Martinez, P., Chiva-Blanch, G., Casas, R., Arranz, S., Martínez-Huélamo, M., Urpi-Sarda, M., et al. (2016). Tomato sauce enriched with olive oil exerts greater effects on cardiovascular disease risk factors than raw tomato and tomato sauce: A randomized trial. *Nutrients, 8*(3), 170. https://doi.org/10.3390/nu8030170

Vallverdú-Queralt, A., de Alvarenga, J. F. R., Estruch, R., & Lamuela-Raventos, R. M. (2013). Bioactive compounds present in the Mediterranean sofrito. *Food Chemistry, 141*(4), 3365–3372. https://doi.org/10.1016/j.foodchem.2013.06.032

Vallverdú-Queralt, A., Regueiro, J., Rinaldi de Alvarenga, J. F., Torrado, X., & Lamuela-Raventos, R. M. (2014). Home cooking and phenolics: Effect of thermal treatment and addition of extra virgin olive oil on the phenolic profile of tomato sauces. *Journal of Agricultural and Food Chemistry, 62*(14), 3314–3320. https://doi.org/10.1021/jf500416n

Weisshaar, R. (2004). Acrylamide in heated potato products – analytics and formation routes. *European Journal of Lipid Science and Technology, 106*(11), 786–792. https://doi.org/10.1002/ejlt.200400988

Zamora, R., & Hidalgo, F. J. (2018). Carbonyl–phenol adducts: An alternative sink for reactive and potentially toxic lipid oxidation products. *Journal of Agricultural and Food Chemistry, 66*(6), 1320–1324. https://doi.org/10.1021/acs.jafc.7b05360

Zhang, X., Julien-david, D., Miesch, M., Geoffroy, P., Raul, F., Roussi, S., et al. (2005). Identification and quantitative analysis of β-sitosterol oxides in vegetable oils by capillary gas chromatography–mass spectrometry. *Steroids, 70*(13), 896–906. https://doi.org/10.1016/j.steroids.2005.06.004

Zhang, H., Yu, D., Sun, J., Liu, X., Jiang, L., Guo, H., et al. (2014). Interaction of plant phenols with food macronutrients: Characterisation and nutritional–physiological consequences. *Nutrition Research Reviews, 27*(1), 1–15. https://doi.org/10.1017/S095442241300019X

Zribi, A., Jabeur, H., Aladedunye, F., Rebai, A., Matthäus, B., & Bouaziz, M. (2014). Monitoring of quality and stability characteristics and fatty acid compositions of refined olive and seed oils during repeated pan- and deep-frying using GC, FT-NIRS, and chemometrics. *Journal of Agricultural and Food Chemistry, 62*(42), 10357–10367. https://doi.org/10.1021/jf503146f